BRITISH CHEMICAL ABSTRACTS

A—PURE CHEMISTRY

JANUARY, 1927.

General, Physical, and Inorganic Chemistry.

Deep-lying terms in two- and three-valency electron system spectra. R. A. SAWYER (J. Opt. Soc. Amer., 1926, **13**, 431—442).—An analysis from the point of view of atomic structure of the following relations: (1) for elements in the first two horizontal rows of the periodic table (*a*) the lowest *PP'* multiplet in the spectra of trebly-ionised atoms is near in frequency to the first line in the principal singlet series of the spectrum of the atom after loss of one more electron, (*b*) the lowest *PP'* multiplet in two-valency electron system spectra is near to the first line of the principal series, both of singlets in that system and of doublets in the once more ionised system; (2) the lowest *PP'* multiplet in the arc spectra of calcium, barium, and strontium is near to the frequency difference of the lowest *S* and *D* terms, both of singlets in the arc spectrum and of doublets in the once-ionised spectrum. It is concluded that the energy difference between the two lowest states in the above spectra is little affected either by the absence of a second electron or by its presence in the normal or the metastable lowest state. Several new combinations have been located. R. A. MORTON.

Specific frequencies associated with continuous spectra. A. WINTER (Ann. Physik, 1926, [iv], **81**, 577—586).—A mathematical paper on the theory of continuous spectra. R. W. LUNT.

Structure in the secondary hydrogen spectrum. V. O. W. RICHARDSON (Proc. Roy. Soc., 1926, **A**, **113**, 368—419).—The bands which were previously shown to be associated with Fulcher's bands (A., 1926, 873) are now shown to form, with other related bands, a set of band systems the null lines of which are connected by a Rydberg–Ritz formula, having the normal value of the Rydberg constant. It is thus possible to apportion the effects observed as between electron jumps and vibration jumps. All the lines in Fulcher's red bands arise as a result of transitions in which the total quantum number (electron jumps) changes from 3 to 2 and the vibrational quantum is unchanged. There is much evidence that the emitters of Fulcher's bands are neutral H_2, although some difficulties are presented. The claims of H_2^+, which should have a band spectrum analogous to the spark spectra, are disposed of in view of the presence of the normal value of the Rydberg constant in the Rydberg–Ritz formula.
E. S. HEDGES.

Hydrogen bands in the ultra-violet Lyman region. S. WERNER (Proc. Roy. Soc., 1926, **A**, **113**, 107—117).—Twelve bands in the spectrum of hydrogen between 1000 and 1230 Å. have been examined. These show a marked temperature effect, indicating that each of the bands originates in the rotation of the hydrogen molecule. The origin of the different bands is the vibration of the molecule. An approximate relation between the bands is of the type to be expected from rotation-vibration bands, but the fact that this relation is not exactly fulfilled indicates that the motion of the particles in the molecule is of a complex character. No complete theoretical description of the structure is yet possible. The probable value of the moment of inertia of the initial states is about 7×10^{-41}, and for the end states, including the normal state, $2-3\times10^{-41}$ g. cm.^{2} The corresponding fundamental frequencies are 6400 cm.$^{-1}$ and 5000 cm.$^{-1}$, respectively, with an error of 10—20%. W. HUME-ROTHERY.

Wave-lengths of new lines in secondary spectrum of hydrogen. D. B. DEODHAR (Proc. Roy. Soc., 1926, **A**, **113**, 420—432).—In addition to the lines tabulated by Merton and Barratt (A., 1922, ii, 461) and Tanaka (*ibid.*, 1925, ii, 909), 450 new lines, not previously recorded, have been found and the measurements are tabulated. The lines 4928·62, 4886·40, 4391·88, 4106·22, 4031·60, 4020·63, and 3858·74, recorded by Merton and Barratt and by Tanaka as single lines, are doublets, but their components have not been measured. E. S. HEDGES.

Low-voltage vacuum arc. Carbon line 4267 A. K. L. WOLF (Z. Physik, 1926, **39**, 883—885).—An arc is described which permits the separation of the 4267 line into its components 4267·261±0·010 and 4267·031±0·010 (weaker). R. A. MORTON.

Structure of second order spectrum [O II] of oxygen. C. MIHUL (Compt. rend., 1926, **183**, 876—877).—Five groups of combinations are given. For the majority of the lines the Zeeman effect has been studied. R. A. MORTON.

Spectrum of fluorine. H. DINGLE (Proc. Roy. Soc., 1926, **A**, **113**, 323—334).—The spectrum of fluorine was obtained by means of discharges through silicon tetrafluoride. Evidence of at least three successive spectra was obtained with gradual intensification of the exciting agency, and measurements were made of the lines in the red and infra-red region of the spectrum, which form under the gentlest stimulus. Analysis of the spectrum showed it to contain doublet and quadruplet systems of terms. The suggested arrangement is consistent with Carragan's observations of the Zeeman effect for fluorine. An ionisation potential of about 17 volts is indicated. It is suggested that lines of fluorine should appear

with maximum intensity at or near type *AO* in the Harvard sequence. E. S. HEDGES.

Large displacements of the spectral lines of chlorine. K. ASAGOE (Mem. Coll. Sci. Kyoto, 1926, **10**, 15—23).—The spectrum of chlorine in the region 5457—2577 Å. has been investigated under two sets of conditions: (*a*) with a Geissler discharge tube containing chlorine, (*b*) with a spark between carbon electrodes mounted in a fused quartz tube containing chlorine at a pressure of 1 atm. Many lines in (*b*) are shifted towards the red as compared with the corresponding lines under conditions (*a*). According to the manner in which they are broadened, the displaced lines are classified into three groups, one of which shows a shift of about 2 Å. towards the red. The broadening may be explained as the Stark effect due to the field of ions in the large current flowing through the gas when the pressure is increased.

R. A. MORTON.

Spectrum of the Pickering type in argon. M. KAHANOWICZ (Atti R. Accad. Lincei, 1926, [vi], **4**, 285—291).—Under suitable pressure and when strongly excited, argon gives rise to an enhanced spectrum of the Pickering type, represented by the series, $x=R[1/2^2-18^2/(2m+1/2)^2]$, with m equal to 35, 39, 40, 49, and 56. The emissive atom exhibits hydrogenoid behaviour. T. H. POPE.

Flash arc spectrum of potassium. F. H. NEWMAN (Phil. Mag., 1926, [vii], **2**, 1042—1046).—Previous work (*ibid.*, 1926, **1**, 721) on the excitation of enhanced lines in an interrupted arc passed between sodium-potassium alloy electrodes has led to the view that in a flash arc at low pressures the actual *P.D.* between the electrodes at each flash or for some period of the duration of the flash will be the full applied voltage; if the vapour pressure is maintained sufficiently low, conditions are favourable for an appreciable fraction of the electrons to attain energy equivalent to that required for the production of the enhanced lines of the vapour. The theory has been tested by examining the spectrum appearing from a flash arc produced by applying an intermittent *E.M.F.* of 120 volts between two potassium electrodes in a tube in which the pressure was maintained below 10^{-3} mm. In this manner, 108 lines of a spectrum comprising almost entirely enhanced lines of potassium were obtained between 6307 and 2986 Å. No lines of wave-length less than 2986 Å. were obtained. Most of the lines measured occur in the spark discharge obtained by passing a heavy electrodeless discharge through a low-density vapour. The spectrum obtained is analogous to the argon red spectrum.

A. E. MITCHELL.

Arc spectrum of copper. Complex spectra of copper. C. G. BEDREAG (Bull. Sci. Acad. Roumaine, 1926, **10**, 95—98, 98—102).—See A., 1926, 651, 766.

Arc spectrum of copper. P. K. KICHLU (Z. Physik, 1926, **39**, 572—587).—The spectra were obtained by using (*a*) weak current, (*b*) strong current, (*c*) under-water spark. Considerable differences were noticeable between spectra (*a*) and (*b*); in the latter many lines were reversed, many new lines were found, some being due to forbidden jumps, others were higher members of known series. Tables are given of the sharp and of the diffuse series.

E. B. LUDLAM.

Excitation of enhanced lines of tin in arcs. Zeeman effect of enhanced lines of tin. M. MIYANISHI (Mem. Coll. Sci. Kyoto, 1926, **10**, 9—13).—The classification of the enhanced lines of tin (Kimura and Nakamura, A., 1925, ii, 166) has been confirmed. The spark lines 6453, 5800, 5589, 5563, 5333 Å. are emitted from a 440-volt a.-c. arc and from a Poulsen water-cooled arc charged with tin. At the instant of break of a heavy d.-c. arc (440 volts, no self-induction, capacity of 0·25 microfarad shunted between arc terminals, 7 amp.) the spark character of the light was intensified, and the super-spark (Sn^{++}) lines 5370, 5344, 5289, 5225, 5101, 5021, 4934, 4858, 4615, 4586 are recorded. The results show that the excitation energy of the super-spark lines is greater than that of the spark lines.

The Zeeman effects of the 5800, 5590, 5563, and 5333 lines were analysed only when the self-induction and capacity in the discharge circuit were adjusted and the field was 15,900 gauss. Their separations were only one third of the normal triplet separations.

R. A. MORTON.

Self-reversal of lines in the explosion spectrum of tin. B. ARAKATSU and M. SHODA (Mem. Coll. Sci. Kyoto, 1926, **10**, 31—34; cf. A., 1926, 875).—In the explosion spectrum of tin, almost all arc lines of wave-length shorter than 3200 Å. are self-reversed. The order of appearance of such lines can be determined by varying the pressure of the air surrounding the exploded tin wire. When explosion occurs in a vacuum, all the lines are sharp; with increasing pressure, however, they broaden, and later show self-reversal. The lines can therefore be classified into four groups according to the stage at which reversal occurs. The results are compared with those of McLennan, Young, and McLay (A., 1925, ii, 454).

R. A. MORTON.

Continuous spectrum of mercury. H. VOLKRINGER (Compt. rend., 1926, **183**, 780—782).—The continuous spectrum of mercury is best excited at 240° and 35 mm. pressure by an oscillatory discharge and a circuit of small capacity. Under these conditions, an intense continuous background is obtained in a spectrum showing the arc lines feebly. The curve of spectral energy distribution has been determined using black body radiation (platinum) at 1520° as a standard for comparison. The curve is symmetrically disposed about a maximum at 512 μμ. It is noted that this wave-length is almost twice that of the resonance line 253·6 R. A. MORTON.

Bands at 2536 and 2540 Å. of mercury. G. NAKAMURA (Mem. Coll. Sci. Kyoto, 1926, **10**, 1—8).—In addition to the 2536 band, an absorption band at 2540 Å. has been found near the mercury cathode of a vertical arc, using a coreless carbon rod as anode. Non-luminous mercury vapour shows a strong absorption band at 2536 extending towards the red, and a very much weaker band at 2540 shading off in the opposite direction. When, however, the luminous vapour which can be isolated from the negative arc with a small horse-shoe magnet is examined, it is seen

that its emission consists of the 2536 line shading off slowly on the red side, whereas its absorption is characterised by marked development of both the 2536 and 2540 bands. When the luminous vapour of the positive column of a vacuum tube is used, the 2540 emission predominates. The 2536 band is regarded as of the arc type of excitation and is connected with the neutral molecule Hg_2, whilst the 2540 band is regarded as of the spark type and is associated with the ionised molecule Hg_2^+. R. A. MORTON.

Scattered X-rays. J-Phenomenon. V. C. G. BARKLA and (MISS) G. I. MACKENZIE (Phil. Mag., 1926, [vii], 2, 1116—1121).—Previous work (A., 1926, 217, 987) has described two alternative ways in which beams of X-rays scattered in directions making angles of 60° and 120° with the direction of the primary radiation differed from one another. In one case, the beam at 120° was absorbed at the same rate as that at 60°, whilst the intensity of the former showed discontinuities when the heterogeneous beam was made to reach certain critical penetrating powers. In the other case, the beam at 120° appeared continuously more absorbable than that at 60°, giving an apparent Compton difference of wave-length with the angle of scattering. When the frequency of interruption of the X-ray tube and the thickness of the absorption medium are varied, the two cases can be made to show the same phenomenon, the beam at 120° behaving similarly to that at 60° above an interruption frequency of 97 per sec. Thus both cases are widely separated forms of the same phenomenon, and what appeared initially to support Compton's theory of scattering is merely the J-phenomenon in the scattered radiation. It is concluded that the factor deciding the degree of activity due to a complex beam acting as a whole is to be found in the details of the method of excitation of the X-rays. A. E. MITCHELL.

Control of the J-phenomenon. VI. C. G. BARKLA and W. H. WATSON (Phil. Mag., 1926, [vii], 2, 1122—1127).—The radiations scattered, from a paraffin cylinder, in the direction making an angle of 90° with that of the primary beam, have been compared with the primary beam itself. The ratio of the ionisation produced by the scattered radiation to that produced by the primary radiation is a constant for various thicknesses of aluminium showing equal absorptions of the scattered and primary beams between the J-discontinuities. The discontinuities show the sudden changes in the ionisation when this is reduced by filtration to certain critical absorbabilities. By careful control of the filament current in the Coolidge tube consistent results were obtained throughout the whole series of experiments, the J-discontinuities appearing in every case. In addition to the J_1-, J_2-, and J_3-discontinuities described previously, further discontinuities between J_1 and J_2 and between J_2 and J_3 have been found. The critical absorbabilities have been found to vary systematically with the current through the Coolidge tube. No difference has been observed between the absorptions of the primary and scattered radiations except by the occurrence of absorption lines (J-discontinuities) in the progressive absorption of the scattered radiation. A. E. MITCHELL.

Measurements in the K-series of X-ray spectra. A. LEIDE (Z. Physik, 1926, 39, 686—710).—Measurements have been made on the lines α_1 and α_2 of most of the elements from copper to tungsten, and on the lines β_1 and β_2 for those from copper to iodine. The line β_3 has been measured for molybdenum, palladium, silver, copper, and tin, and a line has been observed for molybdenum and palladium. The limit-frequencies of the K-series have been measured for elements copper to neodymium, with some exceptions, and also for holmium, and the scheme of energy levels is examined. From the values obtained for the K limit-frequencies for elements below tin, the other limit-frequencies are calculated. By plotting the difference in wave-length of β_1 and β_2 against atomic number, a connexion is shown with the sub-grouping of electrons. The measurements were made by the Seemann method. E. B. LUDLAM.

Secondary and tertiary cathode rays produced by external and internal absorption of homogeneous X-rays. H. R. ROBINSON and A. M. CASSIE (Proc. Roy. Soc., 1926, **A**, **113**, 282—301).—A continuation of previous work (cf. A., 1923, ii, 818; 1925, ii, 728) on the line spectra of the secondary and tertiary cathode radiation produced by targets of uranium oxide, thorium nitrate, bismuth oxide, gold, tungsten oxide, cerium oxide, barium carbonate, silver, molybdenum, zirconium oxide, ammonium bromide, arsenic oxide, copper, and calcium sulphate. The primary X-radiation was an unfiltered beam of molybdenum K-rays. E. S. HEDGES.

Structure of spectra of the third order. C. MIHUL (Compt. rend., 1926, **183**, 1035—1036; cf. this vol., 1).—From the study of the Zeeman effect of some of the rays of the oxygen spectrum of the third order, 5 multiplets have been recognised which result from the combination between 5 terms of multiplicities $r=3$. Data are given for the multiplets represented by the combinations $a^3P-{}^3S$, ${}^3S-b^3P$, ${}^3D-b^3P$, ${}^3P'-b^3P$, and ${}^3P'-a^3P$. J. GRANT.

Scattering of cathode rays. B. F. J. SCHONLAND (Proc. Roy. Soc., 1926, **A**, **113**, 87—106).—The laws governing the encounter of a fast electron with an atomic nucleus have been investigated by measurements of the scattering of fast cathode rays by thin foils of aluminium, copper, silver, and gold. This method avoids the difficulties due to γ-radiation when radioactive β-rays are used. The velocity of the rays was 0·497 of that of light, and their energy 77,300 volts. The ratio of the scattered portion to the rest of the beam was directly determined by a balance method. The variation of scattering with thickness, at first approximately linear, becomes more rapid as the thickness is increased, owing to the incidence of plural scattering, but with aluminium single scattering could be obtained over a range of thicknesses. The variation of scattering with the thickness and atomic number of the material, and with the energy of the rays, confirms Rutherford's theory of single scattering with the relativity correction postulated by Crowther and Schonland (*ibid.*, 1922, **A**, **100**, 526). The inverse

square law of force holds for encounters between a moving electron and the nucleus of an aluminium atom at distances of approach ranging from 1·8 to $3·4\times10^{-11}$ cm., which are the critical distances within which cathode rays of energy 77·3 and 39·0 kilovolts must come to be deflected through 90° by an aluminium nucleus. The atomic numbers of aluminium, copper, and silver calculated from the scattering results are in good agreement with theory, but with gold the calculated value is 86·5 (instead of 79) owing to abnormal secondary emission.

W. Hume-Rothery.

Scattering of positive rays by gases. II. G. P. Thomson (Phil. Mag., 1926, [vii], 2, 1076—1084).—Previous work on the scattering of positive rays by hydrogen (A., 1926, 656) has been extended to helium, argon, and oxygen. Argon and helium show a maximum scattering for protons of velocity $0·75\times10^8$ and $1·4\times10^8$ cm./sec., respectively. These results are analogous to those of Ramsauer and others with electrons of about the same velocity. With both argon and helium the experiments indicate a collision relation of the form $A\theta^{-1·35}$, the index being independent of the velocity. A few results for oxygen show a large scattering, but no maximum has been observed.

A. E. Mitchell.

Effective area of hydrogen and nitrogen molecules towards electrons of slow velocity. E. Bruche (Ann. Physik, 1926, [iv], **81**, 537—571).—From measurements of the weakening of an electron stream in the gases at pressures of the order of 0·001 mm. it has been found that there is a maximum effective area of the hydrogen molecule for electrons of velocity 1·2—1·5$\sqrt{}$volts; and that there are two maxima for nitrogen, one in the same region and a second smaller one at 4·2$\sqrt{}$volts. The experimental procedure is based on that of Lenard and Mayer. Determinations on argon gave values in good agreement with those of Ramsauer. The data obtained are compared with those of other workers in the same field.

R. W. Lunt.

Detection of unimolecular ions in air and the forces between ions and gas molecules. W. Busse (Ann. Physik, 1926, [iv], **81**, 587—602).—The velocity of ions in air at the ordinary temperature and pressure has been examined with respect to the age of the ions and to the partial pressure of water vapour. Ions were generated from a thorium preparation and their velocity was determined by streaming the ionised gas through a cylindrical condenser. The results are construed to indicate the existence of unimolecular ions of short life having velocities, in air dried by phosphorus pentoxide or by liquid air, of the order of 15 cm./sec. per volt/cm., and that Langevin's theory of an inverse fifth power law of force between ions and gas molecules is invalid.

R. W. Lunt.

Ionisation by the slow oxidation of phosphorus. W. Busse (Physikal. Z., 1926, 27, 738—741).—A preliminary account of experiments on the ionisation produced in air streaming over white phosphorus. It is shown that the temperature falls and the ionisation increases with increasing distance of a point in the stream from the phosphorus. From the sizes and charges of the ion clusters, it is held that these are to be identified with the formation of acids corresponding with the oxides formed.

R. W. Lunt.

Long-range particles emitted by the active deposit of actinium-*B*+*C*. P. Mercier (Compt. rend., 1926, **186**, 962—964).—For investigations on long-range particles from active deposits, an apparatus has been employed which eliminates the use of metallic screens by means of a compressed gas placed between the source and screen. The stopping-power of the gas and the distance from the source to the screen being known, the thickness of air equivalent to the gas-screen may be measured for each pressure. The ratio of the number of long-range α-particles to ordinary α-particles emitted from actinium-*C* is 2·8 per 1000. The number of the former falls off slowly to within 2 mm. of the end of their range, when it decreases rapidly, and extrapolation from the curve obtained indicates a maximum range of 6·47 mm. If any particles other than those due to substances such as thorium-*C* of range longer than 6·5 mm. are emitted from this deposit, their number is less than 30 per 10^6 ordinary particles.

J. Grant.

Determination of the mass of particles arising from the disintegration of atoms. G. Stetter (Physikal. Z., 1926, 27, 735—738; cf. A., 1925, ii, 1021).—The method of Aston's mass spectrograph is applied to analyse the particles emitted when α-rays are allowed to impinge on a substance. They are shown to consist of singly-charged helium atoms, reflected α-particles, and positively-charged hydrogen atoms, in confirmation of Rutherford's experiments. The method is discussed at length with reference to the scintillation method.

R. W. Lunt.

Slow β-particles from mesothorium-2. D. K. Yovanovitch and A. Proca (Compt. rend., 1926, **183**, 878—880).—By the classical method of deviation in a magnetic field and registration on a photographic plate, the energy of the β-particles of mesothorium-2 has been investigated down to energies of 2900 volts. The variation of the intensity of the lines on the plate with the energy of the particles is as follows: constant intensity from 2880 to 4500 volts, then diminution almost to zero; from 18,000 to 32,000 a slow increase, until at 38,000 volts great intensity is reached. A further increase occurs at 41,600 and then a decrease to the original intensity. The measurements of intensity are only qualitative, but they support the theoretical conclusions of Curie (A., 1926, 655).

S. J. Gregg.

Calorific effect of the β- and γ-rays of radiothorium. D. K. Yovanovitch and (Mlle.) A. Dorabialska (Compt. rend., 1926, **183**, 1037—1038).—The authors' calorimetric method for the determination of the absorption of β- and γ-rays (A., 1926, 772) has been used in the case of radiothorium prepared from mesothorium-1. The curves obtained for aluminium, copper, and lead show an increase in the calorific effect as a function of the mass per cm.^{2} In terms of the notation previously used, $\mu/\rho=38·3$ for β-rays and aluminium and $Q/I=1·60$ for the γ-rays. The γ-radiation of radiothorium is equivalent to that of 28·95 mg. of radium, as measured through 1 cm. of lead.

J. Grant.

Transmutation of mercury into gold by means of a high-pressure mercury arc of great current density. F. BERNHARDT (Physikal. Z., 1926, **27**, 713—715).—A description is given of the construction and manipulation of a mercury arc working at 600 kg./cm.^{2} carrying 400 amp. at 6 volts. Gold is determined in mercury by applying the borax bead method of Donau to a residual drop obtained by dissolving nearly all of 150 g. of redistilled mercury in pure nitric acid; $0{\cdot}025\times10^{-9}$ g. of gold can be detected in this way. In two experiments working with mercury found to be free from gold by the above method, and operating the arc under the conditions mentioned above with a current consumption of 2092 and 2125 amp.-hrs., the quantities of gold found were, respectively, 81×10^{-7} g. and $3{\cdot}0\times10^{-7}$ g.

R. W. LUNT.

Structure of boron. H. COLLINS (Chem. News, 1926, **133**, 321—323).—Speculative.

Existence of the sub-electron. M. REISS (Z. Physik, 1926, **39**, 631—635).—Polemical.

E. B. LUDLAM.

Spectra of atomic systems with two electrons. W. HEISENBERG (Z. Physik, 1926, **39**, 499—518).—Formulæ are deduced for the motions of the two electrons and applied to helium and Li^+. The agreement with experimental values is not very good.

E. B. LUDLAM.

Ionised hydrogen molecule and [Schrodinger's] wave mechanics. W. ALEXANDROV (Ann. Physik, 1926, [iv], **81**, 603—614).—Mathematical. On the basis of Schrodinger's theory, the relationship between the ionisation potential and the fine-line spectrum is analysed.

R. W. LUNT.

System of orbital planes in the inner region of an atom. *O*-Triplets in *X*-ray spectra belonging to the *L*-series. H. HIRATA (Mem. Coll. Sci. Kyoto, 1926, **10**, 35—55).—Theoretical. Sommerfeld's theory of elliptic orbits is modified by the use of three quantum numbers corresponding with three co-ordinates in space. A selection principle is proposed for electron transitions in the inner region of an atom, and the formation of *O*-triplets in *X*-ray spectra is discussed.

R. A. MORTON.

Excitation by the absorption of light in crystals. Z. GYULAI (Z. Physik, 1926, **39**, 636—643).—The maximum excitation is found to be independent of the intensity of the exciting light for the yellow-coloured sodium chloride; the lower the temperature the greater the excitation. Crystal phosphorescence is regarded as a special case of the more general excitation produced by light.

E. B. LUDLAM.

Band spectra of helium and hydrogen at low temperatures. J. C. MCLENNAN, H. G. SMITH, and C. A. LEA (Proc. Roy. Soc., 1926, **A**, **113**, 183—195).—Bands in the spectrum of helium have been studied at the temperatures given by surrounding the discharge tube with water, liquid air, or liquid hydrogen at approximately 300°, 85°, and 21° Abs., respectively. For certain series the change in the quantum number m corresponding with the maximum intensity is very clearly shown, whilst for other series the first line is the most intense at all temperatures; the lowering of the temperature has only the effect of reducing the relative intensity of the higher members of the series. Where a maximum of intensity is found, it is in all cases shifted to a lower value of m with lower temperatures. The bands studied were at 6400, 5730, 5130, 4650, 4546, 4450, 4000, 3680, and 3630 Å., respectively. Under similar conditions, the relative intensities of the strong lines of the hydrogen spectrum from 6900 to 3850 Å. have been studied at the ordinary temperature and at that of liquid air.

W. HUME-ROTHERY.

Absorption spectrum of nickel. K. MAJUMDAR (Z. Physik, 1926, **39**, 562—571).—The absorption spectra were obtained from an under-water spark and from the vapour in a carbon tube furnace. The absorption lines are tabulated and grouped and a diagram of energy levels is given.

E. B. LUDLAM.

Infra-red absorption spectra of carbonates. C. SCHAEFER, C. BORMUTH, and F. MATOSSI (Z. Physik, 1926, **39**, 648—659).—The spectrum falls into two groups, a short-wave portion common to all the carbonates, due to the internal vibrations of the carbonate ion, and a long-wave portion ($\lambda>9\,\mu$) different for different crystals except for the fundamental frequency at 14 μ. The carbonates examined were: magnesite, calcite, dolomite, spathic iron, witherite, and cerussite. Tables are given and a diagram representing the combinations of frequencies found; both difference and summation frequencies are recognised. Some combinations which might be expected do not appear and others are found for which there is no obvious explanation.

E. B. LUDLAM.

Absorption spectrum of strontianite in the short-wave infra-red. F. I. G. RAWLINS, A. M. TAYLOR, and E. K. RIDEAL (Z. Physik, 1926, **39**, 660—662; cf. preceding abstract).—The absorption spectrum was obtained by means of a spectrometer and thermopile; the results are shown on a curve and the minimum transparency is about 3·4 μ.

E. B. LUDLAM.

Term representation of the aluminium hydride bands. H. LUDLOFF (Z. Physik, 1926, **39**, 519—527; cf. following abstract).—A term system is developed as fully as the data allow for four of the aluminium hydride bands, which are shaded towards the red and indicate a labile molecule.

E. B. LUDLAM.

Molecular binding and band spectra. H. LUDLOFF (Z. Physik, 1926, **39**, 528—546).—The effect on a diatomic molecule of the absorption of light is studied by means of the analysis of the band spectra, particularly the effect of increasing rotation and vibration on the stability of the molecule. The criterion for stability when applied to the spectra of the hydrides of mercury, aluminium, calcium, zinc, and cadmium, and the band spectrum of iodine at 3460 is in good agreement with other evidence. In such compounds as the hydrides of zinc, cadmium, and mercury, in the band spectra of which the shading is on the red side, increase of electronic energy reduces the separation between the nuclei; the molecule is stable in the excited state, but not in the unexcited state; the attraction between the two

atomic cores is greater when the opposing influence of the valency electrons is reduced, as is the case when they are further from the nucleus.

E. B. LUDLAM.

Ultra-violet spectrum of potassium nitrate, and its variations as a function of p_H. (MME.) E. SIEGLER-SORU (Compt. rend., 1926, **183**, 1038—1040).—In the measurement of the absorption spectra of solutions containing 0·1% of potassium nitrate of various p_H values by the method of Vles and Gex (A., 1925, ii, 472), curves have been obtained similar to those previously found. When the p_H is plotted against the ratio $\varphi_1=(\lambda 300)/(\lambda 310)$ or $\varphi_2=(\lambda 300)/(\lambda 289)$, the curves obtained may be divided into 3 parts, included between the p_H ranges 0·2—2·5, 2·5—5·5, and 5·5—13, respectively. It is assumed that these divisions correspond with dissociation equilibria dependent on the law of mass action, and represented respectively by the bivalent systems in which $p_K=0·3—1·8$, and 3·9—4·3, and by the univalent system for which $p_K=7·0$. The equilibria involved appear to be due to successive stages of hydration of the anion, rather than to its acidic nature.

J. GRANT.

Reversing action of red and infra-red rays on sensitised and fogged photographic plates and the absorption of the sensitising dyes. M. MIYANISHI (Mem. Coll. Sci. Kyoto, 1926, **10**, 25—29).—When a photographic plate sensitised with iodo-green and fogged by candlelight is exposed in a spectrograph, reversed spectra of the red and infra-red rays up to 1·13 μ are obtained (Terenin, A., 1924, ii, 363). It is shown that of the dyes tested only those having absorption bands of which the maxima lie on the long-wave side of 5500 Å. are effective in obtaining the reversed impression up to 0·9 μ. Green light appears to be the most effective fogging agency for plates sensitised with iodo-green (absorption maximum near 5700 Å.).

R. A. MORTON.

Technique of photographic spectrophotometry. G. ROSSLER (Ber., 1926, **59**, [*B*], 2606—2615).—Examination of potassium chromate solution by the rotating sector method, using an arc between iron or copper and iron electrodes, shows a mean error of ±2%, which can be reduced considerably by repeated measurement of the plate; if a spark discharge is used as source of light, the absorption curve becomes irregular when the sector is rapidly rotated, but agrees well with the normal curve at slow speeds. Winther's method, slightly modified, gives results agreeing well with those of the sector methods when a single arc light is used, thus establishing the trustworthiness of these methods, since the Winther process under these conditions is theoretically free from error; when a spark discharge is used, the mean error is 2%. The utility of Henri's method depends greatly on the constancy of the source of light, and is considerably influenced by the difficulty of accurate measurement of short intervals of time. Compensation for the absorption of the solvent is best effected by the use of a short layer of the solvent itself.

Ordinary photographic plates are conveniently sensitised to 186 mμ by rubbing them with white vaseline, the excess of which is removed with cotton wool; before development, the plates are bathed in acetone. Similarly, for regions to 800 mμ, the plates are treated for 4 min. at 18—20° with water (50 c.c.), alcohol (96%, 25 c.c.), ethyl-red solution (0·1%, 2·0 c.c.), pinacyanol (0·1%, 1·5 c.c.), and dicyanine (0·1%, 1·5 c.c.). For the region 800—950 mμ, lepidinedicyanine is used as sensitiser.

H. WREN.

Spectrographic investigation of amino-acids, polypeptides, and diketopiperazines. II. Absorptive power of mixtures of known compounds. E. ABDERHALDEN and R. HAAS (Z. physiol. Chem., 1926, **160**, 256—262).—Ultra-violet absorption curves are given for glycylglycine and glycine anhydride, alanylalanine and alanine anhydride, leucylglycine, glycyl-leucine, and leucylglycine anhydride, leucylglycylglycine, and leucylglycyl-leucine. Glycine anhydride absorbs much less than glycylglycine, whereas its diketopiperazine absorbs much more strongly than that of the dipeptide. Mixtures of amino-acids absorb more strongly than would be expected from the additive absorptions of the components. Such molecular mixture (abscissæ)–wave-length (ordinates) curves show maxima when the proportions are: for glycine and alanine, 1 : 1; for alanine and valine, 2 : 1; for glycine and glycine anhydride, 2 : 1; for alanine and leucylglycylglycine, 1 : 1; for glycine and calcium chloride, 2 : 1; and for lævulose and alanine, 1 : 2. The increased absorption of mixtures decreases as the mixture becomes either more acid or more alkaline (cf. A., 1926, 959).

P. W. CLUTTERBUCK.

[Mutability of absorption spectra in solutions in relationship to the distribution of charge of the molecules and connexion between absorption and refraction.] G. SCHEIBE (Ber., 1926, **59**, [*B*], 2616; cf. A., 1926, 774).—The measurements of the absorption spectrum of 0·2939*M* aqueous potassium nitrate by von Halban and Ebert (A., 1924, ii, 824) are affected by a fundamental error; after correction, they agree with those of the author (*loc. cit.*).

H. WREN.

Mutability of absorption spectra in solutions and the distribution of charge of the molecules. IV. G. SCHEIBE [with F. BACKENKÖHLER and A. ROSENBERG] (Ber., 1926, **59**, [*B*], 2617—2628; cf. A., 1926, 774).—The absorption of completely symmetrical molecules, carbon tetrachloride, carbon disulphide, benzene, and hexamethylbenzene, is only very slightly influenced by such solvents as methyl and ethyl alcohols or hexane. Chloroform and, particularly, carbon tetrachloride behave abnormally as solvents. Among unsymmetrically constituted molecules, there are found electrosymmetrical compounds such as the saturated hydrocarbons and unsaturated hydrocarbons like βγ-dimethyl-$\Delta^{\alpha\gamma}$-butadiene. A chromophor made up of electrons which unite two carbon atoms joined only to C–C or C–H groups generally has no dipolar properties. When the chromophor is composed of different atoms, dipolar properties are generally present, as shown by the carbonyl group of acetone; if, however, the methyl groups of the latter are successively replaced

by the ·CMe_3 group, the susceptibility to the influence of dipolar solvents is diminished; the chemical reactivity of the carbonyl group diminishes in the same sequence. Symmetrical chromophors can become asymmetric by the introduction of polar groups, as shown by mesityl oxide and phorone, and particularly by the series of compounds, benzene, hexamethylbenzene, benzophenone, nitrobenzene, ethyl benzoate, and benzonitrile. The groups, ·NO_2, ·CO_2R, CO·R, and ·CN cause the band I of benzene to be displaceable to the regions of longer wave-length, whereas the groups, ·CH_2·CO_2R and, probably, ·NH_2 render it displaceable in the opposite direction. The first group of substituents comprises those which direct halogenation or nitration mainly towards the *meta* position, whereas the directive effect of the second group is to the *ortho* and *para* positions. The extent to which the displaceability of the bands is in harmony with the substitution rules is further examined in the cases of anisole, phenol, benzonitrile, phenylacetonitrile, benzyl alcohol, β-phenylethyl alcohol, *p*-benzoquinone, and aniline. Direct comparison is generally very difficult, since the chemical reactions are commonly effected in solvents such as concentrated sulphuric and nitric acids, which frequently induce profound optical change. H. Wren.

Rate of decay of fluorescence of solutions of dyes. E. Gaviola (Ann. Physik, 1926, [iv], **81**, 681—710).—A more detailed account of work already published (A., 1926, 335).

Rare earths as activators of luminescence. E. L. Nichols and H. L. Howes (J. Opt. Soc. Amer., 1926, **13**, 573—587; cf. Nichols and Slattery, A., 1926, 659).—Observations have been made of the photo- and cathodo-luminescence of solid solutions of traces of salts of samarium, europium, thulium, dysprosium, terbium, neodymium, praseodymium, yttrium, and erbium in calcium fluoride, calcium oxide, borax (bead), sodium phosphate (bead), sodium fluoride (bead), and alumina, and the luminescence spectra have been roughly mapped by means of a hand spectroscope. Solutions in calcium oxide are more brilliantly luminescent than those in any other solvent, and give spectra in which the bands are very bright and line-like. Many cases are noted of the tendency of certain activators to suppress the luminescence due to other elements present in the solvent. Thus, the samarium spectrum is invariably given by solutions of neodymium, assumed to contain infinitesimal quantities of samarium, in calcium oxide. The bands in the spectra of solutions containing traces of thulium, europium, terbium, and samarium may be arranged in sets having a common and constant frequency interval, found to be 18 for europium and 16 for thulium, terbium, and samarium. There are one or more sets of positions in the spectrum which are characteristic of a given activator, and whatever the solvent, all the luminescence bands of substances containing the activator in question are so located that their crests coincide with these positions. This relationship, first established for the spectra of solid solutions containing uranium, is designated as the "principle of essential identity." L. L. Bircumshaw.

Luminescence of potassium vapour in the electrodeless discharge. G. Balasse (Bull. Acad. Roy. Belg., 1926, [v], 12, 193—201).—Wave-lengths below 4427·314 Å. emitted by potassium vapour under the influence of the electrodeless discharge are recorded. With rise in temperature, the luminescence changes in colour, and both limits of the spectrum move towards the infra-red, whilst at a certain temperature modifications appear in the spectral lines, indicating that two types of luminescence are occurring simultaneously. One of these gives the arc spectrum, the other one the spark spectrum. R. Cuthill.

Spectra of phosphorescent flames of carbon disulphide and ether. H. J. Emeléus (J.C.S., 1926, 2948—2951).—The spectra of the cool phosphorescent flames of carbon disulphide and ether have been compared with those of their normal flames. For carbon disulphide, the difference is mainly one of distribution of intensity, although a group of closely-spaced bands between 3400 and 2900 Å. was not observed in the low-temperature flame. The phosphorescent ether flame gives a band spectrum totally different from the normal one. Examination of the corresponding wave-numbers shows the existence of nearly constant differences, indicating that this spectrum has a normal structure. M. S. Burr.

Photo-electric effect in natural blue rock-salt. R. Hilsch and R. Ottmer (Z. Physik, 1926, **39**, 644—647).—The photo-electric conductivity of the rock-salt was measured when the crystal was illuminated with light ranging from 186 to 2000 μμ; curves are given showing the absorption coefficient over this range and the induced conductivity. E. B. Ludlam.

Dielectric constant of solutions of good conducting electrolytes. II. H. Hellmann and H. Zahn (Ann. Physik, 1926, [iv], **81**, 711—756; cf. A., 1926, 778; Physikal. Z., 1926, **27**, 636).—The electrolytes so far investigated are divided into two groups: (*a*) those exhibiting only a small decrease of dielectric constant at high concentrations, *e.g.*, hydrochloric acid, alkali chlorides, etc.; (*b*) those which show a minimum in the dielectric constant when the concentration reaches a critical value beyond which there is a rapid increase in dielectric constant with increasing concentration, *e.g.*, copper sulphate. The sulphates of other heavy metals behave similarly. R. A. Morton.

Variation of dielectric constant of benzene with pressure. L. Cagniard (Compt. rend., 1926, **183**, 873—875).—The variation of the dielectric constant of benzene with pressure has been determined under isothermal conditions up to 22 atm., by a method previously described (*ibid.*, 1926, **182**, 1528). It has been found that the dielectric constant ε varies linearly with the pressure p, and that $d\varepsilon/dp$ increases with rise of temperature. The experimental values of $d\varepsilon/dp$ have been compared with those calculated from Debye's theory of dielectrics using the equation $(\varepsilon-1)/(\varepsilon+2) \cdot d=f(T)$, where d is the density and T the temperature; considerable divergence is obtained, indicating that Debye's theory in its

original form is insufficient. The variation in $d\varepsilon/dp$ per degree is of the same order as that calculated from the theory. S. J. GREGG.

Colour of the ruby [and the sapphire]. C. W. STILLWELL (J. Physical Chem., 1926, **30**, 1441—1466).—The conditions under which chromic oxide imparts colour to corundum and the state of the chromium have been studied. The red colour imparted to α-alumina by chromic oxide is not due to colloidal chromic oxide (cf. Hull, B., 1903, 28) or to the presence of a higher or lower oxide of chromium, or to a change in concentration of the chromium oxide. Correlation of colour and *X*-ray analysis affords strong evidence that it is due to a second modification of chromic oxide having the same crystal structure as the green modification and as α-alumina. The axial ratio of this second form of chromic oxide is nearer to that of α-alumina than to that of the green form, and hence the red modification tends to be produced when chromic oxide is added to α-alumina. This occurs up to a point beyond which α-alumina is unable to stabilise it. The occurrence of the red or green modification depends on the value of the axial ratio of the mixed crystal. Changes in the axial ratio can be effected by changing the chromic oxide content, and by varying the atmosphere in which fusion is accomplished for mixtures containing 30—45% of chromic oxide. The bluish-red colour of certain rubies is due to limited amount of reduction of the red chromic oxide to blue chromous oxide. The chromic oxide content of the natural ruby is approximately 2%, and the cause of colour of the natural ruby is identical with that of the artificial product. When no stabilisation of the red modification occurs, as in the case of the emerald, a green colour is obtained with very low concentrations of chromic oxide. The temporary colour change to green which occurs when rubies are heated is still unexplained.

The cause of the blue colour of the natural sapphire is discussed at length, but with no definite result. Chromium oxide (1%) can impart a typical sapphire-blue colour to a mixture of beryllium, aluminium, and silicon oxides heated in a reducing atmosphere. L. S. THEOBALD.

Systematic errors introduced into the measurement of the depolarisation of light diffused by gases by stray light. Study of some organic vapours. J. CABANNES (J. Phys. Radium, 1926, [vi], **7**, 338—344; cf. A., 1926, 559).—The values obtained by different authors for the depolarisation factor of light diffused by various gases are not concordant; reasons for this divergence are considered. Further values are given for the depolarisation factor ρ and the depolarisation limit ρ_0 of some organic vapours. A. S. CORBET.

Dispersion and molecular refraction of the alkali halides. K. L. WOLF (Ann. Physik, 1926, [iv], **81**, 637—648).—A theoretical paper which extends a previous theory of the dispersion of sodium and potassium chlorides (Herzfeld and Wolf, A., 1925, ii. 1119; 1926, 11) by associating with it the theory of deformation advanced by Fajans and Joos (Z. Physik, 1925, **23**, 1), and from considerations of the relations between the structures of the ions concerned and those of the corresponding rare gases. From Cuthbertson's data for the refractivities of hydrogen chloride, bromide, and iodide, values are calculated for the refractivities of the anions in the halides of the alkali metals; and thence the values for the molecular refractivities of these salts. The values so obtained are held to be in satisfactory agreement with the experimental data of Spangenberg (Z. Krist., 1923, 57, 494). R. W. LUNT.

Anomalous optical rotation-dispersion and magnetic rotation-dispersion of substances of which the optical dispersion of rotation is anomalous. W. PFLEIDERER (Z. Physik, 1926, **39**, 663—685).—Determinations and comparisons are made of the optical and magnetic rotation-dispersion, the absorption, and ordinary dispersion of camphorquinone in toluene, diphenylmethylenecamphor in benzene, phenylmethylenecamphor in benzene, diphenylcamphormethane in benzene, copper tartrate and sodium hydroxide in water, and the copper and ferric compounds of hydroxymethylenecamphor in ethyl alcohol. The curves show a point of inflexion where the dispersion begins to be anomalous, and with increasing concentration this point is displaced towards longer wave-lengths. Measurements of the magnetic rotation of toluene at twenty-four places in the visible region show that it is proportional to $\lambda dn/d\lambda$ (Becquerel's relation, n is the refractive index for wave-length λ). E. B. LUDLAM.

Molecular theory of rotatory power and the calculation of Verdet's constant. R. DE MALLEMAN (J. Phys. Radium, 1926, [vi], **7**, 295—315).—From an analysis of the general equation of motion of an electron when subjected to a magnetic field an expression is developed for Verdet's constant, for substances the permeability of which is approximately unity, involving three constants derived from those characterising the three restraining forces on an electron conceived in a three co-ordinate system. Similarly, the Kerr constant and the molecular refractivity, which is shown to be additive in form, are derived in terms of these three constants. By assigning a fixed number of optically effective electrons to each molecule, an expression is then obtained for Verdet's constant in terms of the Kerr constant, for media in which the molecules are assumed isotropic, whereby the three undeterminable constants are eliminated. The expression so deduced is therefore independent of any assumptions concerning the law of intramolecular forces, and is in a form readily compared with known data. A more complicated expression is then derived for media of anisotropic molecules by expressing the Kerr constant in terms of the Tyndall constant. It is shown that the correction for anisotropy in the case of nitrobenzene, which has a very large value for the Kerr constant, does not amount to more than 3%, and may therefore be neglected for most substances. By assuming that the number of optically effective electrons in *cyclo*hexane is equal to the total number of valency electrons, the value obtained for Verdet's constant agrees within 1% of that observed by Perkin. For a large number of aliphatic compounds a similar

agreement is recorded by assigning the total number of valency electrons in the molecule less four as the number of optically effective electrons. Similarly, by assigning fifteen effective electrons to the benzene nucleus and normal values to substituent groups a similar concordance between observed and calculated values of Verdet's constant is obtained for a large number of benzene derivatives.

It is shown further that an approximate agreement, which is considered satisfactory in view of the difficulty of experimental determination, is obtained for hydrogen, where the number of electrons is known definitely. A further consequence of this derivation of Verdet's constant is that its variation with respect to temperature, pressure, and physical states is independent of assumptions relating to the equivalence of different electrons in the molecule. Data are given showing a satisfactory agreement between the observed and calculated values of the temperature variation for carbon disulphide.

It is shown that the ratio of the magnetic rotatory dispersion to electric double-refraction dispersion is equal to the ratio of the corresponding wave-lengths, which is in agreement with experiment for water, carbon disulphide, and camphor. By introducing the assumption that paramagnetic atoms exert a negative molecular field, the phenomena of negative magnetic rotation and of anomalous dispersion are correlated with the normal phenomena.

R. W. LUNT.

Theoretical and experimental foundations for a general stereochemistry. K. WEISSENBERG (Z. Elektrochem., 1926, **32**, 470—478).—The recent proof of a pyramidal structure for certain carbon compounds has important implications for stereochemistry. Isomerism is discussed from a very general point of view and experiments are suggested.

R. A. MORTON.

Scattering of light by the individual particles of smokes. H. S. PATTERSON and R. WHYTLAW-GRAY (Proc. Roy. Soc., 1926, **A**, **113**, 312—322).—The experiments involved the determination of the size of a particle and of the intensity of light scattered by a particle. The former was determined by the rate of fall, and the latter by comparison with a standard artificial particle. A special eye-piece is described, containing the artificial particle, which consisted of a minute sphere at the end of a glass thread. The measurements were carried out by comparing the intensity of the light scattered by a selected smoke particle with that scattered by the artificial particle, the latter being adjustable by means of a neutral wedge, calibrated so that the relative intensity at different positions could be read off from a curve. The clouds studied were of magnesium oxide, silver, mercuric chloride, and mercury. The results are not in agreement with Rayleigh's law, nor with Mie's theory. It is suggested that the scattering is modified by the close or loose packing of the units of which the larger aggregates are composed.

E. S. HEDGES.

Search for element 61. II. W. PRANDTL and A. GRIMM (Z. angew. Chem., 1926, **39**, 1333—1334; cf. *ibid.*, 892).—A criticism of the work of Harris, Yntema, and Hopkins (A., 1926, 780). The authors consider that the apparatus used for examining the *X*-ray spectrum of the rare-earth oxides was unsuitable; a vacuum tube is essential to obtain sufficient dispersion to differentiate the characteristic lines of element 61 from those of other elements, especially of bromine, platinum, and barium. Harris and his collaborators assumed the absence of these elements without conducting exhaustive tests, but the present authors state that, in their experience, traces are always present under the conditions of working described.

A. R. POWELL.

Element of atomic number 61. II. L. ROLLA and L. FERNANDES (Gazzetta, 1926, **56**, 688—694). Details are given of the principles and procedure of the fractionation methods employed in isolating the element of atomic number 61 (cf. A., 1926, 1083).

T. H. POPE.

Metallography of solid mercury and amalgams. W. ROSENHAIN and A. J. MURPHY (Proc. Roy. Soc., 1926, **A**, **113**, 1—6).—A description of experimental methods for the microscopical examination of solid mercury and of amalgams which are solid only at low temperatures. The low temperatures were maintained by means of carbon dioxide snow, usually made into a paste with acetone. A smooth surface was obtained either by casting on a glass slip or by polishing at the low temperature. The cast surfaces were satisfactorily etched by 25% hydrochloric acid (f. p. −86°), but the polished surface could not be etched, the surface behaving as though passivity were produced by the polishing. Attachments to the microscope to prevent the deposition of frost are described, and photographs of solid mercury and of amalgams of tin and thallium are included.

W. HUME-ROTHERY.

Interpretation of *X*-ray, single-crystal, rotation photographs. J. D. BERNAL (Proc. Roy. Soc., 1926, **A**, **113**, 117—160).—A discussion of the mathematical interpretation of the experimental results obtained by (*a*) the rotation method proper of *X*-ray crystal analysis, in which a small crystal is rotated at uniform speed in front of a narrow beam of homogeneous *X*-rays, and (*b*) the oscillation method, in which the revolving spindle is turned backwards and forwards at a constant speed, through a definite small angle. The determination of the size and shape of the unit cell of the fundamental lattice of the crystal, and of the indices of reflecting planes leading to the determination of the space-group are dealt with. The treatment involves the conception of the reciprocal lattice (Ewald, Z. Krist., 1921, **56**, 129). Tables and charts to save laborious calculations are included.

W. HUME-ROTHERY.

Lead suboxide. A. FERRARI (Gazzetta, 1926, **56**, 630—637).—The results of *X*-ray analysis demonstrate the existence of lead suboxide, which is highly unstable and exhibits monometric structure of the cuprite type. The dimensions of the basic cell containing 2 mols. of Pb_2O are a—5·38 Å., vol.—155·72 Å.^{3}, the corresponding density being 9·16. The value of the diameter for lead calculated from this lattice agrees with that of the non-ionised lead atom.

T. H. POPE.

Polymorphism of silicon dioxide and structure of tridymite. R. E. GIBBS (Proc. Roy. Soc., 1926, **A**, **113**, 351—367).—A review is given of the β-structures of quartz and cristobalite, and, on the assumption of the conservation of the tetrahedron of oxygen atoms around any silicon as the building unit, a structure is suggested for the intermediate form, tridymite. This is justified by *X*-ray analysis, showing that tridymite has a similar structure to ice, with 4 molecules per cell, $a=5{\cdot}03$, $c=8{\cdot}02$. The framework can be considered as a close-packed arrangement of oxygen atoms, whilst the silicon atoms occupy the spaces formed between four neighbouring oxygen atoms. The structures are probably ionic in nature. β–β transitions appear to be characterised by a change of partners between neighbouring ions, whilst the α–β transition of quartz is merely a small atomic rearrangement. The α-states are probably created by distortion of the β-forms, involving lower symmetry and possibly larger cells. α-Tridymite it orthorhombic, $a=9{\cdot}9$, $b=17{\cdot}1$, $c=16{\cdot}3$, in which the units must be polymerised groups $n(SiO_2)$. The existence of a third form, α′, of tridymite was confirmed.

E. S. HEDGES.

***X*-Ray measurements on compounds of the system soda lime–silica.** R. W. G. WYCKOFF and G. W. MOREY (Amer. J. Sci., 1926, [v], **12**, 419—440; cf. A., 1925, ii, 1146, 1161).—*X*-Ray powder photographs show that the orthosilicate Na_2CaSiO_4 is cubic, with four molecules in the unit cell and $a=7{\cdot}497$ Å. The metasilicate $Na_2Ca(SiO_3)_2$, which is also crystallographically and optically cubic, is, however, pseudo-cubic according to the *X*-ray data, with $a=7{\cdot}547$ Å. and two molecules in the cell. The metasilicate $Na_2Ca_2(SiO_3)_3$, which shows weak birefringence and lamellar twinning like leucite, is also pseudo-cubic according to the *X*-ray data. These three compounds show very nearly the same *X*-ray patterns, and they present an anomalous case similar to that of mullite and fibrolite (A., 1926, 664).

L. J. SPENCER.

Mineral component of bones. W. F. DE JONG (Proc. K. Akad. Wetensch. Amsterdam, 1926, 29, 870—872).—See A., 1926, 781.

Solidification temperatures of organic compounds. Fusion temperature and spectrograms in homologous series. J. TIMMERMANS (Bull. Soc. chim. Belg., 1926, 35, 276—283).—A discussion of the relation between the spectrograms of members of homologous series and their fusion temperature. The straight-chain molecular structure of aliphatic hydrocarbons is considered in relation to this and to related crystalline phenomena.

P. V. MCKIE.

Crystal structure of quinol. I. W. A. CASPARI (J.C.S., 1926, 2944—2948).—The crystal structure of quinol has been examined goniometrically, and also by *X*-ray rotation and oscillation photographs. The unit cell is hexagonal, and the lattice unit consists of a group of three molecules forming an asymmetric whole. This association appears to have no connexion with the molecular association in the liquid or gas phase. The results obtained are not in complete agreement with those of Becker and Jancke (A., 1922, ii, 128), who employed only the powder method.

M. S. BURR.

Production of large copper crystals. H. C. H. CARPENTER and S. TAMURA (Proc. Roy. Soc., 1926, **A**, **113**, 28—43).—Large copper crystals exceeding 4 in. in length have been prepared from polycrystalline copper strip of section $0{\cdot}5\times0{\cdot}125$ inch by the method of critical straining and heat treatment previously used for aluminium (A., 1922, ii, 69). The copper crystals, unlike those of aluminium, always contain twin crystals, which may be oriented in as many as three directions in any one crystal. There is no marked difference between the tensile strength of the large crystals and of the polycrystalline material, but the large crystals are much the less ductile, their elongation values being only about one third of those for the polycrystalline strip; this effect is due to the presence of the twin crystals, since single copper crystals prepared direct from the liquid, which are free from twins, are remarkably ductile.

W. HUME-ROTHERY.

Formation of twinned metallic crystals. H. C. H. CARPENTER and S. TAMURA (Proc. Roy. Soc., 1926, **A**, **113**, 161—182).—"Annealing twins" are produced in certain metals by straining, followed by heat treatment, during which recrystallisation and crystal growth occur, and are distinguished from "mechanical twins," produced by straining alone. The formation of annealing twins has been examined with special reference to copper and its alloys and indium. They develop by a process of boundary migration in which crystal growth and twin formation occur simultaneously, and any twin crystals existing in the old crystal grains are consumed. If proper care is taken that cast metals or alloys are free from strain, they do not develop twins on heating. Unlike mechanical twins, annealing twins are very stable thermally. Twinning planes are more stable chemically than crystal boundaries; thus at high temperatures hydrogen attacks the crystal boundaries of copper, but not the twinning planes. The principal cause of twinning is crystal growth, deformation being an indirect cause, because it results in growth on annealing. The mechanism of the atomic rearrangement is discussed, and the suggestion made that twin formation is possible only if the atomic arrangement permits twinning on the planes of densest atomic concentration. Metals crystallising in the face-centred cubic, tetrahedral cubic, or face-centred tetragonal lattices readily produce annealing twins (aluminium being an exception), but not those crystallising in the close-packed hexagonal lattice, and what are called twins in the last-named are probable examples of parallel growth.

W. HUME-ROTHERY.

Properties of electrolytic iron. G. P. FULLER.—See B., 1926, 949.

Specific vibrations of tetrahedral molecules (sulphate ion). K. ROLAN (Z. Physik, 1926, 39, 588—600).—A formula is obtained which gives values for the polarisability and distance apart of sulphate ions in sulphate crystals, using the specific frequencies for 9 μ and 16

E. B. LUDLAM.

Apparent duplication of the optic axis of calcite with Federov's plate. M. PHILIBERT

(Atti R. Accad. Lincei, 1926, [vi], 4, 300—305).—The apparent double refraction of two separate calcite plates, when examined in conjunction with a Federov plate, is found to be due to double refraction of the glass setting of the crystal. T. H. POPE.

Theory of electrical conductivity in metals. S. PROCOPIU (Bull. Acad. Sci. Roumaine, 1926, **10**, 93—95).

Resistance of metals and metal crystals at the temperature of liquid helium. W. MEISSNER (Physikal Z., 1926, **27**, 725—730).—See A., 1926, 1086.

Paramagnetism independent of temperature. [MLLE.] P. COLLET (Compt. rend., 1926, **183**, 1031—1032).—The coefficient of atomic magnetisation of manganese as obtained from measurements of the paramagnetism of solid potassium permanganate is $56{\cdot}5\times10^{-6}$ and is independent of temperature from 15° to 150°. The paramagnetism is raised by the presence of impurities. For solutions of this salt a value of 62×10^{-6} is obtained at the ordinary temperature, and this is approximately constant from 17° to 100° (cf. A., 1924, ii, 586). J. GRANT.

Longitudinal magneto-resistance effect in single crystals of iron. W. L. WEBSTER (Proc. Roy. Soc., 1926, **A**, **113**, 196—207).—The change of resistance in a longitudinal magnetic field has been measured for three directions in single crystals of iron. For the (100) axis there is no change in resistance. For the (111) and (110) axes no change in resistance occurs until a magnetic intensity of about 800 c.g.s.u. is reached; the resistance then increases with the field until magnetic saturation is approached, when the value of dR/R tends to limiting values of 0·40% and 0·28% for the (111) and (110) axes, respectively. The change is probably due to the orientation of the atoms. If in unmagnetised iron the axes of the atoms are parallel to a (100) crystal axis, but may point in either direction, then when the iron is magnetised along the (100) axis there will be reversal of some of the atoms, but without change in orientation, and consequently no change in resistance. For other directions, magnetisation produces a change in orientation and hence a change in resistance. No direct connexion exists between the change of resistance and the net change of length, for there is a large increase in length in the direction of the (100) axis (A., 1925, ii, 369). Magneto-striction is regarded as due to one or both of two effects, change of orientation, and change of structure of the atoms in the magnetic field, and the results are interpreted on this hypothesis. W. HUME-ROTHERY.

Magnetic disturbance of the superconductivity with tin and mercury. W. J. DE HAAS and G. J. SIZOO (Proc. K. Akad. Wetensch. Amsterdam, 1926, 29, 947—963; cf. A., 1926, 230, 667).—Existing measurements have been supplemented by an investigation of the hysteresis figures in longitudinal fields. The figures are very similar to those obtained in transverse fields, discontinuities being again present in the descending lines. New measurements confirm the previously given explanation of the discontinuities. The influence of temperature has been investigated. The threshold value ($H_{\frac{1}{2}}$), *i.e.*, the value of the field at which the resistance has half returned, varies with temperature according to equation $(H_{\frac{1}{2}})=h(T_s^2-T^2)$, where h is a constant characteristic of the metal and T_s the "vanishing point" of the metal. J. S. CARTER.

Ferromagnetic characteristics of stable iron sesquioxide. H. FORESTIER and G. CHAUDRON (Compt. rend., 1926, **183**, 787—789; cf. A., 1925, ii, 1159; 1926, 556).—The coefficient of magnetisation of iron sesquioxide varies with the thermal and magnetic treatment to which the sample is subjected. Starting with an oxide devoid of all magnetisation, the magnetisation–temperature curve shows an increase in the coefficient of magnetisation up to 600°; this is followed by a sharp decrease, which ends at 675°. The magnetisation–temperature curve obtained on cooling is separated from that obtained on heating below 600°, and the coefficient of magnetisation increases on cooling down to the ordinary temperature. On repeating the experiment with the same sample, a curve is obtained which is rigorously reversible and superposable on the cooling curve of the first experiment; moreover, the sample is now polarised. Magnetisation can be destroyed by heating beyond 675° and cooling in a non-magnetic field. Under the same conditions with magnetite and ferrites, a very sharp increase in the coefficient of magnetisation is obtained. M. E. NOTTAGE.

Magnetic susceptibilities of the rare earths. J. ZERNIKE with C. JAMES (J. Amer. Chem. Soc., 1926, **48**, 2827—2831).—The magnetic susceptibilities and their approximate temperature coefficients are recorded for the rare-earth sulphate octahydrates (excluding europium, dysprosium, and thulium). A comparison of the results with those of previous workers indicates that cerium may show different values in the dissolved and solid states, and that the values for holmium, terbium, and ytterbium are still uncertain. It is impossible at present to calculate magneton numbers. S. K. TWEEDY.

Optical constants of molybdenite in the ultra-violet. A. W. MEYER (J. Opt. Soc. Amer., 1926, **13**, 557—560).—By means of the crystalliptometer the optical constants of molybdenite have been measured for wave-lengths 500—330 $\mu\mu$. The apparatus and method were in general the same as those used by Weld (*ibid.*, 1922, **6**, 67), Van Dyke (*ibid.*, 917), and Graber (A., 1925, ii, 1041). Observations were made on thin cleavage surfaces of crystals perpendicular to the optical axis, at settings of 65°, 70°, and 76°, and average results for the refractive index, coefficient of absorption, and reflecting power for each wave-length setting are tabulated. The results are in satisfactory agreement with those obtained by Tyndall (Physical Rev., 1925, [ii], **21**, 162) and Coblentz (A., 1924, ii, 716). L. L. BIRCUMSHAW.

Specific heats of hydrocyanic acid. (MRS.) E. H. INGOLD (J.C.S., 1926, 2816—2817; cf. *ibid.*, 1922, **121**, 1604; A., 1926, 231).—A reply to criticisms (Partington and Carroll, A., 1925, ii, 373; Partington, *ibid.*, 1926, 784) of the author's previous communications. M. S. BURR.

Thermal data on organic compounds. IV. Heat capacities, entropies, and free energies of

n-propyl alcohol, ethyl ether, and dulcitol. G. S. PARKS and H. M. HUFFMAN (J. Amer. Chem. Soc., 1926, 48, 2788—2793).—The specific heats of the above compounds were determined in the manner previously described (A., 1925, ii, 491) over the approximate temperature range 80—290° Abs. The latent heats of fusion were (g.-cal./g.): *n*-propyl alcohol (m. p. 147·0° Abs.) 20·66; ethyl ether (m. p. 156·8° Abs.) 23·54. The calculated entropies at 25° were (g.-cal./1°) 51·2 and 67·7, respectively, and 59·2 for dulcitol, in agreement with the predicted values (A., 1926, 232, 784). The entropy of *n*-propyl alcohol glass exceeds that of the crystals by 1·89 units/mol. at the absolute zero. The calculated free energies at 25° are −44,100, −33,600, and −228,100 g.-cal., respectively. The first and third values agree with those predicted; the value for ether agrees with that calculated from the equilibrium data of Pease and Yung (A., 1924, i, 363; cf. Clark, Graham, and Winter, *ibid.*, 1926, 45). In the case of isomerides, that compound with the lowest m. p. has the largest entropy and free energy. S. K. TWEEDY.

Calculation of the molecular heats of gases from equilibrium constants. W. G. SHILLING (Trans. Faraday Soc., 1926, 22, 377—400).—By means of the reaction isochore $d(\log_e K)/dT = Q/RT^2$, where K is the equilibrium constant of a gaseous reaction; Kirchhoff's equation $dQ/dT = \Sigma C_f - \Sigma C_i = \Sigma C'$, where ΣC_f is the sum of the molecular heats of the resultants of the reaction, ΣC_i the sum of the molecular heats of the reactants, and $\Sigma C'$ the difference between these two quantities; and the equation $Q_T = Q_0 + \int \Sigma C' dT$, where Q_T is the heat of reaction at a given temperature T, and Q_0 that at the absolute zero, the molecular heats, C_p and C_v, of nitrogen, oxygen, nitric oxide, carbon monoxide, carbon dioxide, and ammonia have been calculated up to 3000° Abs. In some cases, Nernst's formulæ for the heat of reaction have been used. By careful correlation of the equilibria and specific heat data, it was possible to eliminate impossible values. The results obtained were found to be in very good agreement with the values given in Partington and Shilling's "The Specific Heats of Gases." L. L. BIRCUMSHAW.

Correction for heat exchanges between a calorimeter and its surroundings. P. E. KLOPSTEG (J. Opt. Soc. Amer., 1926, **13**, 589—595).—A description is given of a graphical method, derived from well-known calorimetric principles, for determining the corrected temperature rise in calorimetric experiments, which appears to yield results of greater accuracy than the usual methods employed. The efficiency of the method is illustrated by applying it to a series of determinations of J by Puluj's method. L. L. BIRCUMSHAW.

Solidification of helium. J. E. VERSCHAFFELT (Natuurwetensch. Tijdschr., 1926, 8, 77—81; cf. Keesom, A., 1926, 893).—The m.-p. curve does not meet the b.-p. curve, so that helium seems to have no triple point. S. I. LEVY.

M.-p. curves of optical isomerides in the camphor series. J. D. M. ROSS and I. C. SOMERVILLE (J.C.S., 1926, 2770—2784).—The m.-p. curves of the optical isomerides of a number of compounds belonging to the camphor series have been determined. Members of the three groups described by Roozeboom have been distinguished. Borneol, camphor, camphoric anhydride, bornyl hydrogen phthalate, and camphene belong to the mixed crystal group, pinene forms a simple (*dl*) conglomerate, whilst camphoric acid and *o*-methyl hydrogen camphorate give definite racemic compounds. A mathematical analysis of the curves has been given, and the experimental curves have been compared with the ideal curves based on the formulæ of Washburn and Read (A., 1915, ii, 738), and on the f.-p. laws of van 't Hoff and Raoult. Associating substances show a strong tendency to form racemic compounds, those in which association is only slight form mixed crystals, whilst non-associating substances form either mixed crystals or a *dl*-conglomerate. M. S. BURR.

Thermal conductivity of vitreous silica and crystalline quartz. G. W. C. KAYE and W. F. HIGGINS (Proc. Roy. Soc., 1926, **A**, **113**, 335—351).—The thermal conductivity of vitreous silica was determined over the range 60—240° by the "divided-bar" method. The value for the conductivity at 100° is 0·00338, increasing with rise of temperature with a mean change of +0·00000185 c.g.s.u. per degree. On the other hand, the thermal conductivity of crystalline quartz decreases with rise of temperature (70—105°) with a mean change of −0·00010 per degree in a direction parallel to the optic axis, and −0·000037 in a direction perpendicular to the optic axis. E. S. HEDGES.

Density of fluids. I. Relation between density, temperature, and the latent heat of vaporisation. J. H. SHAXBY (Phil. Mag., 1926, [vii], 2, 1127—1136).—From kinetic considerations, it has been shown that the density ρ of a fluid can be represented by the equation $\rho^{1/3} - \alpha T \log \rho^{1/3} = \rho_1^{1/3} - \alpha T \log \rho_0^{1/3}$, where ρ_0 is the maximum density of the substance and ρ_1 and α are constants of which $\alpha = \rho_c^{1/3}/T_c$, where ρ_c and T_c are data at the critical temperatures. It is shown also that $\rho_1^{1/3} = 1{\cdot}5\rho_c^{1/3}$ and $\rho_0^{1/3} = e^{1/2}\rho_c^{1/3}$. From these results, a reduced equation of state which contains no constants peculiar to a particular substance has been obtained. The equations hold fairly closely for liquids, but are approximate only for saturated vapours. It is shown that the internal latent heat of vaporisation can be deduced from kinetic considerations and does not depend on any inverse square law for molecular attractions, as assumed by Mills. The molecular diameters of a number of gases have been calculated from the maximum densities. These values are not in good agreement with those determined from viscosity measurements. A. E. MITCHELL.

Density of calcium carbonate hexahydrate. J. HUME and B. TOPLEY (J.C.S., 1926, 2932—2934).—The density of crystals of calcium carbonate hexahydrate, prepared by precipitation with carbon dioxide from calcium oxide dissolved in sucrose solutions at 0°, has been obtained by two different methods. When determined dilatometrically, by measuring the expansion on decomposition, the density at 0° is 1·834, with an average deviation of 0·43%.

The value obtained directly, by displacement of the mother-liquor of the crystals in a specific-gravity bottle, is 1·817, with an average deviation of 0·60%. These values are higher than those obtained by any other investigators. By preparing the crystals from a 10% instead of a 20% sucrose solution, no appreciable difference in density is obtained. M. S. BURR.

Vapour pressures, densities, and some derived quantities for acetone. W. A. FELSING and S. A. DURBAN (J. Amer. Chem. Soc., 1926, **48**, 2885—2893).—The vapour pressure of acetone over the range −70° to +65° is expressed, with an accuracy of at least 0·1 mm. of mercury, by the relation $\log_e p = -2986{\cdot}21241/T + 20{\cdot}7587806 - 40{\cdot}8472641 \times 10^{-4}T + 42{\cdot}6623920 \times 10^{-6}T^2$, where p is expressed in mm. (1/760 normal atm.), and T in degrees absolute. The density of acetone, between −90° and +52°, is given to within 1 in 3000—4000 by the relation $d = 1{\cdot}091301 - 92{\cdot}722 \times 10^{-5}T - 32{\cdot}331 \times 10^{-8}T^2$. The solubility of carbon dioxide in acetone between −75° and +20° is given by the relation $\log_{10} S = 2615{\cdot}017/T - 18{\cdot}085436 + 66{\cdot}55546 \times 10^{-3}T - 79{\cdot}07114 \times 10^{-6}T^2$, where S is expressed in g.-mol. per 1000 g. of acetone when the partial pressure of carbon dioxide is 760 mm. From the vapour pressure–temperature relation given, the heats of evaporation of acetone at different temperatures can be calculated by means of the Clausius–Clapeyron equation. F. G. WILLSON.

Vapour pressure of naphthalene at low temperatures. (MISS) M. R. ANDREWS (J. Physical Chem., 1926, **30**, 1497—1500; cf. A., 1923, ii, 327).—The vapour pressure of naphthalene has been determined over the temperature range −50° to 70° by a modification of Knudsen's method (Ann. Physik, 1909, [iv], **29**, 179), and also a method involving the use of a vibration gauge in which a quartz fibre is replaced by molybdenum. The results given by the two methods are in fair agreement, and the vapour-pressure curve is represented by the equation $\log_{10} P = -4000/T + 12{\cdot}275$ (mm.), which gives a value of 18,280 g.-cal./mol. for the heat of evaporation. It is concluded that every molecule of naphthalene striking a surface of tungsten carbide is decomposed into carbon and hydrogen (cf. *loc. cit.*).

L. S. THEOBALD.

Production of high vacua by using metals of low volatility, especially tungsten. (FRL.) M. A. SCHIRMANN (Physikal. Z., 1926, **27**, 748—751).—A general review of the conditions governing the production of high vacua by absorbing gases on surfaces of metals of high volatility, produced, *e.g.*, by the distillation of the metal from a glowing filament to the walls of a vessel. The efficiency of tungsten is discussed with reference to the formation of tungstic oxide, tungsten nitride, and tungsten carbonyl, which are solids of low vapour pressure. R. W. LUNT.

Surface tension of liquid neon. A. T. VAN URK, W. H. KEESOM, and G. P. NIJHOFF (Proc. K. Akad. Wetensch. Amsterdam, 1926, **29**, 914—916).—With the same apparatus as used for helium (A., 1926, 568), the surface tension of liquid neon has been examined. The molecular surface tension varies linearly with the temperature, Eotvos' constant being 2·1.

J. S. CARTER.

Electrocapillary curve near its maximum. O. K. RICE (J. Physical Chem., 1926, **30**, 1501—1509).—Theoretical. Previous investigators (Frumkin, A., 1920, ii, 578; Chapman, Phil. Mag., 1913, [vi], **25**, 475) in this field have considered the charge to reside on the surface of the mercury, but calculations made on this basis do not agree with experimental results. It is now suggested that there may be a diffuse layer of positive particles and electrons in the mercury as well as the diffuse layer in the solution, and further that, owing to their finite size, ions can approach only within a certain distance of the surface. The difference in surface tension referred to the surface tension of the maximum of the electrocapillary curve may be equal to the sum of the differences which would be caused by the diffuse layer in the solution and that in the mercury for any given *P.D.* across the respective layers. The distribution of the potential drop can also be found. The values of the surface tension calculated in both ways are similar and they agree better with the experimental data. L. S. THEOBALD.

Viscosity of copper and its alloys. J. COURNOT and R. PAGÈS (Compt. rend., 1926, **183**, 885—886).—The viscosities have been determined by a modification of the method previously described (B., 1925, 994) at temperatures up to 700°. It has been verified that there exists a limiting viscosity, and that for slightly greater loads the velocity of flow assumes a constant value, the time required to attain this state being longer the lower the temperature. The experiments at high temperatures have been continued up to the point of rupture, which is preceded by a sudden increase in the rate of flow. The curve limiting viscosity–temperature for the brasses is similar to those for steel; that for copper, however, is approximately rectilinear. S. J. GREGG.

Effect of temperature on the viscosity of air. F. A. WILLIAMS (Proc. Roy. Soc., 1926, **A**, **113**, 233—237; cf. A., 1926, 234).—A reply to criticism by Rankine (*ibid.*, 671). The author's low-temperature results were obtained by an extension of the graph for higher temperatures to Millikan's value (Ann. Physik, 1913, **41**, 759) for the ordinary temperatures; the high-temperature results are confirmed by the work of Fisher (Physical Rev., 1909, **28**, 73). The author's experimental methods are vindicated. W. HUME-ROTHERY.

Dielectric constants of mixtures of organic liquids. R. N. KERR (J.C.S., 1926, 2796—2804).—Mixtures of benzene with methyl benzoate, ethyl benzoate, phenetole, ethyl cinnamate, dimethylaniline, chlorobenzene, bromobenzene, aniline, benzaldehyde, nitrobenzene, benzyl alcohol, and *m*-cresol were examined. Those mixtures which approach most closely to ideal solutions obey Silberstein's volumetric rule, viz., $\varepsilon = (\varepsilon_1 v_1 + \varepsilon_2 v_2)/(v_1 + v_2)$, with fair accuracy. The marked deviations shown by the mixtures of benzene with aniline, benzaldehyde, *m*-cresol, benzyl alcohol, and nitrobenzene, which have curves (ε-volumetric composition) convex to the concentration axis, are attributed to association. With several non-associating mixtures (*e.g.*, benzene–dimethylaniline), the values of ε are slightly greater

than those required by the volume rule. Calculation, from surface tension data, of the relative internal pressures of the components supports the hypothesis that this divergence is due to the different environment of the molecules in the mixture from that in the pure state. A number of mixtures of ethyl ether with benzene derivatives have also been examined, and in the case of mixtures with aniline and chlorobenzene, the curves are concave to the concentration axis. It is inferred that the effect of association on the dielectric constant depends on the nature of the complex formed, this being determined by the sizes of the dipoles and their geometrical positions in the participating molecules. This view is supported by results obtained with aniline–*m*-cresol and acetone–chloroform mixtures. L. L. Bircumshaw.

Double decomposition in absence of a solvent. A. G. Bergmann (Z. anorg. Chem., 1926, **157**, 83—116).—The heating and cooling curves of various fused binary salt mixtures have been studied. The factors involved in the occurrence of double decomposition in such systems are: the degrees of ionisation and heats of formation of reactants and resultants, the heat of reaction, the formation of complex compounds, and the miscibility of the components. Feebly-ionised salts, such as the mercuric halides, show little tendency to enter into double decomposition. Mixtures of the nitrates with the halides of the metals of the alkalis and alkaline earths apparently behave like reciprocal salt-pairs. The following double salts appear to exist in fused mixtures of their components: $TlNO_3,HgCl_2$; $2TlNO_3,HgCl_2$; $TlNO_3,HgBr_2$; $AgNO_3,HgI_2$; and $2AgNO_3,HgI_2$. The first three compounds can be crystallised from aqueous solutions. R. Cuthill.

Azeotropism, particularly of binary systems with chemically related constituents. M. Lecat (Compt. rend., 1926, **183**, 880—882).—It is shown by reference to a table of data that close chemical relationship between the constituents is unfavourable to, but not exclusive of azeotropism. Both chemical dissimilarity and molecular association are favourable to azeotropism, especially if present in only one constituent; if both factors are present together, the difference between the azeotropic b. p. and that of the less remote constituent may amount to 12°. Various other relationships are briefly discussed. S. J. Gregg.

Preparation and hydrolysis of esters by the distillation method. I. L. Gay, P. Mion, and M. Auméras (Bull. Soc. chim., 1926, [iv], **39**, 1329—1349).—A theoretical consideration of mixtures showing a single minimum b. p. R. Brightman.

Internal friction of molten metals and alloys. II. Method of measurement, and internal friction of bismuth–tin alloys and of the alloy Cu_3Sn. F. Sauerwald and K. Topler (Z. anorg. Chem., 1926, **157**, 117—137).—The experimental method has been improved, as a result of which it is found that the viscosity values previously recorded (A., 1924, ii, 553) are all about 3% too small. Measurements of the internal friction of alloys of bismuth and tin have failed to give any indication of the existence of the compounds $BiSn_2$ and Bi_2Sn mentioned by Plüss (*ibid.*, 1916, ii, 294). The temperature–viscosity curve for both the pure metals and their alloys is convex to the temperature axis, the convexity being least for bismuth. The viscosity of the alloy Cu_3Sn, measured at 804°, is unusually large. R. Cuthill.

Serial solubility of some rare-earth bromates. J. Zernike and C. James (J. Amer. Chem. Soc., 1926, **48**, 2871).—A mixture of some rare-earth bromates was fractionally crystallised at 20—25°, and each fraction separated into the elements of the yttrium and cerium groups. The elements were arranged in the following order of decreasing solubility: erbium, lanthanum, yttrium, holmium, praseodymium, dysprosium, neodymium, terbium, gadolinium. The order probably depends on the temperature of crystallisation, and preliminary solubility determinations indicate that below 20—25° neodymium comes between terbium and gadolinium. S. K. Tweedy.

Solubility influences. II. Effect of various salts on the solubility of ethyl acetate in water. S. Glasstone, D. W. Dimond, and E. C. Jones (J.C.S., 1926, 2935—2939; cf. Glasstone and Pound, A., 1926, 18).—The solubility of ethyl acetate has been determined at 25° in aqueous solutions of varying concentrations of sodium, potassium, and ammonium nitrates, ammonium acetate and oxalate, potassium fluoride, chlorate, and chromate, calcium, strontium, barium, and lead nitrates, barium and cupric chlorides, sodium, potassium, magnesium, nickel, copper, and zinc sulphates, and potassium ferro- and ferri-cyanides. Assuming the salting-out power of the iodine ion to be zero, the "hydration numbers" per equivalent of various ions at infinite dilution are deduced. It is found that, in general, the salting-out power of an ion is greater the greater the valency and the smaller the size. It is suggested that the hydration number of an ion is a measure of the intensity of the electrostatic field surrounding the ion, the more intense the electrical field produced by the ions of the added salt the greater being the salting-out power of those ions. Abnormal results are given by nitrates, which have a negligible salting-out power, and, particularly in dilute solutions, tend to increase the solubility of the neutral substance. There appears to be no connexion between the hydration of a salt in solution and its tendency to form stable solid hydrates, since the hydration effect of sodium sulphate in 7·5% solution is the same both below and above the transition temperature of the decahydrate. L. L. Bircumshaw.

Solubility influences. III. Salting-out effect of mixtures on aqueous solutions of ethyl acetate. S. Glasstone, D. W. Dimond, and E. R. Harris (J.C.S., 1926, 2939—2943).—Measurements have been made of the influence of the following mixtures on the solubility of ethyl acetate in water at 25°: dextrose and sucrose, lævulose and sucrose, sucrose and sodium chloride, sodium and potassium chlorides, sodium and ammonium chlorides, potassium and ammonium chlorides, lithium and sodium chlorides, barium and sodium chlorides, potassium and cupric chlorides, and sodium and potassium nitrates. For small concentrations, the effect of the mixture is

almost equal to the sum of the effects of the constituents, taken at a concentration, relative to water, equal to that in the mixture, whilst at higher concentrations each salt has a salting-out capacity which it would have in a pure solution at a concentration corresponding with the sum of the constituents. This is attributed to electrical interaction between the two substances. Erratic values are given by the nitrates (cf. preceding abstract). The results obtained for the mixtures of potassium and cupric chlorides show that, contrary to expectation, salting-out cannot be utilised for the detection of complex-ion formation. L. L. BIRCUMSHAW.

Influence of dissolved salts on the mutual miscibility temperature of the systems ethyl alcohol or methyl alcohol–paraffins. E. J. HOWARD and W. H. PATTERSON (J.C.S., 1926, 2787—2791; cf. Carrington, Hickson, and Patterson, A., 1926, 18).—A continuation of previous work. The changes in the temperature of complete miscibility caused by the addition of various salts to the systems (1) ethyl alcohol–paraffin (b. p. 160—180°) and (2) methyl alcohol–hexane are recorded. In (1), the order of the univalent cations is nearly the same as, and in (2) is still nearer, that for aqueous solutions. The order of the anions in (1) is nearly the reverse of that for aqueous solutions, whilst in (2) intermediate values are obtained. For both systems, the effect of the anions is greater than that of the cations. Univalent ions cause a greater rise than bi- or ter-valent ions in both systems, although in (2) the effect of uni- and bi-valent ions is almost identical. The tests for complexity or association in aqueous solution are applicable to alcoholic solutions. Abnormality is shown by zinc, cadmium, and mercuric halides and mercuric cyanide. L. L. BIRCUMSHAW.

Miscibility tests of dilute solutions of chromic chloride hexahydrates. J. E. HOWARD and W. H. PATTERSON (J.C.S., 1926, 2791—2796; cf. preceding abstract).—Measurements have been made of the rise in critical solution temperature caused by the addition of violet hexa-aquochromic chloride, and green dihydrated dichlorotetra-aquochromic chloride, to the following liquid pairs: water–butyric acid, water–*iso*butyric acid, water–phenol, and ethyl alcohol–paraffin (b. p. 160—180°). Butyric and *iso*-butyric acid systems give identical results. In aqueous solutions up to a concentration of 0·05 g.-mol. of salt per 1000 g. of total solution, the rise in critical solution temperature due to the violet salt is nearly double that due to the green, the ratio becoming gradually less above this concentration. Curves are given showing the rate of change of the green to the violet salt in aqueous solution. In ethyl-alcoholic solutions the green salt causes a greater rise in critical solution temperature than the violet. The results both in aqueous and alcoholic solution support the Werner co-ordination theory, and are at variance with the views of Britton (A., 1925, ii, 1203), who postulates the existence in the green solution of basic aggregates essentially colloidal in nature. L. L. BIRCUMSHAW.

Occlusion of gases by metals and alloys in liquid and solid states. K. IWASÉ (Sci. Rep. Tôhoku Imp. Univ., 1926, **15**, 531—566).—The occlusion of gases by solid and liquid metals has been studied by direct determinations of the volumes of gas absorbed by the metals at various temperatures and 1 atm. pressure. Hydrogen is absorbed by iron from a relatively low temperature, and the solubility increases linearly with the temperature both for the α- and γ-forms, but there is a marked break in the absorption graph at the transformation temperature (910°), the temperature coefficient being greater for the γ-form. The volume absorbed per 100 g. at $t°$ is given by $V=1{\cdot}685+0{\cdot}016(t-200)$, and $V=13{\cdot}445+0{\cdot}1293(t-910)$, for α- and γ-iron, respectively. With steels and cast irons, the solubility diminishes with increasing carbon content, and increases at the m. p. Hydrogen is also dissolved by copper, zinc, antimony, tin, aluminium, silumin (12% Si, 88% Al), and bronze; the absorption for both liquid and solid states increases linearly with temperature, and increases discontinuously at the m. p. Nitrogen is not dissolved by zinc, tin, antimony, or solid copper. It is soluble in iron, but much less soluble than hydrogen; the general form of the absorption–temperature graphs is the same. Cast iron, on the contrary, dissolves more nitrogen than hydrogen. Liquid copper dissolves nitrogen, but the solubility is much less than that of hydrogen. The solubility of nitrogen in aluminium is about the same as that of hydrogen, but with silumin the solubility of nitrogen is less than that of hydrogen; carbon monoxide and dioxide are not absorbed by zinc, antimony, or tin; with solid copper, the absorption of either gas is slight and increases with temperature, but in liquid copper the solubility is greater and diminishes with rise of temperature. With iron, steel, or cast iron, simple occlusion of these gases does not occur, owing to the reaction $2CO \rightleftharpoons CO_2+C$ taking place. From the equilibrium diagram, the composition of mixtures absorbed without change of composition was determined, and simple occlusion of these mixtures was studied. The solubility of the mixed gas decreases with rise of temperature. W. HUME-ROTHERY.

Adsorption of alkali chlorides in aqueous solutions by active carbon. N. ZELINSKY and A. BALANDINE (Bull. Soc. chim., 1926, [iv], **39**, 1508—1515).—The adsorption of alkali chlorides from solutions ($N/10$—$N/160$) by active carbon at 16—18° follows the order: $HCl>LiCl>NaCl<KCl<RbCl<CsCl$ and $NaCl<RbCl<HCl$. The results conform to Freundlich's adsorption isotherm. Experiments with rubidium chloride show that with a given active carbon the amount of salt adsorbed is greater when the carbon is almost powdered. Calcination of the carbon has little effect on the adsorption of hydrochloric acid from solution. Lithium iodide is adsorbed to a greater extent than the chloride at equivalent concentrations (cf. Schilov and others, A., 1922, ii, 350). The experiments indicate that the adsorptive power of a carbon for these salts is not directly connected with its activity. S. K. TWEEDY.

Identity of Langmuir's adsorption equation with the law of mass action. D. I. HITCHCOCK (J. Amer. Chem. Soc., 1926, **48**, 2870).—The simple Langmuir adsorption equation, $q=abp/(1+ap)$, where

q is the amount of gas adsorbed at the equilibrium pressure p, a and b being constants, is deduced from the mass action law, showing that agreement of experimental data with the equation does not determine decisively whether the reaction is one of adsorption or chemical combination. Rinde's conclusion that the reaction between gelatin and hydrochloric acid is not a chemical process is thus rendered invalid (cf. A., 1926, 347). S. K. TWEEDY.

Chemical sorption. II. Sorption and heterogeneous chemical equilibrium. S. LIEPATOV (Z. anorg. Chem., 1926, **157**, 22—26).—The results previously obtained (A., 1926, 571) for the sorption of bases from salts can be satisfactorily accounted for by treating the process as the distribution of a base between two acids and applying the mass law. Experiments on the sorption of bases from basic colouring matters by gels of an acid nature yield analogous results. R. CUTHILL.

Manifestation of interfacial forces in dispersed systems. A. DE WAELE (J. Amer. Chem. Soc., 1926, **48**, 2760—2776).—A qualitative discussion of the interfacial forces in dispersed systems. Three cases arise according as the "spreading coefficient" (Harkins and Feldman, *ibid.*, 1921, **43**, 2665) is positive, zero, or negative. In the first case, the adhesion between the phases is greater than the cohesion, so that the particles of the disperse phase mutually repel. In this case, a positively-held layer is attached to the particles. The second case represents an equilibrium state, the disperse particles having a loosely-held layer. The particles in the last case have no layer, and mutually attract. In a disperse system at rest, the interfacial tension manifests itself in orienting the molecules of the continuous phase normally to the interface. Application of tangential shear to the system causes disturbance of the transversal orientation in a direction tangential to the surface of the dispersed particles, the subsequent rate of re-orientation of the lines of force after removal of the shear being an inverse function of the viscosity of the continuous phase. These ideas are utilised in discussing some well-known phenomena, *e.g.*, lubrication, sintering, sherardising, drying of printers' ink, etc. S. K. TWEEDY.

"Intertraction." N. K. ADAM (Proc. Roy. Soc., 1926, **A**, **113**, 478—479).—The experiments of Wright (A., 1926, 901) have been repeated and some further observations made. The effect described by Wright is produced even more clearly by replacing the albumin by magnesium sulphate, and sodium chloride by hydrochloric acid. The experiments support the former views of Adam and Jessop (*ibid.*, 1925, ii, 772), and indicate that the phenomenon of "intertraction" has not been proved to exist. E. S. HEDGES.

Metal films reduced on the surfaces of silica gel. L. H. REYERSON, O. E. HARDER, and L. E. SWEARINGEN (J. Physical Chem., 1926, **30**, 1623—1627).—Metallised silica gels have been examined by X-ray analysis. Whenever adsorbed hydrogen is used for the reduction to metal, as in the method of Latshaw and Reyerson (A., 1925, ii, 412), the deposited films are too thin to give diffraction patterns, but impregnation of the silica gel by metallic salts or acids such as chloroplatinic acid gives metal aggregates, which afford X-ray patterns when reduced by hydrogen or by heating. Photographs of silica gel metallised by platinum, copper, and palladium are reproduced. L. S. THEOBALD.

Electrostatic theory of anomalous liquids. J. J. BIKERMANN (Physikal. Z., 1926, **27**, 710—711).—From equations relating surface tension to the electric field at an interface and to the dielectric constant of the medium, the ratio of the potential across the interface to $\varepsilon-1$ (ε = dielectric constant) is evaluated for methyl, ethyl, and n-propyl alcohols at various temperatures. The ratio is independent of temperature for each alcohol, in agreement with the theories of Coehn and Raydt (Ann. Physik, 1909, [iv], **30**, 797). R. W. LUNT.

Motion of organic substances on water and other liquid surfaces. C. W. ZAHN (Rec. trav. chim., 1926, **45**, 783—791).—The "camphor movements" exhibited by a large number of substances on the surface of water and their influence on the surface tension of the liquid have been examined. The substances which move are all found to lower the surface tension; those which do not move either raise the surface tension or affect it but little. The motion, which never occurs on the surface of a saturated solution of the substance, is attributed to the preliminary formation of a boundary layer on the surface, which spreads with unequal velocities in different directions. Motion does not occur on a liquid–liquid interface where there is already an oriented boundary layer (*e.g.*, *iso*amyl alcohol–water), but it does occur where such orientation is not already present (*e.g.*, ethylene dibromide–water). Substances which move are positively adsorbed, and their molecules are of an unsymmetrical type. G. M. BENNETT.

Sensitive electrical precision apparatus for the determination of the b.-p. elevation. J. N. PEARCE and M. M. HICKS (J. Physical Chem., 1926, **30**, 1678—1682).—The apparatus of Washburn and Read (A., 1919, ii, 447) has been modified by the introduction of electrical heating and of a thermocouple to replace the Beckmann thermometer. The curve for naphthalene in benzene (data not given) was identical in form with that obtained by Washburn and Read. L. S. THEOBALD.

Cobalt chloride solutions. III. Absorption spectra. IV. Sodium and cobalt chloride solutions. C. MAZZETTI (Gazzetta, 1926, **56**, 589–594, 595—600; cf. A., 1925, ii, 209, 210).—III. Results are given of a spectroscopic examination of aqueous cobalt chloride solutions containing various other chlorides and of solutions of cobalt chloride in methyl, ethyl, propyl, and butyl alcohols. The spectra of the pure aqueous solution and of the solutions containing sodium or barium chloride are characterised by the so-called principal band with its centre at about 5100 Å. For solutions containing hydrogen chloride or aluminium chloride, the spectra show a series of bands in the red with centres at approximately 6120, 6260, and 6580 Å. Intermediate behaviour is shown by solutions containing magnesium or calcium chloride, the principal band being accom-

panied by a secondary band nearer to the red end of the spectrum. These bands in the red are apparently due to the formation of a complex, probably $CoCl_4^{--}$, more or less solvated.

The higher alcohols examined exhibit the effect known as bathochromy, and show increasing tendency to resolve the principal band into a series of bands. The former effect is connected with the increased mol. wt. of the solvent.

IV. The variations in the conductivity of solutions containing sodium and cobalt chlorides with temperature are said to afford evidence of dehydration, and not of scission of complex compounds. This conclusion is in agreement with that reached from a study of the absorption spectra of these solutions.

T. H. Pope.

Rotatory power of tartaric acid. L. Longchambon (Compt. rend., 1926, **183**, 958—960).—Partly polemical against Vellinger's criticism of the author's theory of the lævo-constituent of tartaric acid (A., 1924, ii, 373). The rotatory powers and dispersions of solutions of tartaric acid over a wide range of concentrations increase with decrease in concentration in the same manner. No limit is attained in the dilute solutions, which indicates that the lævo-constituent still exists in appreciable quantities or that it has a high rotatory power. The dispersion and rotatory power of tartaric acid dissolved in calcium chloride solution increase regularly with decrease in temperature from $+43°$ to $-40°$.

J. Grant.

Properties of large molecules in solution. N. Marinesco (Compt. rend., 1926, **183**, 964—966).—The mol. wt. of certain substances the molecules of which become surrounded with a perisphere of solvent cannot be measured by application of the gas laws because of the large volume which the molecules occupy. Stokes' law has been found to hold, however, and by means of a diffusion method, values of 544 and 470 for rhodamine-*B* in water and ethyl alcohol solutions, respectively, and of 1130 for rose-Bengal in water have been found. In terms of the current theory (A., 1926, 673), the ratio of the number of fixed dipoles to the surface of the large molecule is a function of the deformability of the molecule, that of a molecule containing a halogen being high.

J. Grant.

Densities of particles in smokes. H. S. Patterson and R. Whytlaw-Gray (Proc. Roy. Soc., 1926, A, **113**, 302—311).—In determining the radii of ultramicroscopic particles from the rate of fall, it is not valid to use the density of the substance in bulk, except for liquids or homogeneous solids. Particles of smoke have a loose structure possessing a density much less than that of the substance in bulk. A method was devised for measuring the density of such particles by an application of Millikan's "oil-drop" method, assuming the electronic charge instead of the density. The mean observed densities of some smokes were as follows: cadmium oxide, 0·51; silver, 0·94; mercuric chloride, 1·27; mercury, 1·7; magnesium oxide, 1·35; compared with the respective normal densities of 6·5, 10·5, 5·4, 13·6, 3·6. The Cunningham equation was used to determine the true radii of spheres having the same volume as the aggregates, and the results show that the particles are in general much larger than previously supposed. Photomicrographs of particles deposited from the clouds are in complete conformity with the results of the density measurements.

E. S. Hedges

Space distribution of colloid particles. R. Zsigmondy (Z. Physikal. Chem., 1926, **124**, 145—154).—The author's views on the number and constitution of secondary particles in colloidal solution are maintained (cf. "Kolloidchemie," 5th ed., Leipzig, 1925), in opposition to opinions incidentally expressed by Pauli and Valko (A., 1926, 901).

L. F. Gilbert.

Colloidal properties of cellulose nitrate sols in mixed solvents. A. Highfield (Z. physikal. Chem., 1926, **124**, 245—269).—Translated from Trans. Faraday Soc. See B., 1926, 579. L. F. Gilbert.

Emulsions. H. Limburg (Rec. trav. chim., 1926, **45**, 772—782).—A theoretical discussion of the conditions for the coagulation of oil emulsions from the point of view of Freundlich's theory concerning the critical velocity of the particles (cf. Smoluchowski, Z. physikal. Chem., 1918, **92**, 129). The conclusion is reached that the stabilising influence of the electric charge on a particle with respect to coagulation must become smaller with increasing conductivity of the medium. The deductions of Powis (J.C.S., 1916, **109**, 734) are rejected, and the significance of the critical point in his stabilisation curves is discussed. A difference in structure (in the widest sense of the term) between the liquid–liquid interface and the bulk of the two phases tends to hinder coagulation.

G. M. Bennett.

Application of the drop-weight method to the determination of the surface tension of colloidal solutions. W. D. Harkins (Nature, 1926, **118**, 732—733).—By modification of the usual apparatus, the accuracy of the method was increased; the drop may be held for many hours without falling.

A. A. Eldridge.

Hydrates and hydrogels. X. Detection of hydroxides in hydrogels. R. Willstatter and H. Kraut (Ber., 1926, 59, [*B*], 2541—2547).—In reply to Gutbier, Hüttig, and Dobling (A., 1926, 798), it is pointed out that the examination of pressure–temperature curves is not a suitable method for investigating the possible existence of hydroxides in gels. The portion of Gutbier's curve for stannic acid gel lying below 100° is greatly influenced by the presence of adsorbed water. Rise of temperature causes chemical changes in the stannic acid on which the presence of adsorbed water has an important influence. Again, the large number of different compounds which may be present in the gel exert a very considerable influence on the nature of the pressure–temperature curves; even in the case of definite hydrates the change of vapour tension accompanying a given change in composition is not independent of the size of the particles (cf. Hagiwara, A., 1923, ii, 234).

H. Wren.

Photophoresis of colloidal particles in aqueous solutions. W. W. Barkas (Phil. Mag., 1926, [vii], **2**, 1019—1026).—The action of light and *X*-rays on aqueous suspensions of copper, silver, gold, and

gamboge has been examined. The cloud of particles settling under gravitation moves, on the average, towards the light side of the containing vessel. The upper side of the cloud assumes a characteristic form under the action of light, the boundary becoming much more sharply defined. Similar results were obtained with *X*-rays. The drift velocities for particles near the top of the cloud have been calculated, and are shown to be greater in most cases than those found by Ehrenhaft for particles suspended in gases and illuminated by an intense beam from an ultramicroscope. A suspension of gold particles exposed to light showed an increase of mean radius of from $2{\cdot}3\times10^{-6}$ to $2{\cdot}9\times10^{-6}$ cm. Those exposed to *X*-rays showed no increase in size. A. E. Mitchell.

Influence of ageing of a sol on its coagulation. S. Ghosh and N. R. Dhar (J. Physical Chem., 1926, **30**, 1564—1570; cf. A., 1925, ii, 386).—Arsenious sulphide becomes unstable on ageing when coagulated by potassium or barium chloride, aluminium nitrate, aniline hydrochloride, or crystal-violet, the instability decreasing in the order: potassium chloride, aniline hydrochloride, crystal-violet, barium chloride, aluminium nitrate. On the other hand, the same sol becomes stable on ageing when coagulated by quinine and by strychnine hydrochlorides. The stability of ferric hydroxide towards potassium chloride, sulphate, or oxalate is unchanged by ageing, but decreases when coagulated by hydrochloric acid or aluminium nitrate. These results are discussed in the light of adsorption of ions by the sol.

L. S. Theobald.

Mechanical coagulation of cupric oxide [and FeO(OH)] sols. H. Freundlich and H. Kroch (Z. physikal. Chem., 1926, **124**, 155—180; cf. A., 1925, ii, 522).—The properties of cupric oxide hydrosol prepared by Bredig's method are described. Vigorous stirring coagulates the colloid particles. This mechanical coagulation is independent of the temperature (0—20°) and proceeds according to the equation $K=(n_0-n)/t$, where K is the velocity coefficient and n_0 and n are the concentrations at the commencement of stirring and after time t, respectively. The rate of coagulation is proportional to the square of the rate of stirring. No change of the ζ potential of the particles was observed during (mechanical) coagulation. Electrolytes, in concentrations less than certain small "threshold" values, do not affect the rate of coagulation. Salts yielding chloride, bromide, and nitrate ions have threshold values of the order of 10^5 times as great as those yielding ferro- and ferri-cyanide ions. The relative differences between these threshold concentrations are greater than those shown by the coagulation values compared against an electrolyte concentration higher than the threshold value. Hydroxyl ions have a greater influence even than ferro- and ferri-cyanide ions, as in water of p_H 7 (or greater) cupric oxide sol cannot be prepared. The p_H of the sols decreases during mechanical coagulation, whilst the conductivity increases somewhat. With electrolyte concentrations only a little higher than the threshold values, coagulation proceeds according to the formula $K=1/t\,.\,\sqrt{n_0/n-1}$. A FeO(OH) sol, prepared by oxidation of iron pentacarbonyl with hydrogen peroxide, was also coagulated mechanically.

L. F. Gilbert.

Coagulation of weakly solvated sols by acids. Wo. Ostwald (Kolloid-Z., 1926, **40**, 201—209).—The mechanism of coagulation of weakly solvated sols differs from that of strongly solvated sols, the Schultze–Hardy rule applying to the former case and the Hofmeister series being applicable to the latter. A study is made of the effect of a large number of acids on the coagulation of various sols by plotting the time for coagulation against the p_H value of the acid. If the hydrogen-ion concentration is the determining factor, every acid should give the same curve, and this is actually the case with gold sol and with Congo-red. With sols of silver sulphide, arsenious sulphide, sulphur, antimony sulphide, vanadium pentoxide, copper ferrocyanide, paraffin, and stearic acid, the curves for different acids deviate from one another, the amount of deviation increasing in the order of sol given. This is also the order of increasing stability towards coagulation by a given acid. It is noteworthy, also, that some weak organic acids have a stronger coagulative effect than an equivalent amount of hydrochloric acid. Hydrogen-ion concentration cannot therefore alone account for the coagulation of the sols, and the effect of the anion must also be considered. E. S. Hedges.

Antagonistic actions of ions in the neutralisation of sols. II. H. B. Weiser (J. Physical Chem., 1926, **30**, 1527—1537; cf. A., 1926, 242).—Ultramicroscopic examination of an arsenious sulphide sol shows that the addition of an amount of sodium chloride which represents but a small fraction of that required for precipitation results in agglomeration of the particles. In spite of the consequent decrease in stability of the sol, the higher precipitation value of barium chloride in the presence of sodium chloride is maintained, and is due mainly to cationic antagonism rather than to the stabilising influence of the chloride ion. The addition of potassium ferrocyanide to a copper ferrocyanide sol increases the stability of the sol towards electrolytes, owing to strong adsorption of the ferrocyanide ion. The precipitation curves for mixtures of (*a*) potassium chloride and ferrocyanide and (*b*) barium chloride and potassium ferrocyanide each show a maximum, which in the former case is very sharp (cf. Sen, A., 1925, ii, 664, 665). Cationic antagonism plays a minor role in the latter case.

The antagonistic action of salt pairs on protoplasm is determined by their effect on the permeability of the cell membrane, which it is suggested may have a close resemblance to a reversible colloidal sol (cf. Gurchot, A., 1926, 240). A close analogy between the action of salt pairs towards sols such as copper ferrocyanide and arsenious sulphide and the antagonistic action on the permeability, and hence on the life and growth of living cells, could then exist. L. S. Theobald.

Rhythmic, diurnal bands of gold and platinum in silicic acid gel. E. C. H. Davies and V. Sivertz (J. Physical Chem., 1926, **30**, 1467—1476; cf. Holmes, A., 1918, ii, 392).—Rhythmic, diurnal bands of red, colloidal gold have been obtained in a silicic acid gel containing 10 c.c. of 3*N*-hydrochloric acid, 10 c.c. of

water-glass (d 1·16), 0·8 c.c. of 1% gold chloride, and 0·2 g. of oxalic acid, by exposure to light passing through a grid with rhythmic apertures, followed by several days in the dark. The colour of the gold depends on the age of the gel. Freshly-prepared gel gives red gold, older gel blue, and a still older gel yellow gold. Further, reduction to the red form is more rapid in the gel than in the same mixture before setting. Photochemical after-effects occur in the system gold oxalate–silicic acid gel, light producing changes in the gold before any visible effects can be noticed.

Diurnal bands of platinum were produced in ordinary light when oxalic acid or one of its soluble salts diffused into a gel containing 10 c.c. of 3N-acetic acid, 10 c.c. of water-glass (d 1·16), and 0·8 c.c. of 1% platinic chloride. Continuous illumination for 3 weeks was accompanied by reduction, but no bands were formed. Rhythmic, diurnal bands were formed in a gel of the above composition, but containing, in addition, 0·2 g. of oxalic acid, whenever exposure through a grid with rhythmic apertures was followed by a period in darkness. The bands result from light reduction of alternate zones, followed by diffusion.

L. S. THEOBALD.

Behaviour of silicic acid gel during the drying-up process. K. KRISHNAMURTI (Nature, 1926, **118**, 843).—A question of priority (cf. Fells and Firth, A., 1926, 995). A. A. ELDRIDGE.

Swelling of collagen fibres in acids. I. Mineral acids. A. KUNTZEL (Kolloid-Z., 1926, **40**, 264—279).—Tendons from rats' tails were used for single collagen fibres. When placed in acid or alkali, these swell and become shortened in length, although in pure water this does not occur. There is a limit to the contraction—viz., 33%—but the amount of contraction in acid is a measure of the extent of swelling. Using hydrochloric, nitric, and sulphuric acids, the swelling curves, obtained by plotting the contraction against the p_H of the solution, are quite unlike any previously recorded curves. Instead of a well-defined maximum of swelling at a certain p_H value, with these fibres the swelling increases with increasing p_H, reaches a maximum, at which it remains over a wide range, and then suddenly drops to zero. This sudden break occurs at a concentration of 0·0001N, more dilute solutions not causing swelling. A factor influencing the type of curve is the excess of liquid in which the substance is immersed. Theories of swelling are discussed. The exponential law does not hold for the above cases. E. S. HEDGES.

Effect of acids and hydrogen-ion concentration and gelatin. O. GERNGROSS (Kolloid-Z., 1926, **40**, 279—286).—A *resume* of published work, especially on the isoelectric point of gelatin and the firmness of the gels. E. S. HEDGES.

acids. WO. PAULI (Kolloid-Z., 1926, **40**, 185—201).—Proteins can be divided into two groups, according to whether the system is stable or unstable at the isoelectric point. A summary is given of the behaviour of albumins in the neighbourhood of the isoelectric point with respect to viscosity, precipitability by alcohol, hydrogen-ion activity, and conductivity. The phenomena are explained on the basis of Bjerrum's theory of "Zwitterions" (A., 1923, i, 444). At the isoelectric point, the acidic properties of albumins are still more in evidence than the basic properties, although this is no longer the case when excess of acid is added. With increasing quantities of hydrochloric acid, the osmotic pressure, viscosity, activity, and conductivity of albumins rise, pass through a maximum, and subsequently fall.

E. S. HEDGES.

Influence of hydrolysis of gelatin on gold numbers and peptisation of other substances. P. B. GANGULY (J. Indian Chem. Soc., 1926, **3**, 177—186).—Gelatin containing gelatose and other earlier products of hydrolysis of gelatin is more efficient in peptising gold sols than is purified gelatin. When gelatin is boiled with water, the gold number falls to a minimum, and then rises again. Dilute gelatin sols prepared at 70° from a 1% gelatin gel gave the same gold numbers, irrespective of the dilution (cf. Elliott and Sheppard, A., 1921, ii, 720). Partly hydrolysed gelatin is also a better peptising agent for silver and lead chromates than pure gelatin. G. M. BENNETT.

Fractures of acraldehyde gels: rhythmic production of furrows. C. DUFRAISSE and P. GAILLIOT (Compt. rend., 1926, **183**, 967—969).—Regular series of lines resembling furrows are produced on the cut surface of an acraldehyde gel. Spectrograms obtained from these furrows show lines at 4358, 5461, and 5769 Å., and indicate that the greater part of the incident light is diffracted. The distances between the furrows vary slightly in a continuous fashion, but sometimes show a regular and rapid decrease, when the furrows finally converge. The nature of the furrows is probably that of fine fissures (less than 0·5μ long) on a smooth surface. It is suggested that the furrows are present in the gel before fracture, and are part of the gel structure. J. GRANT.

Permeability of collodion membranes. R. E. LIESEGANG (Biochem. Z., 1926, **177**, 239—242).—Collodion membranes possess a much greater permeability than would be expected from the findings of Michaelis and Fujita (A., 1926, 120, 349) when they are dried under tension instead of in a free state.

J. PRYDE.

Stable equilibrium of physico-chemical systems. G. HOMES (Bull. Acad. roy. Belg., 1926, [v], **12**, 20—24).—It is shown thermodynamically that if a mixture of perfect gases is in stable equilibrium at constant temperature and pressure, it is also in equilibrium at constant temperature and volume, and *vice versa*. R. CUTHILL.

Comparison of the effects of the electric spark and thermal dissociation. P. JOLIBOIS, H. LEFEBVRE, and P. MONTAGNE (Compt. rend., 1926, **183**, 784—786; cf. A., 1926, 586, 680).—The limiting dissociation of carbon dioxide depends on the pressure and on the capacity of the condenser. So long as the capacity exceeds 0·1 microfarad, an increase in pressure, or diminution in capacity, lowers the degree of dissociation, and the mode of discharge is of the symmetrical, continuous type. Under a low pressure and with a small capacity, the mode of discharge is of the unsymmetrical type with dark spaces, and it corresponds with a small dissociation. As the

pressure increases even when the capacity is still small, the symmetrical type of discharge reappears, and this is accompanied by an increase in the dissociation. A given volume of carbon dioxide at a pressure p can be brought to a degree of dissociation α by the passage of a large number of discharges of a condenser of capacity c, or by heating the gas to a certain temperature T. Consequently, any point on the diagram ($p \propto T$) corresponds with a point ($p \propto c$), and therefore a given capacity c corresponds with a temperature T on the thermal diagram, which may be called the apparent temperature of the spark. The following results may be deduced from the diagram ($p \propto c$). (1) At all pressures the apparent temperature of the spark increases with the capacity. (2) When the capacity is at least 0·1 microfarad the apparent temperature of the spark is practically independent of the pressure. For a capacity of 10 microfarads it is about 3000° Abs. (3) When the capacity is very small, the apparent temperature of the spark is much lower, but still above 2000° Abs.; its variations are not a simple function of the pressure. (4) With an average capacity, the two types of discharge alternate with one another, but for any given capacity the symmetrical type is more frequent when the pressure of the gas is greater. M. E. NOTTAGE.

Methane equilibrium. I. R. C. CANTELO (J. Physical Chem., 1926, 30, 1641—1645; cf. A., 1926, 798).—The equilibrium constants for the system $C+2H_2 \rightleftharpoons CH_4+21{,}730$ g.-cal. have been calculated for temperatures between 500° and 1100°, using the equation of Saunders (A., 1924, ii, 836), and from these, the equilibrium concentrations of methane and hydrogen for the same temperature range. These values reconcile the apparent disagreement of previous investigators (Coward and Wilson, J.C.S., 1919, **115**, 1380). Experiments at 565°, 670°, and 770° with methane as the initial system and a specially-prepared nickel catalyst are also described. L. S. THEOBALD.

Electrochemical resonance. W. A. PLOTNIKOV (Z. physikal. Chem., 1926, 124, 236—244).—From the point of view of the Nernst–Thomson rule and related theories, apparent anomalies in the degree of ionisation of electrolytes in solution are discussed. It is suggested that conditions favourable to ionisation are: (1) resonance between the oscillations of molecules or portions of molecules of solvent with those of solute: (2) resonance of the oscillations of the (potential) ions of solute molecules with those of solvent molecules. Ionisation will occur when $A=\nu h$, where A is the work of ionisation permolecule, ν is the frequency of the radiation emitted by the ionising medium, and h has the usual significance. L. F. GILBERT.

Experimental methods for determining acid concentration, hydrogen-ion concentration, and acid activity. A. LOTTERMOSER (Kolloid-Z., 1926, 40, 180—185).—A description of electrometric and colorimetric methods of measurement at present in use. E. S. HEDGES.

Actual acidity, potential acidity, and buffering. K. TAUFEL and C. WAGNER (Kolloid-Z., 1926, 40, —180).—The complete acid properties of a system can be summed up in terms of (1) "actual acidity," or hydrogen-ion concentration, (2) "potential acidity," or titration value, and (3) buffering effect. Typical titration curves are discussed, and the properties of buffer solutions are considered, particularly with reference to the control of the taste of beers and wines. E. S. HEDGES.

Hydrogen-ion concentration, hydrogen-ion activity, and the newer solution theories. L. EBERT (Kolloid-Z., 1926, 40, 169—173).—A critical review of theories of solution. E. S. HEDGES.

Hydrogen-ion concentration and pharmacological effect. A. JARISCH (Kolloid-Z., 1926, 40, 259—264).—A *résumé* of the literature concerning the influence of the hydrogen-ion concentration of the medium on pharmacological effect. A comprehensive bibliography is included. E. S. HEDGES.

Importance of hydrogen-ion concentration in pathology. H. SCHADE (Kolloid-Z., 1926, 40, 252—258).—A discussion of the changes of p_H value in blood in pathological cases. E. S. HEDGES.

Hydrogen-ion concentration and plasmolysis. S. PRÁT (Kolloid-Z., 1926, 40, 248—251).—The plasmolysis of plant cells (mainly epidermis of *Allium cepa*) was studied in sea-water of varying hydrogen-ion concentration. Natural sea-water has p_H 8·2, but by addition of acid or alkali this medium lends itself to plasmolytic investigations over the range of p_H 2—10. The results show that with sea-water of p_H 2—4 the contents of the cells were coagulated in 3—5 hrs., yet in neutral or very feebly acid solution the process took several days, or even weeks. The appearance of the precipitated mass also varies with the hydrogen-ion concentration. Hydrochloric acid and sulphuric acid are similar in their effect, but some organic acids differ. Causes affecting the influence of hydrogen-ion concentration are the previous history of the material and the presence of substances of high surface activity. E. S. HEDGES.

Acid taste and hydrogen-ion concentration. R. DIETZEL (Kolloid-Z., 1926, 40, 240—248).—A discussion of previously published work on the methods of comparing taste, and the relation between the sour taste of acids and their hydrogen-ion concentration. The sour taste is not quantitatively proportional to the strength of the acid, although the two are parallel in a qualitative way. It has been sought to relate the difference to surface tension, volatility, and effect on swelling. E. S. HEDGES.

Fermentation and hydrogen-ion concentration. A. FODOR (Kolloid-Z., 1926, 40, 234—240).—A discussion of previously published work on the effect of hydrogen-ion concentration on the rate of fermentation, and the variation of the optimum hydrogen-ion concentration with the nature of the substrate. The author's former theoretical views (A., 1922, i, 92) are further developed. E. S. HEDGES.

Effect of acids and hydrogen-ion concentration in physiology. R. MOND (Kolloid-Z., 1926, 40, 228—233).—A review of the advances made in physiology through the study of hydrogen-ion concentration in colloid systems. The buffer solutions of the blood are considered in particular. E. S. HEDGES.

Amphoteric behaviour of complex systems. I. Theoretical. II. Titration of sulphanilic acid–glycine mixtures. A. E. STEARN (J. Gen. Physiol., 1926, 10, 313—323, 325—336).—Systems consisting of two amphoteric substances in aqueous solution are discussed mathematically, and it is shown that there exists a p_H value between the isoelectric points of the separate components which is virtually the isoelectric point for the complex system. Electrometric titrations of solutions containing both glycine and sulphanilic acid give curves and virtual isoelectric points agreeing with the theoretical. General agreement is also found between experimental and theoretical results in the case of lysine–sulphanilic acid and of glycine–lysine mixtures.

W. O. KERMACK.

Hydration of dissolved sucrose and the expression of the concentration in measuring the activity of ions. I. M. KOLTHOFF (Proc. K. Akad. Wetensch. Amsterdam, 1926, 29, 885—898).—Colorimetric determinations and measurements of the *E.M.F.* of cells containing sucrose show that the apparent hydrogen-ion concentration of solutions of hydrochloric acid is increased appreciably on addition of sucrose. Assuming that hydrogen ions are hydrated and that the hydrogen electrode measures the concentration of anhydrous ions only, a possible explanation is that sucrose has a dehydrating effect on the hydrated ions. Since the colorimetrically and electrometrically determined hydrogen-ion concentrations are in excellent agreement, this explanation involves the further assumption that colour indicators are sensitive only to anhydrous ions. The fact that a corresponding increase in acidity is not observed with solutions of organic acids and that the p_H value of a buffer-mixture is practically uninfluenced by sucrose, renders the proposed explanation untenable. A more plausible suggestion is that sucrose displaces water in the solution, *i.e.*, the quantity of free water is diminished and the concentration of solute is increased. All concentrations should therefore be expressed in mols. of solute (n) in mols. of solution ($n+N$), N being the number of mols. of solvent. Expressing concentrations in this way, a slight increase in the activity of the hydrogen ion is found, which is attributed to the withdrawal of water from the system by hydration of the dissolved sucrose. The calculated hydration of sucrose, 8 ± 2 mols. of water per mol. of sucrose in M-solution, is of the same order of magnitude as that calculated from existing data on the viscosities, osmotic properties, solvent power, and rates of inversion of sucrose solutions. It is unlikely that definite hydrates exist, and it is suggested that, by reason of the affinity of sucrose for molecules of water, some of the latter are retained within the sphere of influence of sucrose molecules, the quantity of free water which remains being consequently decreased.

J. S. CARTER.

Activity coefficients of aqueous hydrochloric acid at extreme dilutions. G. NONHEBEL (Phil. Mag., 1926, [vii], 2, 1085—1090).—The *E.M.F.* at 25° of the combination H_2|HCl aq.|AgCl:Ag have been measured over the concentration range 0·00015 — 0·04M. The results are in good agreement with those of Linhart (A., 1919, ii, 444). The most probable value of E_0 derived from the results is $0{\cdot}2228\pm0{\cdot}0001$ volt, in agreement with the conclusion of Nonhebel and Hartley (*ibid.*, 1925, ii, 1061). The results indicate that the relationship between the activity coefficient and the concentration up to $0{\cdot}003M$ is given by the equation $-\log\gamma=A\sqrt{M}$, in which the constant A is equal to 0·39. The value of the constant is thus smaller than that demanded by the equation of Debye for the interionic attraction in the strong electrolyte.

A. E. MITCHELL.

Law of neutral salt action in concentrated solutions. II. G. SCHMID and R. OLSEN (Z. physikal. Chem., 1926, 124, 97—114).—A general discussion of the salt effect from the points of view of the Bronsted and Debye–Huckel theories is given. The velocity of hydrolysis of cyanamide to carbamide by 0·25N-nitric acid has been measured in presence of potassium, sodium, calcium, and magnesium nitrates at concentrations up to 6N, at a number of temperatures. The equation defining specific neutral salt effect given in the first paper (A., 1926, 474) is found to hold at all the temperatures and concentrations employed. Further, the salt effect is shown to be independent of temperature, which is not compatible with the explanation obtained by assuming it to be due to dehydration of the hydrogen ion.

H. F. GILLBE.

New transformation of cobalt, and the equilibrium diagrams of nickel–cobalt and iron–cobalt. H. MASUMOTO (Sci. Rep. Tohoku Imp. Univ., 1926, 15, 449—477).—Measurements of electrical conductivity, thermal expansion, heat evolution, and magnetisation have been made, and show that cobalt undergoes a transformation between 400° and 500°. With the purest cobalt available, the change occurred at about 477° on heating and 403° on cooling, but these temperatures are depressed considerably by traces of impurity. X-Ray analysis shows that below the transformation point cobalt has a close-packed hexagonal structure, and above it a face-centred cubic structure, both forms being ferromagnetic. On the temperature–magnetisation curves, the transformation is shown only when weak fields are used; the cause of this is discussed. Similar measurements with nickel–cobalt and iron–cobalt alloys have been made, and the equilibrium diagrams constructed for the solid state. In each case, the addition of the second metal lowers the transformation point of cobalt.

W. HUME-ROTHERY.

Separation of pure ice. J. J. VAN LAAR (Chem. Weekblad, 1926, 23, 551—552).—The purity of a solid phase separating from a system of two components is determined by the interval separating the critical pressures; if this is small, the two separate together; if it is great, one component separates in the pure condition over a wide temperature range.

S. I. LEVY.

Apparatus for the dynamic determination of dissociation pressures. Dissociation of silver carbonate. M. CENTNERSZWER and J. KRUSTINSON (Z. physikal. Chem., 1926, 124, 225—244; cf. A., 1926, 1107).—An improved apparatus for the determination of dissociation pressures by the dynamic

method is described (cf. A., 1925, ii, 803). The dissociation pressures of silver carbonate between 180° and 250° have been measured and are in good agreement with Colson's results (*ibid.*, 1901, ii, 238; 1905, ii, 304). Values calculated from the Nernst formula agree closely with those observed. The dissociation pressure of silver carbonate is influenced by the grain size. L. F. GILBERT.

Equilibrium in the binary systems diphenylamine–*p*-nitroanisole and phenol–*p*-toluidine at atmospheric and at higher pressures. N. A. PUSHIN (Z. physikal. Chem., 1926, **124**, 217—224; cf. A., 1913, ii, 852).—The temperature–pressure curves for the eutectic point in the system diphenylamine–*p*-nitroanisole and the second eutectic point in the system phenol–*p*-toluidine (75 mol. % of phenol at 1 atm.) have been investigated at pressures up to 3500 kg./cm.^{2}, by means of a method previously described (A., 1925, ii, 38). No changes in the compositions of the eutectic mixtures were observed. A thermal investigation, at atmospheric pressure, of the system phenol–*p*-toluidine confirms the existence of two forms of the compound p-$C_6H_4Me{\cdot}NH_2,Ph{\cdot}OH$, as reported by Philip (J.C.S., 1903, **83**, 814), but in contradistinction to Kremann (A., 1906, ii, 266). L. F. GILBERT.

Mixtures of antipyrine with phenylurethane and with thiosinamine [allylthiocarbamide]. C. MAZZETTI (Gazzetta, 1926, **56**, 606—611).—Investigation of these systems by the f.-p. method has proved unsuccessful owing to gaps in the crystallisability. By measurements of the viscosity, however, it is shown that antipyrine forms no molecular compound with phenylurethane, whereas, in accordance with cryoscopic determinations (A., 1919, i, 524), it forms at least one additive compound with thiosinamine (cf. Garelli and Barbieri, *ibid.*, 1906, i, 985). T. H. POPE.

Systems sodium iodide–acetone and sodium iodide–methyl ethyl ketone. A. E. WADSWORTH and H. M. DAWSON (J.C.S., 1926, 2784—2786).—The solubility relations underlying the sodium iodide method for the purification of acetone have been examined, and results obtained in agreement with those of Macy and Thomas (A., 1926, 799). At low temperatures, the stable solid phase is the complex NaI,3Me$_2$CO, which is converted into the simple iodide at 25·7°. The solubility of the complex increases rapidly with rise of temperature, whilst that of the simple salt shows a rapid fall. Methyl ethyl ketone forms a similar complex with sodium iodide, with a transition point at about −30°. The system shows great similarity to the acetone system. The conditions for purifying methyl ethyl ketone by means of sodium iodide, as deduced from the solubility curves, differ widely from those prescribed by Lochte (A., 1924, i, 1166), and it is suggested that the crystalline substance which separates out in Lochte's recommended process is really hydrated sodium iodide. L. L. BIRCUMSHAW.

Transition temperature and solubility of sodium sulphate in presence of sodium chloride or sodium bromide. F. J. NORTON and J. JOHNSTON (Amer. J. Sci., 1926, **12**, 477—483; cf. *ibid.*, 467).—The lowering of the transition temperature of sodium sulphate by sodium chloride and sodium bromide of varying concentration has been determined, and also the composition of the liquid phase at the different temperatures. Equimolecular concentrations produce equal lowering, although the reduction in solubility of sodium sulphate is not the same. By comparison with the data obtained by other investigators, it is found that sodium iodide and dextrose exhibit the same behaviour. In the case of the sodium salts, this probably means that only one new ionic species, the halide ion, has been added to a completely ionised solution. The variable effect on solubility is probably due to variations in the attraction of the added solute for water. Alcohol, sodium hydroxide, sodium phthalate, and sodium nitrate are variable in their influence on the transition temperature as well as on the solubility. Addition of sulphuric acid produces approximately the same effect on the transition temperature as addition of sodium chloride or bromide of double the molecular concentration. M. S. BURR.

System sulphuric acid–sodium sulphate–water. O. FAUST and P. ESSELMANN (Z. anorg. Chem., 1926, **157**, 290—298).—The composition of the solid and liquid phases in the above system at 0°, 29·5°, 46°, 60°, and 82·5° has been determined, the solutions containing up to 80% of sulphuric acid. The results are in fair agreement with those of Pascal and Ero (A., 1919, ii, 154). R. CUTHILL.

Solutions of the bi-ternary mixture of the chlorides and nitrates of sodium, potassium, and magnesium. F. FROWEIN and E. VON MUHLENDAHL (Z. angew. Chem., 1926, **39**, 1488—1500).—A phase-rule study at 0°, 20°, 40°, 60°, and 80° with special reference to the manufacture of potassium nitrate. R. CUTHILL.

Systems $CoCl_2$–NaCl–H_2O, $CoCl_2$–KCl–H_2O, and $CoCl_2$–$BaCl_2$–H_2O at 20°. C. MAZZETTI (Gazzetta, 1926, **56**, 601—605; cf. A., 1925, 209, 210).—In no case are double salts formed which can exist in equilibrium with the saturated aqueous solutions at 20° (cf. Engel, A., 1890, 106). T. H. POPE.

Equilibria in systems containing phases separated by a semi-permeable membrane. XVII. F. A. H. SCHREINEMAKERS (Proc. K. Akad. Wetensch. Amsterdam, 1926, **29**, 964—974).—Mathematical. Ternary systems with vapour phases are considered. J. S. CARTER.

Heat of oxidation of beryllium. C. MATIGNON and (MLLE.) G. MARCHAL (Compt. rend., 1926, **183**, 927—929).—The mean values of the heats of solution of beryllium containing negligible quantities of impurities in hydrofluoric and hydrochloric acids are 94·25 and 87·90 g.-cal., respectively. From the heats of solution of beryllium oxide in these acids, a mean value for the heat of formation of this compound is found to be 140·15 g.-cal. A list of modified thermochemical data for beryllium is appended. J. GRANT.

Correction of thermochemical data. W. SWIENTOSLAWSKI and (MLLE.) H. STARCZEWSKA (J. Chim. phys., 1926, **23**, 821—822).—The data of Valeur

(A., 1901, i, 154) have been recalculated using accurate atomic weights, and applying the corrections previously enumerated (*ibid.*, 1925, ii, 1139).

R. CUTHILL.

Heats of mixture of partly miscible couples. System methyl alcohol–*cyclo*hexane. P. MONDAIN-MONVAL (Compt. rend., 1926, **183**, 1104—1106).—The heats of mixture of various proportions of methyl alcohol and *cyclo*hexane have been measured at 18°, 29°, 40°, and 52°, the critical temperature (above which the liquids are miscible in all proportions) being 49·1°. At 52°, the curve obtained is continuous and similar to those for systems in which total miscibility occurs at all temperatures. At temperatures below 49·1°, where two layers separate for certain proportions of the constituents, discontinuous curves result. The specific heats of the mixtures are greater than those obtained by calculation from the rule of mixtures, and are 0·64 and 0·43 for methyl alcohol and *cyclo*hexane, respectively.

J. GRANT.

Heat of adsorption of carbon monoxide on a copper catalyst. R. A. BEEBE (J. Physical Chem., 1926, **30**, 1538—1544).—The integral and differential values for the heat of adsorption of carbon monoxide on a copper catalyst have been found by the method previously employed (Beebe and Taylor, A., 1924, ii, 159). The values of the former vary from 11,200 to 12,200 g.-cal. per mol. The differential values are much higher for the initial than for the later amounts of carbon monoxide adsorbed, but never less than 8000 g.-cal. per mol. Accidental poisoning of the catalyst by an unknown substance resulted in decreased adsorptive capacity, but the integral heat of adsorption increased. A similar result was obtained with hydrogen and nickel (*loc. cit.*), although Foresti (A., 1925, ii, 692) found no increase in heat of adsorption with decreasing adsorptive capacity.

It is questionable whether the points of highest energy level and greatest unsaturation in a metal surface are always the most active catalytically for every reaction.

L. S. THEOBALD.

Theory of electrolytic ions. XXXIV. Application of extrapolation method of Lorenz and Lande. R. LORENZ and J. WESTENBERGER (Z. anorg. Chem., 1926, **157**, 313—318; cf. A., 1926, 1008).—The relations between ionic mobilities discovered by Lorenz and Lande (A., 1923, ii, 9) receive further confirmation from the results of recent measurements (*ibid.*, 1926, 910).

R. CUTHILL.

Electrical conductivity of solid oxide mixtures. P. FISCHER (Z. Elektrochem., 1926, **32**, 538—543).—Previous work on salt mixtures (A., 1926, 478) has been extended to include metallic oxides. The systems examined fall into three groups: (1) salt mixtures: no regular variation of conductivity with percentage composition; (2) oxide–salt mixtures, *e.g.*, manganese dioxide and potassium bromide: the conductivity–composition curve shows a maximum; (3) oxide mixtures, *e.g.*, cupric oxide and manganese dioxide: continuous increase or decrease of conductivity with composition. Whereas in group (1) values obtained with direct current and with alternating current often show wide divergences, they agree fairly closely in the other groups.

H. J. T. ELLINGHAM.

Conductivity of stable aqua regia. E. BRINER, R. HEBERLEIN, and A. ROTHEN (Helv. Chim. Acta, 1926, **9**, 951—956).—The conductivity of the aqueous phase in the equilibrium $HNO_3+3HCl \rightleftharpoons NOCl+2H_2O+Cl_2$ (cf. Briner, A., 1916, ii, 231) has been measured, using pure iridium electrodes, equilibrium being maintained by the use of a closed cell. The values of K, 0·326—0·324 and 0·465 ohm^{-1} at 0° and 20°, respectively, are independent of the proportions and concentration of the acid mixture.

J. W. BAKER.

Electrical conductivity of mixtures of hydrochloric and sulphuric acids with orthophosphoric acid prepared in various ways. A. KAILAN and J. SCHROTH (Monatsh., 1926, **47**, 1—10; cf. Pessel, A., 1923, ii, 396).—The low conductivity found for solutions of hydrochloric or sulphuric acid with orthophosphoric acid prepared from lead pyrophosphate is shown to be due to phosphates present as impurities, the observed values agreeing with those calculated from the content of sodium salt found to be present. When the orthophosphoric acid is prepared from pure pyrophosphoric acid, the results agree with those obtained with the ortho-acid from phosphorus pentoxide. Pessel's observations on the velocities of hydration are confirmed.

G. M. BENNETT.

Potential differences at phase boundaries at which partition equilibria exist. E. BAUR and E. ALLEMANN (Z. Elektrochem., 1926, **32**, 547—550).—Improved methods are described for setting up cells of the types previously described (A., 1925, ii, 1164), whereby errors due to the presence of membranes are avoided. Revised values for these phase-boundary potentials are recorded. Measurements have now been made on cells of the type: Hg, HgCl|*N*-KCl in water (1)|*N*-KCl in amyl alcohol (2)|salt AB in amyl alcohol (3)|salt AB in water (4)|3·5*N*-KCl in water (5)|*N*-KCl in water (6)|HgCl, Hg. The *P.D.* between (2) and (3) is made zero by using a solution of the salt in (3) of such a concentration that it has the same electrical conductivity as (2). When the salt AB is a chloride, (5) and (6) are omitted. The *P.D.* at the various junctions are now either zero or capable of determination, except that between (3) and (4), which can thus be obtained from a measurement of the *E.M.F.* of the complete cell. The results are true "ionic partition potentials," and a comparison of their values for various salts suggests that each ion makes a specific contribution to such a potential, although this rule is probably not exact. The significance of these potentials is discussed.

H. J. T. ELLINGHAM.

Potential of the fluorine electrode from thermal data. W. M. LATIMER (J. Amer. Chem. Soc., 1926, **48**, 2868—2869).—From recent thermal data of von Wartenberg (A., 1926, 476) the potential of the normal fluorine electrode is calculated to be 2·85±0·04 volts at 25°.

S. K. TWEEDY.

Reduction–oxidation potentials. II. Colorimetric determination of reduction–oxidation potentials. P. HIRSCH and R. RUTER (Z. anal.

Chem., 1926, 69, 193—232; cf. A., 1926, 930).—The reduction-oxidation (R–O) potential of a solution containing a substance and its oxidation or reduction product is shown from theoretical considerations based on the ionic hypothesis and the mass action law to be a function of the ratio of the two substances present; *i.e.*, for the reversible R–O process $E_h=E_0+(0{\cdot}0577/n)\log([O]/[R])$ at 18°. Certain substances which undergo colour changes in the presence of oxidising or of reducing agents may be used as indicators for R–O potentials in the same way that certain dyes act as indicators of p_H; similarly, R–O buffer solutions of well-defined potential may be prepared for standardising the indicator solutions. The most suitable buffer solutions are mixtures of cuprous and cupric chlorides in potassium chloride solution when the acidity is greater than p_H 2·2, ferrous–ferric oxalate in sodium oxalate–oxalic acid solutions for p_H 2·7—4·2, and ferrous–ferric oxalate in citric acid–trisodium citrate solutions for p_H 5·2—6·0. The colour of methylene-blue in these buffer solutions has been fully investigated; the system methylene-blue–leuco-base is reversible in all solutions more acid than p_H 7. For a 50% reduction at 20°, the R–O potential of a methylene-blue solution decreases from +0·4206 volt at p_H 1·2 to +0·0920 volt at p_H 5·2, measured against the normal hydrogen electrode, and this fall is directly proportional to increase of p_H. A temperature change of 1° causes a change of 1 millivolt in the potential and a change of 2% in the depth of colour. To determine the R–O potential of a solution by means of the methylene-blue indicator, the p_H is first determined colorimetrically or otherwise; to 20 c.c. of the solution is added 1 c.c. of a 0·045% solution of methylene-blue, and the volume of water required to be added to a further 1 c.c. of the indicator solution to match the colour of the test solution is then determined. From this result, the colour intensity, $f/(1-f)$, is calculated and the value of A_h (a constant depending on the p_H of the solution) is read from a graph. Then the R–O potential of the solution is calculated from the equation $E_h=A_h+0{\cdot}02935\log f/(1-f)$; the result is the potential for 23°. The work of Clark and his collaborators on reduction potentials of certain dyes in equilibrium with their reduction products is discussed at length and shown to be in agreement with the theories recorded in this paper.

A. R. Powell.

Electrochemical investigations on the metallic properties of iodine. W. Finkelstein (Z. physikal. Chem., 1926, 124, 285—298; cf. A., 1925, ii, 546).—Measurements of the decomposition potentials of solutions of iodine trichloride, chloride, and bromide, and of the potentials of iodine electrodes in these solutions, have been made. The results are in accordance with the existence of iodine cations ($I^{\cdots}$ and $I^{\cdot}$). Other considerations support this view.

L. F. Gilbert.

Influence of traces of alkali or alkaline-earth metals on the normal cathode fall of potential of mercury. A. Gunther-Schulze (Z. Physik, 1926. 39, 491—494).—The cathode fall of potential is greatly reduced by minute quantities of metals of the alkalis or alkaline earths.

E. B. Ludlam.

Electrometric determination of small amounts of ferric iron. J. F. King and R. N. Washburne (J. Physical Chem., 1926, 30, 1688—1697; cf. Hostetter and Roberts, A., 1919, ii, 480).—A method is described for the determination of 0·0003—0·0005 g. of ferric iron by electrometric titration with titanous sulphate with an error of less than 0·1%. The apparatus includes an electrode of fine platinum wire (0·0085 mm. diameter) for use in hot solutions and a satisfactory means of storage of 0·0003*N*-titanous sulphate. Titrations are best carried out in 20% sulphuric acid solution and at the b. p. of the solution.

L. S. Theobald.

Overvoltage. I. Hydrogen overvoltage. T. Onoda (J. Fac. Sci. Tokyo, 1926, 1, 223—247).—The overvoltage of hydrogen at electrodes of platinum, gold, copper, or nickel depends to a considerable extent on the previous treatment of the electrode. After anodic polarisation, the value is a minimum, which is characteristic of the metal employed. With rise of temperature, this minimum decreases in a linear manner.

R. Cuthill.

Apparatus for determining oxidation-reduction potentials. J. M. Ort (J. Opt. Soc. Amer., 1926, 13, 603—608).—By means of a reduction flask and a movable burette, solutions can be reduced, stored, and transferred to the electrode chamber without contact with air during the run. Active gases are removed by flushing with nitrogen. The electrode chamber is a large pyrex test-tube, closed with a rubber stopper, and provided with a gas outlet through a mercury trap. Extending nearly to the bottom of the chamber are the platinum electrodes, the glass tube of the nitrogen inlet, and the glass tube leading to the salt bridge. The latter tube dips into a beaker of saturated potassium chloride, into which three saturated calomel electrodes also dip. At any time during a run, the electrode chamber can be raised out of, or lowered into, the oil thermostat in which readings are taken. Full details of the method of using the apparatus are given.

L. L. Bircumshaw.

Electrolytic polarisation. IV. Electrodeposition potentials of iron, cobalt, and nickel. V. Electrodeposition potentials of alloys of iron, cobalt, and nickel. S. Glasstone (J.C.S., 1926, 2887—2897, 2897—2902).—IV. Measurement of the initial deposition potentials of iron, cobalt, and nickel, at temperatures ranging from 15° to 95°, and in a series of solutions of known hydrogen-ion concentration, ranging roughly from p_H 2 to 6, shows that for each temperature the deposition potential has a definite value, depending only on the concentration of metal in the solution, and independent of the p_H of the electrolyte and of the nature of the anions present. The presence of a depolariser (*e.g.*, hydrogen peroxide) causes scarcely any change in the deposition potential. In each case, a considerable overvoltage is required to cause the initial deposition of metal, after which increase of current density produces only slight increase of polarisation. The results obtained do not appear to be in agreement with any of the theories previously advanced to account for the retarded deposition of the metals of

the iron group. As an alternative hypothesis, it is suggested that the metals are primarily deposited in a metastable form which has a different electronic arrangement from the ordinary form (perhaps 2, 8, 16, 2, as compared with 2, 8, 17, 1 for the normal form), and a different deposition potential.

V. By means of the commutator–extrapolation method of measuring the potentials of polarised electrodes, the initial deposition potentials of alloys of iron, nickel, and cobalt, in pairs or all together, from solutions of various metallic and hydrogen-ion concentrations, have been measured at 15°, 55°, and 95°. Acetate buffer solutions were used to maintain a definite p_H. The initial deposition potential is independent of the p_H, but decreases with rising temperature, and with decreasing iron ratio (in the case of the iron alloys) or cobalt ratio (in the case of nickel–cobalt alloys) in the electrolyte. With iron–cobalt and iron–nickel alloys, the deposition potential is much closer to that of pure iron than would be expected. Applying this fact to the theory previously advanced to account for the retardation of the deposition of the iron-group metals, it is shown that for a given electrolyte the proportion of iron in the deposit should increase at first rapidly with increasing current density, then more slowly, and finally reach an almost constant value. L. L. Bircumshaw.

Periodic electrochemical passivity of iron, cobalt, nickel, and aluminium. E. S. Hedges (J.C.S., 1926, 2878—2887; cf. A., 1926, 807, 1213).—A study has been made of the periodic passivation of anodes of iron in sulphuric acid, nitric acid, and phosphoric acid, of cobalt in sulphuric acid, of nickel in sulphuric acid, and of aluminium in nitric acid and in sodium hydroxide. Experiments in which a passivated anode is progressively activated, (*a*) by raising the temperature, (*b*) by diluting the reagent, and (*c*) by addition of some agent favouring the active state (*e.g.*, ammonium chloride to an ammonium sulphate solution in which a nickel anode has been made passive), support the view that periodicity ensues whenever the anode is given equal opportunities of existing in the active or passive state. Evidence in favour of the suggestion that passivity is a special case of film formation is drawn from a comparison of the behaviour of a nickel anode in 5% sulphuric acid with that of a zinc anode in sodium hydroxide. In every case investigated, passivation is immediately preceded by the formation of a visible film on the metal, which disappears at the moment the electrode assumes the passive state. L. L. Bircumshaw.

Electrolysis of molten alloys. XVII. Zinc with lead, bismuth, and cadmium, antimony with lead and bismuth, and cadmium with lead and bismuth. R. Kremann and A. Troster (Monatsh., 1926, 47, 285—293).—Experimental difficulties were met with in all cases specified except that of the bismuth–cadmium alloys. Electrolysis of these mixtures containing 25, 50, and 75 atomic-% of bismuth was maintained for 20 hrs. The exceptionally large electrolytic effect, involving accumulation of bismuth near the anode, increased with rising current density up to 5—6 amp./mm.^{2} The maximum effect, obtained with an alloy containing 50 atomic-% of bismuth, produced a difference of concentration of 65·5% of bismuth. G. M. Bennett.

Electrolysis of molten alloys. XVIII. Summary of preceding papers. R. Kremann (Monatsh., 1926, 47, 295—306; cf. A., 1924, ii, 723; 1925, ii, 132, 312, 678, etc.).—The accumulation of one constituent metal of a molten alloy in a higher concentration near the cathode during electrolysis is compared with the analogous case of gas mixtures (Skaupy, A., 1916, ii, 466, 469). For a given alloy, this effect is remarkably constant when the temperature is varied over a range of several hundred degrees, which indicates that the electrolytic transport increases with rise of temperature to the same extent as the opposed diffusion. The relatively small effect observed in certain alloys (*e.g.*, Bi–Pb) studied at high temperatures is to be attributed to the specific character of the individual metals rather than to the influence of increased diffusion. For production of the maximum effect, an alloy containing 50 atomic-% of each metal must be electrolysed with a current density of an upper limiting value for 3—24 hrs. The following series shows in descending order the tendency to migrate to the cathode: He, Ne, A, Bi, Sb, Hg, Pb, Sn, Zn, Cd, Cu, Ag, Al, Na, K. This series gives approximately the order of diminishing ionisation potentials, but the difference between the ionisation potentials of two metals is not a quantitative indication of the magnitude of the electrolytic effect. The current is carried both by liberated electrons and by the metal ion M^+. The positions of aluminium and lead in the above series are not in accord with their positions in the series of ionisation potentials, which may be due partly to the liberation of a second electron from the metal and partly to the electrolysis of intermetallic compounds M_1M_2 $M_1^+ + M_2^-$. Wherever one constituent of the alloy is of markedly metalloid character (*e.g.*, Bi, Sb), the effect of electrolysis is large. G. M. Bennett.

Electrolysis of glass. I. H. Hurter (Helv. Chim. Acta, 1926, 9, 1069—1073).—The quantity of sodium (as measured by the increase in weight of the lamp) introduced into the high vacuum of an electric light bulb in accordance with the method of Burt (A., 1925, ii, 921) is in exact agreement with Faraday's laws. Contrary to the conclusion of Burt, substitution of potassium for sodium ions occurs when the bulb is immersed in a bath of molten potassium nitrate during the passage of the current, the substitution again being in agreement with Faraday's laws; both the red potassium lines are shown by the spectrum. J. W. Baker.

Electrolysis of dichromic acid under a mercury vapour lamp of high intensity. G. S. Forbes and P. A. Leighton (J. Physical Chem., 1926, 30, 1628—1633).—Electrolysis of 0·006—0·05*N*-chromate solutions in *N*- and 3*N*-sulphuric acid between platinum electrodes has been carried out at different current densities, and the electrochemical yields in light and in the dark compared. At the illuminated cathode, 0·5% greater efficiency was observed, but part or all of this can be attributed to local heating in the thin diffusion layer at the cathode. The curves obtained by plotting electrochemical yields against

current densities show maxima and minima, explicable, for the most part, in terms of the formation of hydrogen and of hydrogen peroxide.

A quartz–mercury lamp, consuming 1500 watts and intensely illuminating a horizontal surface, is described. L. S. THEOBALD.

Apparently unimolecular reaction. Homogeneous decomposition of gaseous propaldehyde. C. N. HINSHELWOOD and H. W. THOMPSON (Proc. Roy. Soc., 1926, **A**, **113**, 221—229).—The decomposition of propaldehyde has been studied between 722° and 877° Abs. Carbon monoxide is removed from the molecule in almost theoretical amount, and the residual fragments give rise to a mixture consisting principally of methane and ethane, with small amounts of more highly-condensed products, whilst about 2% of carbon dioxide and ethylene are also formed. The relative proportion of methane increases with rise of temperature. The decomposition is a homogeneous reaction which is very nearly unimolecular at pressures above 100 mm. The velocity coefficients rise from $0{\cdot}052\times10^{-3}$ at 722° to $39{\cdot}4\times10^{-3}$ at 877° Abs. The heat of activation is 55,000 g.-cal. At 800° Abs., the number of molecules reacting is approximately 2×10^{16} per c.c. per sec. at 760 mm., whilst the number of collisions is only about 5×10^{13}. At low pressures, the unimolecular velocity coefficients appreciably diminish, but not in the manner characteristic of a bimolecular reaction (cf. following abstract). W. HUME-ROTHERY.

Theory of unimolecular reactions. C. N. HINSHELWOOD (Proc. Roy. Soc., 1926, **A**, **113**, 230—233).—It is usually supposed that the energy of activation is confined to a few degrees of freedom, in which case the chance that a molecule possesses energy in excess of E is $e^{-E/RT}$. The rate of bimolecular reactions is adequately expressed by the equation, number of molecules reacting$=Ze^{-E/RT}$, where Z is the number entering into collision. If molecules are activated by collision in unimolecular reactions and Lindemann's mechanism (Trans. Faraday Soc., 1922, **17**, 599) operates, the energy E ought in unit time to be communicated to more molecules than the number reacting, but actually many more molecules react than the expression $Ze^{-E/RT}$ allows for (cf. preceding abstract). Lindemann suggested (private communication) that there might be enough collisions for unimolecular reactions if the total energy E could be made up by any distribution among a number of degrees of freedom. Calculation shows that for propaldehyde (cf. preceding abstract) from 12 to 14 degrees of freedom would be required for this mechanism to operate; for acetone and nitrogen pentoxide, even more degrees of freedom would be required. The mechanism is thus possible only in the case of molecules of complex internal structure, in agreement with the fact that all known unimolecular changes involve molecules of complex structure, whilst bimolecular reactions, where the simple activation theory holds, usually involve simpler molecules. W. HUME-ROTHERY.

Supposed law of flame speeds. W. A. BONE (Nature, 1926, **118**, 837).—Experiments with acetylene–hydrogen–oxygen and ethylene–hydrogen–oxygen mixtures do not support the claim that Wheeler and Payman's law of flame speeds is of universal application. A. A. ELDRIDGE.

Effect of hydrogen-ion concentration on the rate of hydration of sodium pyrophosphate. S. J. KIEHL and W. C. HANSEN (J. Amer. Chem. Soc., 1926, **48**, 2802—2814).—The rate of hydration of sodium pyrophosphate, $Na_4P_2O_7+H_2O \rightarrow 2Na_2HPO_4$, was followed by hydrogen-ion concentration measurements in 0·125, 0·175, and 0·225*M*-solutions, each containing 0·350, 0·425, and 0·500*M*-hydrochloric acid. When the hydration exceeded 50%, the orthophosphate was determined by a gravimetric method with the aid of "magnesium chloride mixture." The results indicate that pyrophosphoric acid is more active than orthophosphoric acid. S. K. TWEEDY.

Inversion of sucrose by acids. H. COLIN and A. CHAUDUN (J. Chim. phys., 1926, **23**, 808—813; cf. A., 1925, i, 233).—Addition of glycerol or increase in the concentration of sugar raises or lowers the velocity coefficient of the above process according as the catalyst is a strong or a weak acid. For weak acids, the ratio of the velocity coefficients for two concentrations of acid and a fixed initial concentration of sugar is nearly equal to the ratio of the conductivities of the solutions; with strong acids, the former value is the greater. The velocity coefficient is increased by the addition of a salt of an acid other than the catalyst, whether the latter is a strong acid or a weak acid. These facts can be accounted for on the basis of the mechanism previously suggested for the inversion (A., 1926, 580). R. CUTHILL.

Esterification of malonic acid by glycerol and hydrogen chloride. A. KAILAN and J. SCHROTH (Monatsh., 1926, **47**, 63—81; cf. A., 1914, ii, 41; 1925, i, 880, ii, 49).—The esterification of malonic acid in a glycerol solution of hydrochloric acid with or without the addition of water (2/3 and 4/3 mols. per litre) proceeds according to a unimolecular law with a velocity which is proportional to the concentration of hydrochloric acid. The variation of the velocity coefficient with the varying concentration of acid and of water at 25° and 35° follows a relation of the simple type previously used for the values for malonic acid in ethyl alcohol. The effect of water in depressing the reaction velocity is much less in glycerol than in ethyl alcohol. The values of the coefficient decrease more than can be accounted for by the effect of the water produced in the reaction; this is attributed to a velocity of esterification of the first carboxyl group somewhat higher than that for the second.
G. M. BENNETT.

Stability of benzenediazonium chloride solutions. II. Reaction of benzenediazonium chloride with certain organic hydroxy-substances. H. A. H. PRAY (J. Physical Chem., 1926, **30**, 1477—1486; cf. A., 1926, 1214).—The velocity of reaction of benzenediazonium chloride with various alcohols and organic acids has been determined at 20°, 30°, 40°, and 50°. The reactions are unimolecular or pseudo-unimolecular, and the values of $0{\cdot}4343k\times10^{1}$ at 30° and 40°, respectively, are for the alcohols as follow: methyl, 53·5, 227; ethyl, 53·5,

218; *n*-propyl, 52·0, 204·2; *iso*propyl, 69·0, 288; *n*-butyl, 50, 201; *iso*butyl, 54, 208; amyl, 46·3, —; allyl, 41·7, —; benzyl, —, 153·0; and for the acids: formic, 18·6, 73·1; acetic, 18·7, 82·0; propionic, 18·9, 82·0; butyric, 23·0, 102·0; dichloroacetic, —, 53·1, and for water, 25·0, 107·0. The temperature coefficients vary markedly with temperature. The rate of reaction of benzenediazonium chloride in methyl alcohol–water mixtures is an additive function of the mol. percentage of the components of the solvent. Benzenediazonium chloride is insoluble in a large number of organic liquids with which it does not react. It is slightly soluble in furyl alcohol, pyridine, and quinoline, but the addition of water or alcohol does not cause the liberation of nitrogen in these cases. Selenium and phosphorus oxychlorides and arsenic trichloride dissolve and decompose the diazo-compound, and in the last-named case the rate of decomposition is the same as in water. Collodion has no effect on the velocity of reaction between benzenediazonium chloride and ethyl alcohol.

The theory of the mechanism of diazo-decomposition of Hantzsch is inadequate for the above results, and further, there is no simple relation between the physical properties of the solvent and the velocity of decomposition. L. S. THEOBALD.

Velocity of hydrolysis of pentaerythritol tetra-acetate. A. SKRABAL and M. ZLATEWA (Monatsh., 1926, 47, 39—56).—The hydrolysis of pentaerythritol tetra-acetate is an apparently bimolecular reaction in both acid and alkaline solution. The velocity coefficients at 25°, referred to molar concentrations of hydrogen and hydroxyl ions, respectively, are 0·00432 and 20·5. The latter figure was determined in sodium carbonate solution; the value for the reaction in sodium hydroxide solution is computed to be 26·6. The reason for the simple course of the hydrolysis of the esters of glycol, glycerol, and pentaerythritol is discussed. The following influences are distinguished, which together determine the velocity of such reactions: (*a*) depressing effect of steric hindrance, (*b*) increase of velocity with any increase of acid character of either the acid or the alcohol component of the ester, (*c*) mutual reinforcement of active groups in the molecule, and (*d*) a depression with increasing symmetry of the molecule. The case of glyceryl esters with one group in a less favourable position than the others involves a diminishing velocity of reaction, particularly in alkaline solution. The effect of migration of acyl groups is discussed. G. M. BENNETT.

Influence of the alcohol component on velocity hydrolysis of acetic esters. A. SKRABAL and [illegible] (Monatsh., 1926, 47, 17—38; cf. A., 1924, II, 1926, 1010).—The following velocity coefficients for alkaline hydrolysis (k_a) and for acid hydrolysis (k_s), respectively, have been found at 25°, the values being expressed in minutes and referred to unit molar concentration of hydrogen or hydroxyl ions: *iso*propyl acetate, 1·57, 0·00360; *tert.*-butyl acetate, 0·090, 0·00758; phenyl acetate, 82·0, 0·00469; benzyl acetate, 11·8, 0·00654. The alkaline hydrolysis of phenyl acetate was carried out with sodium phenoxide. The general question of the variation of the velocity of hydrolysis of esters with the nature of the alcohol component is discussed, and the results are compared with those obtained in the study of other reactions. G. M. BENNETT.

Velocity of saponification of mono- and di-substituted chloro- and methoxy-derivatives of ethyl benzoate. W. BLAKEY, H. MCCOMBIE, and H. A. SCARBOROUGH (J.C.S., 1926, 2863—2868).—The velocities of saponification of ethyl benzoate, *o*-, *m*-, and *p*-methoxy- and -chloro-benzoate, 2 : 3-, 2 : 4-, 2 : 5-, 3 : 4-, 3 : 5-dimethoxy- and -dichloro-benzoate have been determined in 95% and 70% alcohol–water mixtures. With one exception, the *m*-chloro- and *m*-methoxy-esters are the more reactive. The values for k for the dimethoxy-esters bear a definite relation to those of the monomethoxy-esters; for the dichloro-esters, no relationship was observed. Change of solvent changes the order of the velocity coefficients for the monomethoxy-esters. W. THOMAS.

Initial stages of dehydrogenation and isomeric change of allyl alcohol. F. H. CONSTABLE (Proc. Roy. Soc., 1926, **A**, **113**, 254—258).—When the vapour of allyl alcohol is passed over a heated copper catalyst, two simultaneous reactions occur, producing respectively propaldehyde and a mixture of acraldehyde and hydrogen. A study of the two reactions was made over the temperature range 245—280°. The rate of dehydrogenation is approximately equal to that of ethyl alcohol, and has a temperature coefficient of 1·5, whilst the isomeric change to propaldehyde is considerably faster, but has a diminished temperature coefficient of 1·16. The isomeric change is more easily catalysed by sintering the catalyst than is the dehydrogenation. It appears that there are two sets of centres of activity, one characteristic of each reaction, and it is therefore considered that true isomeric change occurs, and not rehydrogenation. E. S. HEDGES.

Corrosion of steel by acids. V. DUFFEK.—See B., 1926, 949.

Acid and salt effects in catalysed reactions. II. Minimum reaction velocities for acid–salt mixtures. H. M. DAWSON and N. C. DEAN (J.C.S., 1926, 2872—2878).—The significance of the reaction velocity minimum for acid–salt mixtures of the type C·HA–x·MA is discussed. The hydrogen-ion concentration of the minimum velocity mixture depends on the catalytic coefficients of the hydrogen and acid ions, on the dissociation constant of the acid, and on its concentration. The velocity–p_H curve is symmetrical with respect to the minimum velocity point. Results indicate that salts in aqueous solutions are completely ionised, and that the catalytic activity of a catalyst is proportional to its concentration and has no apparent connexion with the thermodynamic activity. The results are confirmed by the study of the catalytic effect of 0·05N-acetic acid + $x$$N$-sodium acetate on the rate of interaction of iodine and acetone. W. THOMAS.

Dehydration by means of acetic anhydride. J. B. MENKE (Chem. Weekblad, 1926, **23**, 552—553).—The reaction between acetic anhydride and water is accelerated by mineral acids and their salts;

hydrated salts may be rapidly and completely freed from water by addition of the anhydride.

S. I. Levy.

Role of certain metallic ions as oxidation catalysts. S. F. Cook (J. Gen. Physiol., 1926, **10**, 289—312).—Measurements have been made of the rate at which pyrogallol is oxidised by hydrogen peroxide in the presence of an iron or a copper salt as catalyst. The reaction is also catalysed, but less strongly, by salts of silver, gold, cobalt, and nickel. In the case of silver and gold salts, the reaction rate suddenly decreases and at the same time the metal separates from the solution. Although gold salts act as catalysts, colloidal gold is inert. It is concluded that the activity of metal catalysts depends on their ability to form metallic peroxides and at the same time to remain in solution. W. O. Kermack.

Autoxidation and anti-oxygens. XX. Catalytic action of another series of nitrogen compounds. General observations on nitrogen compounds. C. Moureu, C. Dufraisse, and M. Badoche (Compt. rend., 1926, **183**, 823—826).—The action of 37 nitrogen compounds in exalting or diminishing the autoxidation of acraldehyde, benzaldehyde, and styrene has been studied. The nitrosobases are the most frequently inactive or only slightly active, but the other results are difficult to summarise. Although 177 substances have so far been investigated, few general rules can yet be given. However, the presence of nitrogen in a molecule usually confers an exalting or a diminishing action with respect to autoxidation reactions. It might be thought that this would be of great importance biologically, but actually the effect is not large, owing to the simultaneous presence of carboxyl groups, which tend to diminish the activity of the amino-groups, and also to the fact that the nitrogen is often combined in the inactive amido-form. S. J. Gregg.

Catalytic activity of contact substances. IV. H. Remy (Z. anorg. Chem., 1926, **157**, 329—338).—The results previously obtained (cf. A., 1926, 134) for the catalysis of the combination of hydrogen and oxygen are examined in the light of Bodenstein's theory (*ibid.*, 1925, ii, 216) that in heterogeneous catalysis the molecules are rendered active by being deformed by the unsaturated surfaces of crystalline substances. If, as Hofmann and Ebert suppose (*ibid.*, 1917, ii, 25), the catalyst first activates both the hydrogen and the oxygen, its activity will depend on its affinity for oxygen as well as on its solvent power for hydrogen. If the former quantity be small but the latter great, then on charging the catalyst with oxygen the small amount that it takes up will be in a highly reactive state, whilst the affinity for hydrogen will still be great. On the other hand, the catalyst charged with hydrogen will have little activating effect on oxygen, so that the catalytic activity will be small. As would therefore be expected, the results show that if the pure metals examined are arranged in order of increasing solvent power for hydrogen and increasing affinity for oxygen, a metal which occurs earlier in the first series than it does in the second is more active when charged with hydrogen than when charged with oxygen, and *vice versa*. Alloys of metals of the eighth group of the periodic classification behave in a similar manner, except those composed of metals of the iron group. The catalytic activity is also dependent on the readiness with which the deformed molecules combine with the catalyst. If this be assumed, for oxygen, to run parallel with the heat of formation of the oxides, metals the oxides of which have large heats of formation would be expected to be relatively poor catalysts; this probably accounts for the small catalytic activity of metals of the iron group. R. Cuthill.

Catalytic oxidation of carbon monoxide in contact with quartz glass. A. F. Benton and T. L. Williams (J. Physical Chem., 1926, **30**, 1487—1496).—Langmuir's explanation (A., 1917, ii, 19) of the results obtained by Bodenstein and Ohlmer (*ibid.*, 1905, ii, 692) has been examined by measuring the amount of carbon monoxide, and oxygen in certain cases, adsorbed by powdered quartz glass at 760 mm. and at 0°, 25°, 218°, 300°, and −79°, and also at low pressures. The adsorption is practically immeasurable and certainly less than 3% of the surface is involved.

Measurements of reaction velocity showed that quartz glass, when carefully freed from impurities, is a poor catalyst, and although the surface of the catalyst was greater, the rates of reaction found at 500° were smaller than those obtained by Bodenstein and Ohlmer (*loc. cit.*). This difference is attributed to the presence of impurities in the latter case. Further, the retarding influence of carbon monoxide found by the last-named workers was not confirmed. The reaction velocity is directly proportional to the pressure of the oxygen and to the square root of the pressure of the carbon monoxide, but quantitative results are difficult to reproduce.

L. S. Theobald.

Mechanism of activation of catalytic surfaces. H. S. Taylor (Proc. Roy. Soc., 1926, **A**, **113**, 77—86).—The mechanism of catalytic activation is discussed with special reference to recent experimental work indicating that the activation of diatomic molecules at metallic surfaces involves the production of adsorbed atoms. The following explanations are given of the unimolecular decomposition of hydrogen iodide and of ammonia at platinum surfaces discovered by Hinshelwood and Burk (A., 1925, ii, 691). In the gaseous phase, the unimolecular and bimolecular decompositions of hydrogen iodide involve the following amounts of energy: $HI=H+I-68$ kg.-cal. and $2HI=H_2+I_2-3$ kg.-cal. Since the bimolecular critical increment is only 44,000 g.-cal. per 2 mols., the gaseous decomposition is bimolecular. At the platinum surface, it is assumed that the first stage is the adsorption of hydrogen iodide on the platinum and its decomposition to give a free iodine atom, and an adsorbed hydrogen for which the thermal change is $Pt+HI=Pt(H)+I-15$ kg.-cal. The adsorbed hydrogen atom is then struck by a hydrogen iodide molecule, when the following changes occur: (i) $Pt(H)+HI=Pt(H_2)+I+x$ kg.-cal., (ii) $Pt(H_2)=Pt+H_2+y$ kg.-cal., where y lies between −10 and −25 kg.-cal., and x between −8 and +7 kg.-cal., according to different workers. By this

mechanism, the unimolecular decomposition is changed from a single stage requiring 68 kg.-cal., to a series of changes none of which requires more than 25 kg.-cal., so that the energy of activation is probably reduced and the catalytic action is understood. The decomposition of ammonia is somewhat similarly explained, but the removal of adsorbed hydrogen atoms with colliding ammonia is not possible. The adsorbed hydrogen atoms are removed by evaporation or reaction with adjacent atoms, in agreement with the observation of Hinshelwood and Burk (*loc. cit.*) that the surface is poisoned by hydrogen atoms.

W. HUME-ROTHERY.

Dissociation of methane. F. E. C. SCHEFFER, T. DOKKUM, and J. AL (Rec. trav. chim., 1926, **45**, 803—816; cf. Mayer and Altmayer, A., 1907, i, 457; Coward and Wilson, J.C.S., 1919, **115**, 1380).—Determinations have been made of the compositions of mixtures of hydrogen and methane brought to equilibrium at 480—680° and atmospheric pressure by continuous circulation over finely-divided carbon and catalytic nickel. The mixture contains 59% of methane at 480°, falling to 18% at 680°, similar figures being obtained when the equilibrium is approached from either direction. The reaction involved is $C+2H_2=CH_4+18{\cdot}8$ kg.-cal. (at constant pressure). At lower temperatures, a carbide of nickel is involved which is exothermic and stable between 340° and 420°, and also occurs in a metastable state at higher temperatures. The carbide produces methane by the following reaction: $Ni_xC+2H_2=xNi+CH_4+11{\cdot}4$ kg.-cal.

G. M. BENNETT

Poisoning action of oxygen on iron catalysts for ammonia synthesis. J. A. ALMQUIST and C. A. BLACK (J. Amer. Chem. Soc., 1926, **48**, 2814—2820).—The effect of oxygen (0·02—0·24 vol.-%) on the reaction $N_2+3H_2=2NH_3$ at 444° and 1 atm., in presence of promoted and unpromoted iron catalysts is to diminish the yield of ammonia to a constant amount, which is the lower the higher is the oxygen content, and for a given oxygen concentration is lower for the less active catalysts. Similar results are obtained when the oxygen is replaced by water vapour, which bears out the results obtained previously, *i.e.*, that the poisoning action of oxygen compounds is proportional to the oxygen content in those cases in which the oxygen is converted into water under the conditions of the experiment. Oxygen is retained by the catalyst during the reaction, probably in the form of an iron oxide.

S. K. TWEEDY.

Nature of the catalyst surface and the effect o promoters. J. A. ALMQUIST (J. Amer. Chem. Soc., 1926, **48**, 2820—2826; cf. preceding abstract).—A consideration of the previous results indicates that iron catalysts contain atoms of various degrees of unsaturation capable of catalysing the ammonia synthesis and of forming oxide in presence of water vapour at low concentrations (cf. Kubota and Yoshikawa, A., 1925, ii, 1174). Calculations based on the amounts of oxygen retained by the iron in the above show in pure iron about 1 atom in 5000 atoms is active and in iron promoted with alumina about 10 times this number.

S. K. TWEEDY.

Influence of added substances on the mode of fixation of nitrogen by mixtures of barium carbonate and carbon. P. ASKENASY [with J. BRING].—See B., 1926, 978.

Negative catalysis in the oxidation of benzaldehyde. O. M. REIFF.—See this vol., 57.

Reversal of chemical reactions by electrolysis. R. SAXON (Chem. News, 1926, **133**, 342).—An attempt to reverse certain precipitation reactions. A porous pot surrounds a carbon anode, and in this anode chamber are placed ammonium chloride solution and a sparingly soluble or an insoluble salt (gypsum, Iceland spar, calamine, etc.). Using high voltages, it is found that the metallic salt undergoes partial decomposition, appreciable quantities of the corresponding chloride being found in the solution.

J. S. CARTER.

Electrolytic preparation of sodium perborate. U. SBORGI and D. LENZI.—See B., 1926, 985.

Decomposition of nitrogen pentoxide by light. C. S. FAZEL and S. KARRER (J. Amer. Chem. Soc., 1926, **48**, 2837—2839).—Previously recorded results on the decomposition of nitrogen pentoxide and dioxide mixtures by light are accounted for if the energy absorbed by the dioxide molecules is transferred to the pentoxide molecules by collisions of the second type (cf. Klein and Rosseland, A., 1921, ii, 291; Dickinson, *ibid.*, 1924, ii, 841). The dioxide molecules absorb light of wave-length 0·460 μ and transfer this energy to, and so cause decomposition of, the pentoxide molecules, which are unable to absorb light corresponding with their critical energy increment.

S. K. TWEEDY.

Colour produced by the action of light on concentrated solutions of ammonium thiocyanate. E. A. WERNER and K. C. BAILEY (J.C.S., 1926, 2970—2971).—The pink coloration developed in ammonium thiocyanate or its concentrated solution on exposure to light is believed to be due to the dissociation of the salt into ammonia and thiocyanic acid, and not to the formation of sub-microscopic sulphur (Holmes, A., 1926, 920). The possibility of the colour being due to traces of iron is being investigated.

W. THOMAS.

Photochemical decomposition of aqueous formic acid solutions. A. J. ALLMAND and L. REEVE (J.C.S., 1926, 2852—2863).—Light of wave-length 250—300 μμ decomposes formic acid according to the two primary reactions $H{\cdot}CO_2H \longrightarrow CO_2+H_2$, and $H{\cdot}CO_2H \longrightarrow CO+H_2O$, the former taking place to the extent of about six times the latter, and this relative occurrence is not dependent on wave-length (cf. Berthelot and Gaudechon, A., 1910, ii, 814). With concentrated solutions, the greater part of the nascent hydrogen and carbon monoxide molecules, especially the former, reduce the formic acid to formaldehyde and other more highly-reduced products. For 0·11—2·43*M*-solutions, the quantum efficiencies for formic acid decomposition are of the order 1·0 for 300, and 2·7 for 260 μμ.

W. THOMAS.

Photochemical decomposition of aqueous oxalic acid solutions. A. J. ALLMAND and L. REEVE (J.C.S., 1926, 2834—2851).—The initial stages

of the photolysis of aqueous oxalic acid have been quantitatively investigated by specially developed experimental methods. Monochromatic light of wave-length between 254 and 365 $\mu\mu$ was employed, the extent and nature of the decomposition being followed by measurement and analysis of the evolved gases. Contrary to the statements of Berthelot and Gaudechon (A., 1914, ii, 602), there is, under these conditions, only one primary reaction: $C_2H_2O_4 \longrightarrow H{\cdot}CO_2H+CO_2$. Neither hydrogen nor carbon dioxide is produced. Formaldehyde (the vapour of which is liable to be analysed as a mixture of carbon monoxide and hydrogen) is formed in small quantity, probably by the interaction between nascent carbon dioxide molecules and water. The amount of formaldehyde formed increases with the frequency of light used, and increases with dilution of the oxalic acid. For solutions of concentration 0·6—0·7M, the numbers of quanta required for the decomposition of 1 mol. of oxalic acid are as follows: 265 100; 300 $\mu\mu$, 245; 365 1060. Quantum efficiencies are probably greater for solutions of concentration 0·01M and particularly 0·001M. This is interpreted by assuming a finite life for the photo-activated oxalic acid molecules before decomposition, coupled with deactivation from collision with another oxalic acid molecule (cf. Ghosh and Mukherjee, A., 1925, ii, 1179).

W. THOMAS.

Photochemical studies. IV. Thermal decomposition of anhydrous oxalic acid and its relation to photochemical decomposition. D. E. WOBBE and W. A. NOYES, jun. (J. Amer. Chem. Soc., 1926, 48, 2856—2868).—The thermal decomposition of anhydrous oxalic acid (d^{25} 1·873) between 130° and 170°, $(CO_2H)_2=H{\cdot}CO_2H+CO_2$, is nearly of zero order, the constants being given by the equation $\log_{10} k=22{\cdot}548-11227/T$. The reaction probably takes place on the surface of the crystals. The progressive increase of k with time at the lower temperatures indicates adsorption of the reaction products by the glass and by the acid itself. The results confirm those published previously (Noyes and Kouperman, A., 1923, ii, 527). The critical increment is about 51,400 g.-cal. The photochemical decomposition of the acid is brought about by radiation of wave-length 0·250 μ or less, the wave-length predicted by the radiation hypothesis, viz., 0·550 μ, being without measurable effect. The suitability of the reaction for testing the radiation hypothesis is queried.

S. K. TWEEDY.

Chemical action of cod-liver oil and of adrenaline on the photographic plate. P. NIEDERHOFF (Biochem. Z., 1926, 176, 478—482).—The action of cod-liver oils from various sources and of adrenaline on photographic plates is a purely chemical effect comparable with the darkening action of resins, oils, and hydrogen peroxide on silver bromide and is not due to radiation.

C. RIMINGTON.

Chemical reactions of hydrogen atoms. H. S. TAYLOR (J. Amer. Chem. Soc., 1926, 48, 2840—2848).—Two simple quartz mercury arcs suitable for the preparation of atomic hydrogen are described. The chemical properties of atomic hydrogen prepared by the methods of Wood (A., 1922, ii, 759) and of Cario and Franck (*ibid.*, ii, 809) are detailed, and the preliminary results of some investigations by the author and co-workers are mentioned. Thus hydrogen atoms react with oxygen to form hydrogen peroxide as an initial product, which decomposes to water in ultra-violet light. Ethylene is quantitatively reduced to ethane. Contrary to the results of Hirst (*ibid.*, 1926, 583), and in agreement with those of Bonhoeffer (*ibid.*, 583, 586), no reaction occurs with nitrogen. Carbon dioxide reacts slowly, forming the monoxide and oxygenated organic compounds. Rideal and Hirst's suggestion (*ibid.*, 486) that excited hydrogen molecules, and not atomic hydrogen, cause certain reactions attributed to the latter is considered to be improbable in the light of published results (Senftleben, *ibid.*, 1925, ii, 883). The presence of hydrogen atoms at cathodes during electrolysis, as well as in oxy-hydrogen flames, is indicated. Experiments by Compton and Turner (A., 1924, ii, 639) point to the mechanism $Hg'+H_2=HgH+H$ for the production of atomic hydrogen by the Cario–Franck method (cf. Taylor and Marshall, A., 1925, ii, 1078).

S. K. TWEEDY.

Displacement of metals from solutions of their salts by less electropositive elements. III. Action of liquid ammonia solutions of salts of the alkali and alkaline-earth metals on magnesium and other elements. F. W. BERGSTROM (J. Amer. Chem. Soc., 1926, 48, 2848—2856; cf. A., 1925, ii, 885).—The extremely slow reaction $Mg+2NH_3=Mg(NH_2)_2+H_2$ is catalysed by salts of the alkali and alkaline-earth metals (excluding cæsium chloride, sodium tetrasulphide, strontium and barium iodides, and sodium nitrate): $2NaCl+Mg \longrightarrow MgCl_2+2Na$; $2Na+2NH_3=2NaNH_2+H_2$; $2NaNH_2+MgCl_2=Mg(NH_2)_2+2NaCl$. When heated at 350—400° in a vacuum, magnesium amide yields light yellow deammonation products. Sodium chloride or potassium cyanide in liquid ammonia has little or no action on metals less electropositive than magnesium. Potassium thiocyanate in liquid ammonia removes all trace of magnesium from its amalgam, forming soluble magnesium thiocyanate and potassium amalgam. The ultimate product of the action of potassium amide on magnesium in ammonia solution is the sparingly soluble potassium ammonomagnesiate, which is also produced by the action of a solution of potassium on magnesium. The sodium salt reacts with water to form sodium and magnesium hydroxides and ammonia. It reacts with magnesium to form magnesium amide; the latter is also formed by the action of amides of lithium and sodium and a solution of sodium in ammonia on magnesium. By analogy, the reaction between magnesium and sodium iodide in aqueous solution, in so far as it is exclusive of electrochemical influences, may be represented: $2NaI+Mg \rightleftharpoons MgI_2+2Na$; $2Na+2H_2O=2NaOH+H_2$; $2NaOH+MgI_2=Mg(OH)_2+2NaI$.

S. K. TWEEDY.

Dehydration of metallic salt hydrates. I. Sodium borate, carbonate, and sulphate. M. A. RAKUSIN and D. A. BRODSKI.—See B., 1926, 1011.

Basic sulphate of copper. H. T. S. BRITTON (J.C.S., 1926, 2868—2872).—A criticism of Fowles'

paper (A., 1926, 922). Phase-rule studies at 25° and 100° indicate that the compound $4CuO,SO_3,4H_2O$ is the only basic sulphate of copper. W. THOMAS.

Changes in heterometallic complex compounds on heating. A. GRUNBERG and N. PSCHENITZIN (Z. anorg. Chem., 1926, **157**, 173—189).—*Triethylenediaminezinc chloroplatinite*, $[Zn(en)_3][PtCl_4]$ (red), and *triethylenediaminecadmium chloroplatinite*, $[Cd(en)_3][PtCl_4]$ (red), have been prepared by the action of potassium chloroplatinite on the complex triethylenediamine sulphate. The corresponding copper *compound*, $[Cu(en)_3][PtCl_4]$ (lilac), is obtained by adding potassium chloroplatinite to an aqueous solution of copper sulphate saturated with ethylenediamine. When these salts and the analogous nickel salt are heated, part of the ethylenediamine is driven off, and the remainder wanders to the platinum atom, so that the residue consists of the chloride of the particular metal concerned and the compound $[Pt(en)_2]Cl_2$. With the zinc and cadmium salts these combine to form the *compounds* $[Pt(en)_2]Cl_2,ZnCl_2$ and $[Pt(en)_2]Cl_2,CdCl_2$, respectively. In the case of the copper compound, *diethylenediaminecopper chloroplatinite*, $[Cu(en)_2][PtCl_4]$ (reddish-violet), is an intermediate product. The temperatures at which the above migration occurs increase in the order: copper, zinc, cadmium, nickel. The compound $[Ag(en)]_2[PtCl_4]$ behaves when heated in the same way as the above, except that no ethylenediamine is given off.

R. CUTHILL.

Displacement reactions of complex compounds. A. GRUNBERG (Z. anorg. Chem., 1926, **157**, 201—210).—The equilibrium $[M(en)_3]X_2 + 2nH_2O \rightleftharpoons [M(en)_{3-n}(H_2O)_{2n}]X_2 + n\,en$, where M is a metal and X an acid radical, seems to exist in aqueous solutions of the triethylenediaminates of bivalent metals. If to a solution of triethylenediaminezinc sulphate there is added nickel sulphate, the ions $[Ni(en)_3]$ and $[Ni(en)_2]$" are formed, the amine passing to the metal capable of forming the more stable complex ion. Analogous results are obtained if the zinc salt is replaced by the corresponding cadmium compound, or if copper sulphate is used instead of nickel sulphate.

R. CUTHILL.

Precipitation of metals from non-aqueous solutions. II. Reactions of zinc and cadmium with nickel and cobalt chlorides in absolute ethyl alcohol. R. MULLER and F. R. THOIS (Z. anorg. Chem., 1926, **157**, 349—370; cf. A., 1926, 1016).—The precipitation of nickel and cobalt from solutions of their chlorides in absolute alcohol by zinc and cadmium at the ordinary temperature is slow and incomplete, the precipitated metal being in the form of a loose powder. If even minute traces of water are present, some hydroxide is produced in the process. The general phenomena observed are very similar to those previously recorded (*loc. cit.*) for solutions in 98% alcohol. After being annealed by heating at 150°, the precipitates have an electrode potential equal to that of the precipitating metal.

R. CUTHILL.

Element 61. L. ROLLA and L. FERNANDES (Z. anorg. Chem., 1926, **157**, 371—381).—A claim for priority over Harris and Hopkins (A., 1926, 810) in the discovery of the above element. By fractional crystallisation of the double thallium, ammonium, and magnesium nitrates of the constituents of commercial didymium oxide, solutions were obtained the absorption spectra of which showed irregularities ascribed to the presence of a new element. Confirmatory evidence was afforded by the application of *X*-ray methods.

R. CUTHILL.

Germanium. III. Salts of germanic acid. W. PUGH (J.C.S., 1926, 2828—2832).—The rate and extent of displacement of carbon dioxide from the carbonates of lithium, sodium, and potassium by germanium dioxide are parallel with the extent to which the various carbonates lose carbon dioxide by dissociation. The salts $Na_2GeO_3,7H_2O$ and $Li_2GeO_3,\frac{1}{2}H_2O$ have been crystallised from water; the potassium salt is too soluble to be crystallised. Metagermanates of lithium, barium, lead, and silver have been prepared by precipitation with sodium metagermanate.

W. THOMAS.

Oxidation of stannous to stannic salts. S. KOMARETZKYJ (Z. anal. Chem., 1926, **69**, 257—260).—When a solution of stannous chloride is boiled with sodium thiosulphate, the pale brown precipitate obtained consists of monothio-β-stannic acid, $SnS(OH)_2$, which is decomposed by dilute hydrochloric acid into stannic chloride and stannic sulphide. Addition of thiosulphate to a hot acid solution of stannous chloride results in the direct formation of stannic chloride according to the equation $SnCl_2 + Na_2S_2O_3 + 4HCl = SnCl_4 + 2NaCl + H_2O + H_2S + SO_2$. Similar reactions occur when stannous chloride is boiled with ammonium or potassium disulphide, and it is shown that the oxidising agent in all cases is the colloidal sulphur first produced by the decomposition of the precipitant by the acid formed in the hydrolysis of the stannous salt or originally present in the solution.

A. R. POWELL.

Action of molecular oxygen and hydrogen on sodium azide. K. A. HOFMANN and U. HOFMANN (Ber., 1926, **59**, [*B*], 2574—2579; cf. A., 1926, 370).—Sodium azide when rendered unstable thermally in an atmosphere of oxygen is converted almost quantitatively into sodium nitrite and oxygen. Catalysts or carriers are unnecessary, but the presence of free alkali is essential to delay the transformation $3NaN_3$ into $Na_3N + N_2$ until the oxygen molecule can penetrate the nitrogen zone. Oxidising agents such as copper oxide, manganese dioxide, and lead dioxide merely facilitate the removal of nitrogen by oxidising the sodium, whereas peroxides such as barium peroxide have the same effect as gaseous oxygen, since they furnish molecular oxygen. It therefore appears probable that the direct combustion of ammonia to nitrite and subsequently to nitrate at a basic contact depends on an unstabilising of the molecule, previously to thermal dissociation, which may be represented by the scheme $HN \leftrightarrow H_2$; molecular oxygen then penetrates the molecule and displaces hydrogen, which is subsequently oxidised to water. In a similar manner, hydrogen converts sodium azide into hydrogen and sodamide, the greater velocity of diffusion of hydrogen allowing it to penetrate the nitrogen zone so rapidly that the presence of alkali is not

necessary to prevent the transformation $3NaN^{-} \longrightarrow Na_3N+N_2$. If sodium azide is decomposed in an atmosphere of carbon dioxide, the NaN--- residues unite with loss of nitrogen and production of sodium azoimide, which is very readily hydrolysed to sodium hydroxide and ammonia, even when the concentration of aqueous vapour is very low. H. WREN.

Tervalent vanadium. II. J. MEYER and E. MARKOWICZ (Z. anorg. Chem., 1926, **157**, 211—250; cf. A., 1924, ii, 558).—Pure ammonium vanadium alum is blue in colour, the red variety described by Bültemann (A., 1904, ii, 266) owing its colour to the presence of traces of vanadic oxide or hydroxide. By electrolysis of a solution of ammonium metavanadate in dilute sulphuric acid after reduction with sulphur dioxide, a *compound*, $NH_4V(SO_4)_2,4H_2O$, is obtained as a green powder (cf. Brierley, J.C.S., 1886, **49**, 823). Using excess of sulphuric acid, the ammonium *salt* of Stahler and Wirthwein's acid, $HV(SO_4)_2,6H_2O$ (A., 1906, ii, 33), is formed. If a suspension of vanadium pentoxide in glacial acetic acid is reduced with hydrazine, and the resulting solution of vanadic acetate treated with fuming sulphuric acid, a mixture of *acids* of the formula $HV(SO_4)_2,nH_2O$, where n is 5, 6, or 8, is obtained. The ammonium salt $NH_4V(SO_4)_2,4H_2O$ and the *salt* $NH_4V(SO_4)_2,5H_2O$ are prepared by substituting ammonium metavanadate for vanadium pentoxide. Addition of 60% sulphuric acid to a vanadic acetate solution yields a number of dark green *hydrates* of vanadic sulphate, $V_2(SO_4)_3,nH_2O$, where n is 9 or 10—11. A yellowish-green *trihydrate* and a pale green *dihydrate* are obtained by the action of concentrated sulphuric acid on solid vanadic acetate. A *monohydrate* is formed when excess of concentrated sulphuric acid is added to a vanadic acetate solution and the acetic acid then evaporated off. If only part of the acetic acid is removed and pyridine is then added, green crystals of *triaquopyridinemonosulphatovanadic hydrogen sulphate*, $[V(H_2O)_3(C_5H_5N)(SO_4)]HSO_4$, appear. When this is heated at 300°, yellow *monoaquopyridinevanadic sulphatesulphuric acid*, $[V(H_2O)(C_5H_5N)(SO_4)_2]H$, results. The vanadic sulphates and sulphatesulphuric acids are able to give three kinds of solutions, two green in colour and one yellow. These seem to correspond with the various solutions of chromic sulphate. By addition of selenic acid to a solution of vanadic acetate, three *acetatovanadic selenates*, $V_3(CH_3\cdot CO_2)(SeO_4),nH_2O$, ($n$=10, 14, or 18), have been prepared

R. CUTHILL.

Tantalum and niobium and their mineral associates. VI. Precipitation of the earth acids by sodium compounds. W. R. SCHOELLER and C. JAHN (Analyst, 1926, **51**, 613—620).—If tantalic and niobic oxides are fused with potassium carbonate until the product is clear, and a fragment of potassium hydroxide is added to the cooled mass, the whole dissolved in hot water, and an excess of solid sodium chloride gradually added, dense micro-crystalline precipitates of 4 : 3 sodium tantalate and of 7 : 6 sodium niobate, respectively, are formed. The small amount of non-precipitated earth acid contained in the filtrates may be substantially recovered by partial neutralisation to the hydrogen carbonate stage and digestion on the water-bath, when hydrolytic dissociation takes place and precipitation of the earth acid. The salts are decomposed by dilute acids and the volume of hydrochloric acid required is proportional to the quantity of alkali in the precipitates. The application of the reaction to the volumetric determination of the earth acids was attempted.

D. G. HEWER.

Formation of sulphur trioxide during the burning of sulphur. J. CORNOG, W. DARGAN, and P. BENDER (J. Amer. Chem. Soc., 1926, **48**, 2757—2760).—Sulphur sealed in a tube with a capillary orifice was vaporised at 460° and the vapour burned at the orifice in a current of oxygen. The effluent gases were passed through 0·1*N*-iodine solution, potassium iodide solution, and a Hawley filter, and contained about 3·6% of sulphur trioxide. In absence of the filter, inconsistent results were obtained, some of the trioxide escaping unabsorbed. Blank experiments with sulphur dioxide–oxygen mixtures indicated that the catalytic action $2SO_2+O_2=2SO_3$ does not occur. S. K. TWEEDY.

Compound of sulphur trioxide with nitric oxide. Theory of the lead chamber process. W. MANCHOT [with J. KONIG and S. REIMLINGER] (Ber., 1926, **59**, [*B*], 2672—2681).—Nitric oxide readily reacts with sulphur trioxide at 60°, yielding the *product*, $2SO_3,NO$, m. p. 215—220° after darkening and softening at 180°, b. p. 275°/715 mm. The substance is readily decomposed by water into sulphuric acid and nitric oxide, but does not react with ferrous sulphate or cupric sulphate dissolved in concentrated sulphuric acid. When heated, it becomes decomposed into sulphur dioxide and nitrogen peroxide, from which it may be prepared at 200—300°. If, however, the gases are moist, nitrosylsulphuric acid is formed in which drops of "blue acid" appear after some time (cf. Manchot, A., 1912, ii, 637). The "acid" is regarded as an oxide of nitrogen intermediate between $NO_{1\cdot5}$ and NO. Raschig's conception that "blue acid" has the composition H_2SNO_5 is rendered improbable by the observation that its absorption spectrum does not resemble those of the compounds $CuSO_4,NO$ and $FeSO_4,NO$. The production of the "copper salt of the blue acid" throws no light on its constitution, since the formation of copper–nitric oxide compounds by the action of "blue acid" on copper sulphate depends on the "acid" serving simply as a source of nitric oxide. H. WREN.

Sulphurous acid and its salts. IV. Action of sulphites on polythionates. F. FOERSTER and K. CENTNER (Z. anorg. Chem., 1926, **157**, 45—82; cf. A., 1925, ii, 120).—The reaction between equivalent quantities of sulphite and tetrathionate or pentathionate leads to the equilibria $S_5O_6''+SO_3'' \rightleftharpoons S_4O_6''+S_2O_3''$, and $S_4O_6''+SO_3'' \rightleftharpoons S_3O_6''+S_2O_3''$ being set up. If, however, a slight excess of sulphite is present, both reactions occur practically to completion to the right in accordance with the ordinary bimolecular law, the speed of the former reaction being much greater than that of the latter. When hydrogen sulphite acts on pentathionate and tetrathionate, the equilibria $S_5O_6''+HSO_3' \rightleftharpoons S_4O_6''+S_2O_3''+H^{\cdot}$ and $S_4O_6''+HSO_3' \rightleftharpoons S_3O_6''+S_2O_3''+H^{\cdot}$

are slowly established, the reactions probably being brought about entirely by the sulphite ions present in the hydrogen sulphite solutions. The second equilibrium is disturbed by the decomposition of the trithionate, according to the equation $S_3O_6''+H_2O=SO_4''+S_2O_3''+2H^{\cdot}$, and by its re-formation from hydrogen sulphite and thiosulphate, $S_2O_3''+4HSO_3'+2H^{\cdot}=2S_3O_6''+3H_2O$. As a result of these reactions, the hydrogen-ion concentration increases until sulphur is deposited by the reaction $S_2O_3''+H^{\cdot}\rightleftharpoons HSO_3'+S$. Finally, a stationary state is reached, and sulphate and free sulphur are formed from thiosulphate and sulphite, corresponding with the equation $S_2O_3''+2HSO_3'=2SO_4''+2S+H_2O$. Since hydrogen sulphite and free sulphur can be obtained from thiosulphate by the action of acids, thiosulphate itself can, under suitable conditions of acidity, be converted into sulphate and sulphur.

R. CUTHILL.

Decomposition of ammonium thiocyanate into carbon disulphide and "mellon," and decomposition of "mellon" into ammonia and carbon dioxide. W. GLUUD, K. KELLER, and W. KLEMPT.—See B., 1926, 1011.

Action of gaseous hydrogen chloride on tungsten compounds. V. SPITZIN and L. KASCHETANOFF (Z. anorg. Chem., 1926, **157**, 141—164).—If tungsten trioxide is heated in hydrogen chloride, the dioxydichloride commences to be formed at 300°. The sodium tungstates gradually lose tungstic oxide, which is converted into the dioxydichloride and volatilised, and finally sodium chloride remains; in no case are lower tungstates formed as intermediate products. Metallic tungsten is not attacked at 500—600°. The dioxide and the pentoxide form the dioxydichloride, and leave a residue of the metal; it is concluded that their structures are $W(WO_3)_2$ and $W(WO_3)_5$, respectively. Tungsten bronzes form the dioxydichloride, and leave a residue of sodium chloride and the metal, the results indicating that their formula is $(Na_2W_2O_6)_3$ rather than the single formula.

R. CUTHILL.

Hydrogenomolybdotungstates. L. FERNANDES (Gazzetta, 1926, **56**, 655—681).—Derivatives of definite hetero-poly-acids are obtained by (1) neutralisation of a solution containing a molybdate and a tungstate in stoicheiometric proportions by addition of acetic acid, followed by crystallisation, (2) addition of molybdic anhydride to a boiling solution of a tungstate, or (3) mixing solutions of a polymolybdate and a polytungstate. Guanidine derivatives may be obtained by adding a soluble salt of the base to a boiling alkali molybdotungstate solution. Addition of concentrated hydrochloric acid to aqueous solutions of the salts results in the precipitation of the free tungstomolybdic acids as white, amorphous powders, and repeated treatment with hydrochloric acid fails to effect separation of the two acids; the barium salts form sparingly soluble white, microcrystalline precipitates.

The following compounds were prepared and analysed: $2WO_3,4MoO_3,2K_2O,12H_2O$;
$2WO_3,3MoO_3,2K_2O,10H_2O$;
$3WO_3,3MoO_3,3K_2O,9H_2O$;
$3WO_3,3MoO_3,3K_2O,3H_2O$;
$5WO_3,MoO_3,3K_2O,5H_2O$;
$3WO_3,MoO_3,2K_2O,4H_2O$;
$4WO_3,2MoO_3,3K_2O,11H_2O$;
$10WO_3,MoO_3,5K_2O,12H_2O$;
$4WO_3,MoO_3,2K_2O,9H_2O$;
$WO_3,10MoO_3,3Gu_2O,7H_2O$;
$WO_3,5MoO_3,2Gu_2O,6H_2O$;
$4WO_3,MoO_3,2{\cdot}5Gu_2O,6{\cdot}5H_2O$;
$2WO_3,4MoO_3,3Gu_2O,11H_2O$;
$2WO_3,3MoO_3,2{\cdot}5Gu_2O,H_2O$;
$3WO_3,3MoO_3,3Gu_2O,5H_2O$;
$4WO_3,2MoO_3,3Gu_2O,5H_2O$.

The constitution of these compounds is discussed.

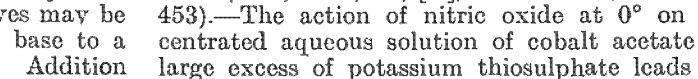
T. H. POPE.

Heterotriphosphates. III. Tungstovanadophosphates. G. CANNERI (Gazzetta, 1926, **56**, 642—651).—The tungstovanadophosphates, which are perfectly analogous in constitution and behaviour to the tungstovanadoarsenates (A., 1926, 258), form a continuous series of mixed crystals, the miscibility in the solid state taking place in every case between definite chemical species of analogous molecular constitution. Solutions especially rich in tungstic acid yield red crystals of type (1) (*loc. cit.*), whilst solutions somewhat enriched in vanadic acid give ruby or wine-red crystals of type (2), and those still richer in vanadic acid yield reddish-brown or pitch-black crystals of type (3).

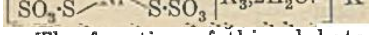
T. H. POPE.

Tervalent manganese. VI. J. MEYER and W. SCHRAMM (Z. anorg. Chem., 1926, **157**, 190—200; cf. A., 1924, ii, 555).—If manganic hydroxide is added to a concentrated solution of oxalic acid at 0°, a reddish-violet solution results which probably contains *trioxalatomanganic acid*, $H_3[Mn(C_2O_4)_3]$. The normal *thallous* salt appears to be formed when manganese dioxide is treated with thallous tetraoxalate in a freezing mixture. *Sodium diaquodioxalatomanganate*, $Na[Mn(H_2O)_2(C_2O_4)_2]$, is precipitated as green crystals when alcohol is added to a solution of manganese dioxide in sodium tetraoxalate solution at a low temperature. The free *acid*, $H[Mn(H_2O)_2(C_2O_4)_4]$,aq. (green), is obtained by adding manganic hydroxide to cooled oxalic acid. Both the oxalatomanganic acids form salts with organic bases, but only the *quinoline* salt, $(C_9H_7N)_3,H_3[Mn(C_2O_4)_3]$,aq. (black), has been isolated.

R. CUTHILL.

Univalent iron, cobalt, and nickel. W. MANCHOT (Ber., 1926, 59, [*B*], 2445—2453; cf. A., 1926, 453).—The action of nitric oxide at 0° on a concentrated aqueous solution of cobalt acetate and a large excess of potassium thiosulphate leads to the separation of the *salt*,  is somewhat unstable in solution, but may be preserved for some days in the solid state. In more dilute solution, the corresponding *dihydrate* is produced. A similar reaction occurs in the presence of potassium sulphide or ethyl mercaptan. Bivalent nickel does not appear to give compounds with nitric oxide, which readily combines with salts containing univalent nickel such as red potassium nickelocyanide (cf. Bellucci, A., 1919, i, 526; 1920, i, 296). Nickel

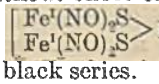
acetate in presence of potassium thiosulphate and nitric oxide in aqueous-alcoholic solution suffers reduction with formation of the *salt*,



The function of thiosulphate during the reduction of cobalt by nitric oxide of which 3 mols. are necessary lies in the removal of oxidised nitric oxide, but an excess of the substance above that required for this purpose is highly advantageous. With iron and nickel, reduction is less complete than with cobalt.

The nickel compound is transformed by potassium cyanide without evolution of nitric oxide into the *compound*, $(NO)Ni(CN)_3K_2$, obtained also from red potassium nickelocyanide and nitric oxide. The cobalt salt appears to act similarly with dilute potassium cyanide solution, whereas the iron compound evolves nitric oxide vigorously when treated with concentrated potassium cyanide, but reacts without liberation of gas from the cold, dilute solution.

The proof of the actual existence of compounds containing univalent iron permits the constitution $\begin{matrix}N\\NO\end{matrix}>Fe^{I}\text{–}SK$ to be assigned to the red series of Roussin's salts (in which nitric oxide is regarded as neutral portion without effect on the valency of iron) and the structure



to be given to the black series. H. WREN.

Oxidation by alkaline ferricyanide and composition of higher oxides of cobalt. D. BHADURI and P. RÂY (J. Indian Chem. Soc., 1926, **3**, 213—228; cf. Howell, J.C.S., 1923, **123**, 65).—The oxidation of freshly-precipitated cobaltous hydroxide by ferricyanide in solutions of various concentrations of alkali has been followed by titrating with permanganate the ferrocyanide produced. The amount of available oxygen used up is plotted against the increasing amounts of either ferricyanide or potassium hydroxide present. The oxidation rapidly affords the oxide Co_2O_3, and, further, a small amount of peroxidation may occur, especially in the presence of large excesses of alkali. A slight discontinuity in one of the curves is interpreted as indicating the formation of the compound Co_3O_4. Direct analysis of the precipitate, carried out in only one series of experiments, indicates that somewhat less available oxygen is combined than was deduced from the indirect measurements. Nickel and iron salts retard the oxidation of cobalt hydroxide. Nickel hydroxide is not oxidised readily to a higher oxide by a similar method. G. M. BENNETT.

Mol. wts. of the isomeric platinous salts. A. GRÜNBERG (Z. anorg. Chem., 1926, **157**, 299—310).—By the action of thiocarbamide on the two isomeric dithiocyanatodiammineplatinums, the *compounds* $[Pt,4CS(NH_2)_2]Cl_2$ (yellow) and $[Pt(NH_3)_2,2CS(NH_2)_2]Cl_2$ (white) have been prepared. On the basis of Kurnakov's rule (J. Russ. Phys. Chem. Soc., 1893, **25**, 585), it is therefore concluded that the latter compound is derived from the *trans*-isomeride and the other one from the *cis*-isomeride. The mol. wt. of both isomerides in acetone solution corresponds with the single formula $[Pt(NH_3)_2(CNS)_2]$, and the solutions are very poor conductors, as Werner's theory requires. It seems, by analogy, that Peyronne's chloride and the chloride of Reiset's second base are geometrical isomerides, and that they do not differ in mol. wt., as Reihlen and Nestle have suggested (A., 1926, 699). R. CUTHILL.

Platinum metals. VI. Role of carbon monoxide in the preparation of ruthenium trichloride by direct union of its elements. H. REMY and T. WAGNER (Z. anorg. Chem., 1926, **157**, 339—344; cf. A., 1924, ii, 770).—Ordinary metallic ruthenium is only partly attacked by pure chlorine, but in presence of carbon monoxide and at temperatures above red heat the reaction is complete. If the product is reduced again to the metal, it can be completely chlorinated with chlorine alone, in absence of carbon monoxide. It is therefore concluded that, as Manchot and König have suggested (A., 1925, ii, 149), carbon monoxide promotes the reaction by exerting a disintegrative effect on the solid phases. If oxygen is present in the chlorine, the trichloride first formed is converted into the dioxide, but carbon monoxide, by itself combining with the oxygen, prevents this. R. CUTHILL.

Preparation of cyanides from calcium cyanamide and dicyanodiamide. A. E. KRETOV.—See B., 1926, 1012.

Kuhlmann micro-balance, and use of porcelain, quartz, and glass filters in quantitative micro-chemical analysis. E. SCHWARZ-BERGKAMPF (Z. anal. Chem., 1926, **69**, 321—341).—Close examination of the variations of the balance with temperature and atmospheric conditions showed that a hitherto unobserved cause of variation is the differential expansion of the knife-edge supports, a metastable temperature equilibrium being established in the interval between weighings. The balance should be kept in a room maintained at about 18—20°, with a maximum difference of 1°, and after being so maintained for several days, may be used without correction, save for pressure variations, for weighings made on the same day; the necessary precautions are described. A porcelain micro-filter which suffers no change in weight after treatment with hot concentrated hydrochloric acid, or with ammonia, or after ignition in a Teclu burner, is described, and details of micro-chemical analyses carried out with it are given. Suitable quartz filters are also described, but are found slower in operation; glass filters are satisfactory, and are more rapid. The use of a new glass filter vessel is described. S. I. LEVY.

Temperature correction in volumetric analysis. W. J. COUVÉE (Chem. Weekblad, 1926, **23**, 550—551; cf. Schlösser, Chem.-Ztg., 1905, **29**, 510).—A volume-correction table for reduction of burette readings to a standard temperature of 20° is given. Temperatures should be read in the burette itself after reading, by means of a thermometer suspended from a soda-lime or an empty tube. S. I. LEVY.

Hydrogen electrode. J. M. LEWIS (Austral. J. Exp. Biol., 1926, **3**, 189—191).—A modification of Michaelis' apparatus whereby the usual tape or wick completing the chain between the hydrogen and calomel electrodes is replaced by the column of fluid

lying between a lightly-fitting, ungreased glass stopper and the neck of the containing vessel. W. ROBSON.

Electrolytic preparation of calomel for use in the calomel electrode. S. W. PENNYCUICK and R. J. BEST (Austral. J. Exp. Biol., 1926, 3, 173—176).—A mercury dropping electrode forms the anode, and the calomel is precipitated on the falling stream of mercury which carries down the finely-divided calomel and simultaneously presents a new mercury surface to the current. Introducing the product into the chain H_2, Pt, 0·1*N*-HCl, sat. KCl, *N*-KCl, Hg_2Cl_2Hg gave an *E.M.F.* value of 0·3483 volt. Of the substances required in the preparation, only the potassium chloride and mercury need be pure. A method for purifying mercury is detailed. W. ROBSON.

Graphical interpretation of electrometric titration data. H. S. SIMMS and P. A. LEVENE (J. Biol. Chem., 1926, **70**, 319—325).—The titration curve of an unknown or complex substance, obtained by plotting corrected equivalents of base, b', against p_H, is compared with the curve of a known compound of similar constitution; a third "comparison" curve is then constructed, by subtracting values of b' for the known curve from those of the unknown, from which may be deduced the properties of the unknown compound. C. R. HARINGTON.

Method of differential potentiometric titration. D. A. MACINNES and P. T. JONES (J. Amer. Chem. Soc., 1926, 48, 2831—2836).—A method of potentiometric titration described previously (COX, A., 1925, ii, 999) is improved by inserting the two electrodes in the same solution and temporarily isolating the solution round one of the electrodes while the next small increment of titrating agent is added to the bulk of the solution. A simple device for isolating the solution is described. The improved method is very accurate. S. K. TWEEDY.

Buffering in homogeneous and heterogeneous systems. K. TAUFEL and C. WAGNER (Biochem. Z., 1926, **177**, 389—399).—The reciprocal of the buffering capacity of a system in heterogeneous equilibrium equals the sum of those of the participants in the equilibrium multiplied by 0·4343. Formulæ for the determination of changes of p_H of systems of known buffering capacity on addition of weak acids and bases and for the calculation of the p_H of mixtures of buffer systems are deduced. P. W. CLUTTERBUCK.

Titration acidity and true acidity. W. MANG (Chem.-Ztg., 1926, 50, 781).—The true acidity of a solution is measured by the hydrogen-ion concentration, and as this may be reduced by the presence of a neutral salt of the acid radical in the solution, it is possible for the acidity as determined by titration with an alkali to appear to be much higher than it really is. This difference may cause serious errors in work involving colloidal phenomena, *e.g.*, in determining the conditions under which flocculation of colloidal solutions takes place. In all such cases, determinations of the p_H of the solution should be made in preference to titrations with alkalis.
A. R. POWELL.

Potassium di-iodate as a standard in alkalimetric and iodometric titrations. I. M. KOLTHOFF and L. H. VAN BERK (J. Amer. Chem. Soc., 1926, 48, 2799—2801).—Pure potassium di-iodate, prepared according to the method of Shaffer and Hartmann (A., 1921, ii, 417), and crystallised two or three times from water, is a suitable substance for the standardisation of thiosulphate and, because of its high mol. wt., especially of alkali. Indicators showing a colour change between dimethyl-yellow and phenolphthalein may be used in the latter case.
S. K. TWEEDY.

Detection and rapid determination of chlorides in presence of bromides and iodides. R. BERG (Z. anal. Chem., 1926, 69, 342—348).—On treatment of the acidified solution with bromic acid in presence of acetone, the chloride remains unoxidised in the solution, whilst the liberated bromine and iodine attack the acetone, forming derivatives from which the halogen is not precipitated by means of silver nitrate. The chloride is determined gravimetrically, or, after removal of the excess of bromic acid by addition of a ferrous salt, by Volhard's method.
S. I. LEVY.

Determination of silicic acid and fluorine in fluorspar, sand, and silicates. H. DUBIEL.—See B., 1926, 978.

Complete analysis of fluorspar. E. BAILLEUX.—See B., 1926, 1012.

Micro-analytical determination of sulphur and the halogens. A. RECSEI (Chem.-Ztg., 1926, 50, 785).—For the determination of sulphur in organic substances that are not too easily volatile, 2—8 mg. of the substance are heated in a nickel crucible with 0·2—0·8 g. of a mixture of potassium sodium carbonate and sodium peroxide in the ratio 2 : 1. The fused mass is dissolved in water, the solution acidified with hydrochloric acid and boiled with a few drops of bromine water, and the sulphur precipitated by addition of 1—2 c.c. of 0·5*N*-barium chloride solution. The halogens may be determined in a somewhat similar manner; the fusion is conducted as before, the solution of the mass boiled with a little sodium sulphite, acidified with nitric acid and treated with 1 c.c. of 0·5*N*-silver nitrate solution, and the precipitate collected on a filtering crucible, washed successively with very dilute nitric acid and alcohol, dried at 125°, and weighed. A. R. POWELL.

Use of the potassium iodide and iodate method for the titration of Kjeldahl distillates. H. F. WILSON and F. MATTINGLEY (Analyst, 1926, 51, 569).—Carbonic acid seriously interferes with the iodide–iodate method of titration of Kjeldahl distillates by retarding the end-point, and since it is almost certain to be present in such distillates, the latter should be boiled. D. G. HEWER.

Spectrometric determination of nitrates and nitrites by diphenylamine sulphate. E. TASSILLY and R. SAVOIRE (Compt. rend., 1926, 183, 887—888).—The reagent was prepared by dissolving 0·2 g. of diphenylamine (recrystallised from alcohol) in 1 litre of pure sulphuric acid. A mixture of 15 c.c. with 3 c.c. of nitrite solution of known titre, added drop by drop with cooling, was poured into one cell of Fery's spectrometer, the other being filled with 15 c.c. of reagent together with 3 c.c. of water, the

reading being taken after 15 min. Absorption varied linearly with concentration. The lower limit of sensibility of the method is 0·1 mg. and freshly-prepared reagent is essential. With nitrates, there is intermediate formation of nitrite, since the characteristic blue colour was not formed in the presence of carbamide. S. J. Gregg.

Determination of arsenic in small quantities of organic compounds. O. Wintersteiner and H. Hannel.—See B., 1926, 994.

Thiele's test for arsenic with sodium hypophosphite. H. Matthes (Pharm. Ztg., 1926, **71**, 1509).—Although this material for detection of arsenic is frequently known as Bougault's reagent, it was first employed by Johannes Thiele in 1890. S. I. Levy.

Apparatus for the direct determination of carbon dioxide. J. E. Underwood.—See B., 1926, 977.

Colorimetric determination of minute amounts of compounds of silicon, phosphorus, and arsenic. W. R. G. Atkins and E. G. Wilson (Biochem. J., 1926, 1223—1228).—The amounts of phosphate and arsenate usually present in natural waters do not interfere with Diénert and Wandenbulcke's method for the determination of silicate (A., 1923, ii, 507; 1924, ii, 253), nor does the reagent used by these authors give any colour with moderate quantities of phosphate, arsenate, or arsenite. Denigès' methods for phosphates and arsenates (*ibid.*, 1920, ii, 770; Compt. rend. Soc. Biol., 1921, **84**, 875) are satisfactory. Bell and Doisy's method (Briggs' modification, cf. A., 1922, ii, 659; 1924, ii, 498) is not as convenient and delicate as Denigès' method. The amounts of silicate ordinarily found in natural waters do not interfere with the accuracy of the latter method. Glycerophosphate, triphenyl phosphate, and tritolyl phosphate do not react with Denigès' reagent, the last one not even after hydrolysis, nor do vanadates, tungstates, or phosphotungstates. Pouget and Chouchak's reagent for phosphates (*ibid.*, 1909, ii, 266; 1911, ii, 823) reacts definitely with arsenates on heating, but only faintly in the cold. It does not react with arsenites. S. S. Zilva.

Sensitive reagent for sodium ions. Possible differentiations and separations among the alkali and alkaline-earth metals. F. Díaz de Rada (Anal. Fís. Quím., 1926, **24**, 442—451; cf. Gaspar y Arnal, A., 1926, 591).—Lithium ferrocyanide (0·13—0·26%) in aqueous ethyl alcohol solutions gives precipitates with solutions of the chlorides of alkali and alkaline-earth metals. Using the chlorides in 1% solution, precipitates are obtained at the following concentrations of ethyl alcohol: ammonium, 90%; sodium, 84%; potassium, 78%; rubidium, 72%; cæsium, 62%; magnesium, 83%; calcium, 68%; strontium, 61%; barium, 51%. With the alkali metals, at least, the precipitates consist of the corresponding ferrocyanides. Each ferrocyanide can serve as a precipitating reagent for those ions which follow it in the above series. If to a solution of lithium ferrocyanide in 72·8% alcohol as much magnesium chloride be added as will just fail to give a precipitate, the resulting solution is a very sensitive reagent for sodium, yielding sodium magnesium ferrocyanide. Potassium and sodium may also be distinguished by the precipitate obtained on adding dilute copper sulphate solution to a solution of lithium ferrocyanide in 80% alcohol, containing a small quantity of one of their salts. Sodium gives a dense dark precipitate which settles, leaving a clear supernatant liquid, whilst potassium affords a light pink, flocculent precipitate, and the supernatant liquid is turbid and light yellow. G. W. Robinson.

Detection and determination of minute quantities of beryllium. H. Fischer (Wiss. Veroff. Siemens-Konz., 1926, **5**, 99—117).—Addition of a violet alkaline solution of 1 : 2 : 5 : 8-tetrahydroxyanthraquinone (quinalizarin) to a neutral solution of a beryllium salt produces a pure blue colloidal solution of a complex in which 1 mol. of quinalizarin appears to be united to 2 atoms of beryllium. Phosphates and tartrates do not interfere with the test, but magnesium produces a similar blue colour. Sufficient sodium hydroxide must be present to retain any aluminium in solution, and sufficient tartaric acid to prevent precipitation of iron. Much iron produces a yellow solution in which the violet to blue colour change cannot be detected. If the test is carried out by the addition of an ammoniacal solution of the reagent to the neutral beryllium solution, the addition of bromine water to the blue liquid causes flocculation of the complex; in the case of the magnesium compound, addition of bromine completely destroys the colour, hence beryllium may be detected by this means in the presence of a great excess of magnesium. The delicacy of the reaction is such that 1·5 μg. of beryllium per c.c. may be detected in a solution containing 2 mg. of magnesium or 6 mg. of aluminium per c.c. For the determination of minute amounts of beryllium in a solution free from other metals, 1 g. of ammonium nitrate is added per 10 c.c. of solution, followed by an excess of a 0·05% solution of quinalizarin in 2*N*-ammonia. After centrifuging, the precipitate is collected in a filtering crucible, washed with slightly ammoniacal 3% ammonium nitrate solution, and dissolved in 25 c.c. of 0·5*N*-sodium hydroxide. The blue colour is compared with that of freshly-made standards prepared in the same way from a beryllium solution of known strength. Beryllium may also be determined by direct titration with a 0·05% solution of the dye in 0·25*N*-sodium hydroxide if the solution is first treated with sodium hydroxide until it is 0·25*N*-alkali. The end-point is marked by the appearance of a violet tint in the previously blue liquid, and may most easily be discerned by comparison with the blue tint of a beryllium solution of approximately equal concentration containing a slight deficiency of the reagent. Aluminium does not interfere in this method. Equally good results may be obtained by adding an excess of the quinalizarin solution to obtain a violet tint and titrating back to blue with standard beryllium nitrate. A. R. Powell.

Co-ordination studies on the analytical behaviour of heavy metal sulphides. II. F. Feigl (Z. anorg. Chem., 1926, **157**, 251—268; cf. A., 1925, ii, 70).—A reply to the criticisms of Ruff and Hirsch (A., 1926, 345). It is pointed out that since certain properties, and particularly the value of the solu-

bility product, of metallic sulphides prepared in the wet way depend on the mode of preparation and their age, their formation is not entirely represented by the equation $M''+S''=MS$; and indeed instances are known of such sulphides being formed in solution from their un-ionised components. The ordinary insoluble coloured sulphides are probably polymerides of soluble colourless sulphides, corresponding in composition with the usually accepted formulæ, polymerisation being effected by the residual affinity of the sulphur atoms. In some cases, mixed sulphides may be formed in a similar way, this being a probable explanation of the " induced precipitation " of one sulphide by another. R. CUTHILL.

Co-ordination studies on the analytical behaviour of heavy metal sulphides. III. F. FEIGL [with H. GLEICH and R. SCHACHERL] (Z. anorg. Chem., 1926, **157**, 269—289; cf. preceding abstract).—The suggestion of Ruff and Hirsch (A., 1926, 345) that the partial insolubility in acids of manganous sulphide when precipitated along with mercuric sulphide is due to the protective action of a coating of the latter sulphide seems to be incorrect. Thus barium carbonate is not protected from the action of acetic acid by having mercuric sulphide precipitated on its surface, and manganous sulphide coated with mercuric sulphide by treatment with mercuric chloride does not resist acids as well as when it is itself precipitated on the surface of the mercuric sulphide. Similar experiments show that reduction of the solubility of mercuric sulphide in sodium sulphide when co-precipitated with manganous sulphide is not attributable to a protective action of the latter. Further, there is no evidence that manganous sulphide is oxidised when heated with ammonium sulphide solution, as Ruff and Hirsch have claimed. All the experimental facts can, however, be satisfactorily explained by the hypothesis that mixed sulphides are formed. R. CUTHILL.

Determination and separation of rare metals from other metals. VII. Determination of tungsten and its compounds by distillation in a current of air and carbon tetrachloride vapour. L. MOSER and K. SCHMIDT (Monatsh., 1926, **47**, 313—326).—The method of Jannasch and Leiste (A., 1918, ii, 460) is modified by the substitution of air for carbon dioxide as a carrier for the carbon tetrachloride vapour, this mixture being more active. Amorphous tungsten requires to be oxidised to the oxide before volatilising it as chloride, but provided that the gas mixture is rich enough in air, a separate preliminary oxidation is unnecessary. Drawn tungsten wire, however, requires heating for 1 hr. in oxygen, followed by 0·5 hr. in hydrogen before it is subjected to the distillation. The distillate may be collected in water, the solution boiled and made alkaline with ammonia, and the tungsten precipitated in the presence of a little sulphuric acid as benzidine tungstate and weighed as the trioxide. The application of the method to various tungstates is described. Where iron is present, the tungstic anhydride, obtained by evaporation with nitric acid, contains ferric oxide, which is quantitatively removed by heating at 300° with a mixture of equal parts of ammonium chloride and bromide. G. M. BENNETT.

Acidimetric determination of nickel as the dicyanodiamidine salt. P. FLUCH (Z. anal. Chem., 1926, **69**, 232—243).—The precipitate of nickel dicyanodiamidine obtained by Grossmann's method (A., 1906, ii, 903), after washing with 2·5% ammonia, then with 95% alcohol, dissolves readily in 0·2*N*-hydrochloric acid, with the formation of nickel chloride and dicyanodiamidine hydrochloride, both of which react neutral towards methyl-red. The excess of acid is therefore readily determined by titration with 0·2*N*-potassium hydroxide, provided that less than 0·2 g. of the nickel compound is present per 200 c.c. of acid solution; 1 c.c. of acid=0·002934 g. of nickel. Precipitation is carried out in ammoniacal tartrate solution if iron is present, or the iron may be separated by the basic acetate or barium carbonate methods. Copper interferes and is best separated by electrolysis. The method is applicable to the determination of nickel in ores and alloys, examples of which are given. A. R. POWELL.

Two sources of error in the electrolytic determination of nickel in presence of iron. C. MARIE and J. BERTHELOOT (Compt. rend., 1926, **183**, 793—795).—In the determination of nickel in presence of iron by the electrolysis of an ammoniacal solution of the sulphates, two sources of error occur: (1) The precipitate of hydrated iron sesquioxide retains nickel; this adsorption may be reduced to a minimum by displacement of the adsorbed nickel ions by means of magnesium ions (cf. Charriou, A., 1926, 899). (2) The hydrated iron sesquioxide is reduced at the cathode and deposited with the nickel; this source of error may be suppressed by preventing the hydrate from coming into contact with the cathode by means of a diaphragm (a sheath of filter-paper). When the nickel content is small, a preliminary separation in the presence of magnesium is necessary; this gives an impure nickel compound which can be reduced and electrolysed. M. E. NOTTAGE.

Oxidation of chromic salts in acid solution with chlorine and bromine in presence of silver salts. E. POSNER (Z. anorg. Chem., 1926, **157**, 311—312).—If a solution of chrome alum containing sulphuric acid and silver nitrate is treated with chlorine or bromine, and boiled, it becomes orange-yellow in colour, due to the formation of chromate, which is precipitated as the silver salt when the solution is neutralised. This reaction may be used to detect 1 part of chromium in 100,000 parts of water. R. CUTHILL.

Apparatus for vacuum sublimation. E. TIEDEMANN (Wiss. Veroff. Siemens-Konz., 1926, **5**, 229—232).—The apparatus consists of a thick-walled glass tube 8 cm. in diameter and 35 cm. long blown into a slight bulb at the lower end, and provided with side tubes for connexion to the vacuum pump and for the insertion of a thermometer. The upper end of the tube is closed with a rubber stopper carrying a wide tube ending in a bulb, and provided with an inner tube for the circulation of water, so as to cause the sublimed substance to condense on the bulb. The outer tube is heated either electrically or by immersion in an oil-bath. The sublimation temper-

ature of naphthalene in this apparatus is 100° (0·05 mm.), of 1 : 5-dihydroxynaphthalene 270° (1 mm.), of "1-hydroxy-5-tetralone" 220° (1 mm.), of "α-diphenol" 280° (0·025 mm.), of "α-dinaphthol" 320° (0·025 mm.), and of salicylic acid 140° (0·05 mm.). No decomposition takes place in subliming any of these substances, and the products obtained are very pure. A. R. POWELL.

Arrangement for alternating-current electrolysis. H. J. S. SAND and W. V. LLOYD (J.C.S., 1926, 2971—2973).—The circuit makes use of a source of continuous current and a revolving three-point commutator. The ammeter may be a direct-current instrument. To measure electrode potentials during each pulse, a second two-point revolving commutator is mounted on the same shaft as the first. W. THOMAS.

[Laboratory] filtering devices. H. B. GORDON. —See B., 1926, 967.

Flask for recovery of volatile liquids. M. NIERENSTEIN (Analyst, 1926, **51**, 569).—Volatile solvents may be recovered with a loss of about 5% by means of a round-bottomed flask with a bent-over neck for attachment to the condenser, and with a vertical arm from the bend of the neck to carry a reflux condenser. D. G. HEWER.

Rapid dialyser. A. GUTBIER and R. FAHR (Z. anorg. Chem., 1926, **157**, 345—348).—A new model of the well-known apparatus. R. CUTHILL.

Vacuum dryer for laboratory work. A. RIECHE (Chem.-Ztg., 1926, **50**, 891).—A simple glass apparatus for keeping the drying tube at any desired temperature by means of a liquid of suitable b. p. is described. S. I. LEVY.

Duplex m.-p. apparatus. F. J. F. MUSCHTER (Chem. Weekblad, 1926, **23**, 552).—A simple apparatus is described by which two or more thermometers may be employed in different parts of the apparatus, which may be heated separately or together. It consists of two or more wide vertical tubes connected by narrower tubing so arranged as to permit the desired heating. S. I. LEVY.

Titration apparatus. BAADER (Chem.-Ztg., 1926, 50, 891).—The titration is carried out in a wide-mouthed conical flask provided with a narrow glass side tube sealed in at the top and bottom, which facilitates observation of colour changes. S. I. LEVY.

Mineralogical Chemistry.

Constitution of the chalcedons and quartzines. L. LONGCHAMBON (Compt. rend., 1926, **183**, 1116—1118).—The identity of quartzine (occurring in crystalline, fibrous form in chalcedons) with quartz has been established by means of dilatometric analysis, radiograms, and density determinations of the constituents of pure chalcedons. The chalcedons consist of opal and crystalline silica in a fibrous form, chalcedony itself containing 4% and 96% of the former and latter, respectively. Its high degree of hydration (50%) accounts for its permeability. The quartzine fibres are agglomerated by the opal. J. GRANT.

Relation between kaolin and clays. G. CALSOW (Chem. Erde, 1926, **2**, 415—441).—Partial analyses are given of eight samples of kaolin, montmorillonite, and other clays. These materials were heated under 4 mm. pressure, and curves show the loss of water with rise of temperature. Kaolin loses the bulk of its water between 400° and 450°. L. J. SPENCER.

Relation between kaolin and clays. G. LINCK and G. CALSOW (Chem. Erde, 1926, **2**, 442—445; cf. preceding abstract).—From the amount of water lost between 400° and 450° the amount of crystalline kaolin present in the clays examined is calculated, the remainder being assumed to be amorphous clay material. L. J. SPENCER.

Noteworthy Vesuvian sublimates. G. CAROBBI (Atti R. Accad. Lincei, 1926, [vi], **4**, 306—311).—A deposit from a boric acid fumarole on Vesuvius contained appreciable traces both of soluble vanadium compounds and of soluble titanium compounds. T. H. POPE.

Application of *X*-rays to chemical analysis. I. Analysis of molybdenite from Zovon. G. NATTA (Gazzetta, 1926, **56**, 651—654).—Deformed laminæ, weighing in some cases as little as 0·02 mg., found in trachite from Zovon, are identified as molybdenite by the rotating crystal method of *X*-ray analysis. For the side of the base of the crystal unit the value 12·22 Å. is obtained. T. H. POPE.

Organic Chemistry.

Stereochemistry of ethylene derivatives. J. A. LE BEL (Compt. rend., 1926, **183**, 889).—The existence of three isomeric forms of a substance of the type CHR':CR''R''' (Dufraisse and Gillet, this vol., 58), which cannot be explained by the classical theory, may be ascribed to the possibility of three equilibrium positions of the molecule under the mutual attractions and repulsions of the four different radicals. H. E. F. NOTTON.

Δ$^{\alpha}$-Hexene. H. VAN RISSEGHEM (Bull. Soc. chim. Belg., 1926, **35**, 387).—Δ$^{\alpha}$-Hexene obtained by Brooks and Humphrey's method is contaminated with a halogen derivative, probably allyl bromide. The following constants are given for pure Δ$^{\alpha}$-hexene : b. p. 63·35°/760 mm. (±0·05°), d_4^{15} 0·67875, m. p. −139°, and for αβ-dibromohexane, b. p. 87°/16 mm. (±0·2°), d_4^{15} 1·5872 (cf. Kirrmann, A., 1926, 934). R. BRIGHTMAN.

Action of perbenzoic and peracetic acids on unsaturated substances. J. BOESEKEN (Rec. trav. chim., 1926, 45, 838—844).—When the double linking in an organic substance is conjugated with the carbonyl group, either free, as an acetal, or in the carboxyl group, it is not attacked. Thus ethyl fumarate and maleate on treatment with perbenzoic acid yield only polymerides. Diallyl on treatment with the peracid in chloroform solution yields the dicyclic oxide, which was not isolated, since it is completely volatile in chloroform, and on hydrolysis with dilute sulphuric acid yields an undistillable *substance*, d_4^{20} 1·2332, n_D^{20} 1·4845, which is probably the furan derivative $OH\cdot CH_2\cdot CH\cdot[CH_2]_2\cdot CH\cdot CH_2\cdot OH$ (—O—) or $OH\cdot CH_2\cdot CH\cdot[CH_2]_2\cdot CH(OH)\cdot CH_2$ (—O—) but not the expected hexane-αβεζ-tetrol, since it does not form a cyclic derivative with acetone. On oxidation with potassium permanganate in neutral solution at —45°, diallyl yields Δ$^{\alpha}$-hexene-εζ-diol (b. p. 60—85° in an absolute vacuum) and hexane-αβεζ-tetrol, which yield the cyclic *isopropylidene ethers*, b. p. 166—167°/760 mm., and m. p. 65°, respectively. γ-Methyl-Δ$^{\alpha}$-butene on oxidation with perbenzoic acid yields the cyclic *oxide*; this on hydrolysis yields γ-methylbutane-αβ-diol, b. p. 97—98°/18 mm., which on treatment with a 1% solution of hydrochloric acid in acetone yields the *isopropylidene ether*, b. p. 136—137°/760 mm., n 1·4110. β-Methyl-Δ$^{\alpha}$-butene on oxidation with peracetic acid yields β-methylbutane-αβ-diol, b. p. 187°/760 mm. (after liberation from the *diacetate*, which is originally formed), which with acetone yields the corresponding *isopropylidene ether*, b. p. 129°/760 mm. J. W. BAKER.

Δ$^{\alpha\eta}$-Octadi-inene. R. LESPIEAU and DELUCHAT (Compt. rend., 1926, 183, 889—891).—βδ-Dibromo-Δ$^{\alpha}$-butene reacts with magnesium in ethereal solution, forming *βη-dibromo-Δ$^{\alpha\eta}$-octadiene*, b. p. 112—114°/11 mm., d^{15} 1·517, n_D^{15} 1·525, together with a magnesium compound which is converted by chloromethyl ether into (?) *β-bromo-ε-methoxy-Δ$^{\alpha}$-pentene*, b. p. 63·5°/11 mm., d^{19} 1·3089, 1·474. The dibromo-octadiene is converted by alcoholic potassium hydroxide into *Δ$^{\alpha\eta}$-octadi-inene*, b. p. 135—136°, d^{21} 0·8169, n_D^{21} 1·453 (*silver* salt, $C_8H_8Ag_2,2AgNO_3$), which readily absorbs atmospheric oxygen. H. E. F. NOTTON.

Preparation of β-chloroallyl chloride. L. BERT and P. C. DORIER (Bull. Soc. chim., 1926, [iv], 39, 1573—1575).—Substitution of technical glycerol αγ-dichlorohydrin for the purified material in Hill and Fischer's process (A., 1923, i, 8) gives 470 g., as against 312 g., of pure β-chloroallyl chloride per kg. of crude dichlorohydrin. Certain experimental precautions are described. M. CLARK.

Nitrosyl derivatives of bivalent sulphur. II. Nitrosylethylmercaptide [ethyl thionitrite]. H. LECHER and W. SIEFKEN (Ber., 1926, 59, [*B*], 2594—2601; cf. A., 1926, 819; Tasker and Jones, J.C.S., 1909, 95, 1917).—Even at very low temperatures, nitrosyl chloride and ethyl mercaptan react violently, giving mainly hydrogen chloride, nitric oxide, and diethyl disulphide, with a little hydroxylamine hydrochloride and ethyl thionitrite. In the presence of decahydronaphthalene at —50°, ethyl thionitrite is formed in 80% yield, but its isolation is accompanied by very considerable loss, so that the method is less convenient than that starting from ethyl nitrite and ethyl mercaptan. Ethyl thionitrite is very stable towards alcoholic potassium hydroxide, probably owing to the inability of the —N:O group to add water or alkali hydroxide. This inability explains the ready formation of ethyl thionitrite from ethyl mercaptan and ethyl nitrite according to the scheme: $EtO\cdot N{:}O + HSEt \quad EtO\cdot N(OH)\cdot SEt \longrightarrow EtOH + O{:}N\cdot SEt$, and the failure of the thionitrite at its b. p. to react with amyl alcohol. The remarkable colour of the thionitrites is attributed to the loosely-united valency electrons between the sulphur and nitrogen atoms, and not to the nitrosyl group, which, in these compounds, is an unusually stable complex. The formation of thionitrite from ethyl or amyl nitrite may be used as a colour test for mercaptans, but the method is less sensitive than the mercuric chloride test.

Ethyl nitrite and triphenylthiolmethane afford triphenylmethyl thionitrite, m. p. 99° (decomp.) after darkening at 95° when slowly heated, in theoretical yield. H. WREN.

Dihalogenomethanesulphonic acids. H. J. BACKER (Rec. trav. chim., 1926, 45, 830—837).—Dihalogenomethanesulphonic acids have been prepared in good yields by the action of the halogen (or an acidified mixture of the barium halide and halate) on barium sulphoacetate in sealed tubes at 159—210°, according to the individual case. All the acids obtained are extremely deliquescent, but lose a portion of their water of crystallisation on exposure to phosphoric oxide in a vacuum. They are best purified by crystallisation of their barium salts, the solubilities of which have been determined. The following acids have been prepared (the solubility data refer to g. of anhydrous salt per 100 g. of aqueous solution at 25°): dichloromethanesulphonic acid $+1H_2O$, m. p. 70° (*barium* $+1H_2O$, solubility 47·86 g., anhydrous, 91·79 g., and *potassium* salts); dibromomethanesulphonic acid $+1H_2O$, m. p. 73° (barium $+1H_2O$, solubility 33·30 g., anhydrous, 49·92 g.; *potassium*, *sodium*, and *thallous* salts); *di-iodomethanesulphonic acid* $+2H_2O$, m. p. 61° (*barium* $+2H_2O$, $+3H_2O$, and $+6H_2O$, solubility of last-named 14·70 g., anhydrous 17·23 g.; *potassium* and *sodium* salts); chlorobromomethanesulphonic acid $+1H_2O$, m. p. 63° (barium $+1H_2O$, solubility 42·88 g., anhydrous 75·07 g.; *potassium*, *sodium*, and *thallous* salts); chloroiodomethanesulphonic acid $+2H_2O$, m. p. 64° (*barium* $+1H_2O$, solubility 45·40 g., anhydrous 83·15 g., and *sodium* salts); *bromoiodomethanesulphonic acid* $+1H_2O$, m. p. 87° (*barium* salt $+1H_2O$ and $+3H_2O$, solubility of the latter 35·11 g.; anhydrous 54·11 g.). J. W. BAKER.

[Decomposition of formic acid by ultra-violet light.] A. KAILAN (Ber., 1926, 59, [*B*], 2493; cf. A., 1920, ii, 576).—A claim for priority against Müller and Hentschel (A., 1926, 1124). H. WREN.

Manufacture of acetic anhydride. H. DREYFUS. —See B., 1926, 995.

Separation of fatty acids. A. H. LEWIS (Biochem. J., 1926, 20, 1356—1363).—Saturated and un-

saturated fatty acids and their triglycerides form phenylhydrazides, but these are unsuitable as a means of separating fatty acids owing to the similarity of their solubility in various media. Hydroxylamine in the presence of sodium ethoxide reacts with the triglycerides of the fatty acids to give hydroxamic acids. The sodium salts of the hydroxamic acids from palmitic and stearic acids are completely insoluble in alcohol, but with decrease of mol. wt. the solubility increases. The lauric acid derivative is appreciably soluble, whilst that of heptoic acid is totally soluble in alcohol. The sodium salts of the hydroxamic acids from unsaturated fatty acids and from the hydroxy-fatty acids are completely soluble in alcohol. The above groups of fatty acids can therefore be separated by this method when present as glycerides in natural oils. S. S. ZILVA.

Use of phosphorus pentachloride in the preparation of glycerides. R. K. NEWMAN, V. M. TRIKOJUS, and G. HARKER (J. Proc. Roy. Soc. New South Wales, 1925, **59**, 293—300).—Glycerides are readily obtained by heating glycerol with phosphorus pentachloride (1 mol.) and the sodium salt of a fatty acid (5½ mols.) at 200° for 9 hrs. Tributyrin (yield 93%) has b. p. 310° (corr.) and 192—196°/26 mm., d_4^{20} 1·0350, n_D^{20} 1·43585. Tri*iso*valerin, b. p. 330·5°, 209·5—210·5°/27 mm., d_4^{20} 0·9984, n_D^{20} 1·43535. The method is also general for the preparation of esters, ethyl acetate being obtained from phosphorus pentachloride (1 mol.), ethyl alcohol (3 mols.), and sodium acetate (4 mols.). Tributyrin results from heating glycerol with butyric acid (6 mols.), so that the water produced is continuously fractionated away (yield 80%). G. M. BENNETT.

Undecenoic acid and its homologues. I. P. CHUIT, F. BOELSING, J. HAUSSER, and G. MALET (Helv. Chim. Acta, 1926, **9**, 1074—1093).—The action of dry hydrogen bromide on undecenol (*acetate*, b. p. 125—127°/7 mm., d^{15} 0·8858; *undecenoate*, b. p. 225°/8 mm., d^{15} 0·877) at 130°, yields mainly *undecenyl bromide*, CH_2:CH·[CH_2]$_8$·CH_2Br, b. p. 117—118°/8 mm., d^{15} 1·070, which on treatment with ozone yields *ι-bromodecoic acid*, m. p. 39·5—40·5°, b. p. 160°/1 mm. (*methyl* ester, b. p. 161—163°/12 mm., 135—136°/1·5 mm., d^{15} 1·177), and the corresponding *aldehyde*, b. p. 128—130°/3 mm., d^{15} 1·22 (*semicarbazone*, m. p. 85·5—86·5°), which rapidly oxidises in the air. When the bromo-acid is boiled with potassium acetate and glacial acetic acid, it yields the acetyl derivative, m. p. 36—37°, b. p. 172—174°/2 mm., of ι-hydroxydecoic acid, m. p. 75·5—76·5° (methyl ester, m. p. 15°, b. p. 165—166°/13 mm.; cf. Grün and Wirth, A., 1922, i, 804). The action of hydrogen bromide on undecenol in a freezing mixture yields *κ-bromoundecan-α-ol*, b. p. 168—169°/15 mm., d^{15} 1 152, which on treatment with acetic acid and potassium acetate and subsequent hydrolysis yields *undecane-ακ-diol*, m. p. 48—48·5°, b. p. 168—169°/8 mm. [*diphenylurethane*, m. p. 93—94°, not identical with the phenylurethane of undecane-αλ-diol (Chuit, A., 1926, 499), m. p. 139—140°], together with *iso*undecenol, CHMe:CH·[CH_2]$_5$·CH_2·OH, b. p. 124—125°/8 mm., d^{15} 0·8507, 1·4535 (*acetate*, b. p. 127—128°/7 mm., d^{15} 0·8841; *phenylurethane*, m. p. 65—66°). The action of hydrogen bromide under either of the conditions mentioned above yields also *ακ-dibromoundecane*, b. p. 164—165°/8 mm., d^{15} 1·323, which on treatment with acetic acid and potassium acetate and subsequent hydrolysis yields the ακ-diol. This glycol, on oxidation with chromic acid in acetic acid solution, yields *κ-ketoundecan-α-ol*, m. p. 42—43°, b. p. 175—176°/16·5 mm. (*acetate*, b. p. 167—168°/11 mm., 135°/1 mm.; *semicarbazone* of the acetate, m. p. 100—100·5°), and *ι-ketoundecoic acid*, m. p. 58·5—59·5°, b. p. 166—167°/1 mm. (*methyl* ester, m. p. 17°, b. p. 163—164°/13·5 mm., d^{20} 0·959). Oxidation of undecenol with sodium dichromate yields undecoic acid (chief product) and sebacic acid, which is also obtained when undecenoic acid is oxidised with chromic acid, potassium permanganate, or ozone. Oxidation of *iso*undecenol similarly yields *iso*undecenoic acid (Krafft and Seldis, A., 1901, i, 115) and azelaic acid, which is also obtained by the oxidation of *iso*undecenoic acid. Attempts to prepare *iso*undecenoic acid (1) by the action of potassium hydroxide at 220—240° on undecenoic acid or (2) by the dehydration of ι-hydroxyundecoic acid (below) with β-naphthalenesulphonic acid yield a mixture of *iso*undecenoic acid (80%) and undecenoic acid, together with a little of the *allo*-form of the former, which lowers the m. p. of the mixture below the eutectic mixture of the main products. Treatment of methyl ι-bromoundecoate (obtained by the action of hydrogen bromide on undecenoic acid at 0°) with potassium acetate and acetic acid yields the *acetyl* derivative of the methyl ester, b. p. 178°/15 mm., d^{15} 0·960, of *ι-hydroxyundecoic acid*, m. p. 49·5°, which is liberated on hydrolysis (*methyl* ester, m. p. 21·5°, b. p. 152°/8 mm.). On oxidation, this acid yields ι-ketoundecoic acid, and on reduction it gives undecane-ακ-diol. J. W. BAKER.

Preparation of α-substituted valerolactones. G. DARZENS (Compt. rend., 1926, **183**, 1110—1112).—The conversion of β-phenyl-α-allylpropionic acid into methyltetrahydronaphthalenecarboxylic acid by the action of 80% sulphuric acid at 90° (A., 1926, 1239) is accompanied by the formation of *α-benzylvalero-γ-lactone*, b. p. 188—190°/20 mm., which is not itself convertible into the tetrahydronaphthalene derivative. The reaction is general for α-alkyl-α-allylacetic acids, and thus are obtained α-iso*butylvalero-lactone*, b. p. 119—120°/16 mm., and α-iso*octyl-valerolactone*, b. p. 165—170°/18 mm. J. W. BAKER.

Carbon suboxide. O. DIELS and K. HANSEN (Ber., 1926, **59**, [*B*], 2555—2560; cf. Diels and Lalin, A., 1908, i, 939).—Carbon suboxide reacts with sulphur dioxide at a low temperature in the presence of minute traces of rubber or sulphur, yielding a colourless solid substance which is very unstable and sensitive to air. Its composition has not been established with certainty, but, since its formation is attended by production of carbon dioxide, the constitution CO:C:SO is suggested. Carbon suboxide gives yellow to orange, amorphous additive compounds with tertiary bases. The mode of union is not established, but does not appear very intimate. The following *compounds* are described: with *iso-*

quinoline, C_9H_7N,C_3O_2, m. p. 112—115° (decomp.) after darkening at 100°; with quinoline, $C_9H_7N,2C_3O_2$, m. p. about 115° (decomp.), which is converted by phenylhydrazine into the *compound*, $C_9H_7N,2C_3O_2,NHPh\cdot NH_2$; with 2-methylquinoline, $C_{10}H_9N,2C_3O_2$; with nicotine, $C_{10}H_{14}N_2,3C_3O_2$, m. p. about 100°; with codeine, $C_{18}H_{21}O_3N,5C_3O_2$, m. p. 155—160° (decomp.); with atropine, $C_{17}H_{23}O_3N,5C_3O_2$, m. p. 115—120° after darkening; with quinine, $C_{20}H_{24}O_2N_2,7C_3O_2$, m. p. 135° (decomp.). Triethylphosphine (1 mol.) and carbon suboxide (4 mols.) give an amorphous additive compound.

H. WREN.

Addition of alkali alkoxide to esters. II. F. ADICKES (Ber., 1926, **59**, [*B*], 2522—2533; cf. A., 1925, i, 1378).—Esters of oxalic acid are not able to add more than 1 mol. of alkali alkoxide. The formation of additive compounds is not observed with esters of formic, carbonic, benzoic, acetic, mono-, di-, or tri-phenylacetic acids. Trichloroacetic esters and sodium ethoxide immediately yield sodium chloride. Ethyl malonate immediately gives ethyl sodiomalonate (conveniently prepared by treating sodium with a slight excess of ethyl malonate dissolved in ether and addition of light petroleum to the solution); the possibility of intermediate formation of an additive compound is not excluded. Ethyl diethylmalonate does not unite with sodium ethoxide. Reaction is not observed with compounds in which the carboxyl groups are separated by a greater number of carbon atoms (succinic and phthalic esters). If, however, the carboxyl groups are united by an aliphatic ·C:C· linking, reactivity is again observed, as instanced by ethyl fumarate. In general, addition of sodium alkoxide appears invariably possible with molecules containing the system R·CO·CO·R′, even when neither R nor R′ is a carboxyl group. Thus benzil unites with sodium ethoxide, as apparently do also ethyl glyoxylate and ethyl mesoxalate. Ethyl pyruvate combines very readily with 1 mol. of sodium alkoxide, but the constitution of the additive compound could not be established with certainty by reason of its great reactivity. It is, however, highly probable that addition occurs at the carboxyl, and not at the carbonyl group, since pyruvic acid is present in the additive compound in polymerised form, and, further, the compound is not converted by ethyl iodide into diethoxypropionic ester, as would be expected if reaction had occurred at the carbonyl group. The second necessary C:O double linking can be replaced by the aliphatic C:C linking, as shown by the reactivity of acrylic, crotonic, and cinnamic esters.

Arguments are advanced against the constitution, $COMe\cdot CH_2\cdot C(OEt)_2\cdot ONa$, assigned by Scheibler and Voss (A., 1920, i, 366) to the intermediate product of the acetoacetic ester synthesis. The assumption of the formation of an additive product from ethyl acetate and sodium ethoxide does not appear to be supported by experimental evidence. H. WREN.

Stereochemistry of the tetrahedral carbon atom. IV. Isomerism of the chloromalic acids. R. KUHN and R. ZELL (Ber., 1926, **59**, [*B*], 2514—2521; cf. A., 1925, i, 780; 1926, 505).—(−)-*trans*-Oxidoethylene-αβ-dicarboxylic acid is conveniently prepared by treating methyl monoacetyl-*d*-tartrate with thionyl chloride in pyridine solution, followed by successive treatment of the product with acid and alkali hydroxide. The mixture of (−)-*trans*-oxidoethylene-αβ-dicarboxylic acid (96%) and chloromalic acid-II is separated into its components by means of the barium salts. (−)-*trans*-Oxidoethylene-αβ-dicarboxylic acid, m. p. 180° (corr. decomp.), $[\alpha]_D^{18}$ −100° in water, gives a *potassium hydrogen* salt (+H_2O), $[\alpha]_D^{18}$ −100° in water, normal *calcium* salt (+H_2O), and anhydrous *barium* salt. The mother-liquors from the barium (−)-*trans*-oxidoethylene-αβ-dicarboxylate when treated with an excess of alkali hydroxide afford *cis*-oxidoethylene-αβ-dicarboxylic acid, thus confirming the conclusion of Freudenberg and Brauns (A., 1922, i, 623) that partial inversion occurs during the replacement of the hydroxyl group of methyl monoacetyltartrate by chlorine by means of thionyl chloride. Hydrolysis of (−)-*trans*-oxidoethylene-αβ-dicarboxylic acid affords *d*-tartaric acid mixed with a little *meso*tartaric acid. Ethereal hydrogen chloride transforms it quantitatively into (−)-chloromalic acid-I, m. p. 165—166° (decomp.), $[\alpha]_D^{18}$ −8·0° in water, $[\alpha]_D^{22}$ −31·1° in ethyl acetate, $[\alpha]_D$ −11·5° in 96% alcohol [Sonn and Rosinsky (A., 1925, i, 1237) give m. p. 153°]; the *potassium hydrogen*, *barium* (+$3H_2O$), and *calcium* salts, the *dimethyl* ester, b. p. 140°/14·5 mm., d_4^{20} 1·3598, n_D^{20} 1·4594, $[\alpha]^{22}$ −22·05°, and *diethyl* ester, b. p. 147°/11 mm., d_4^{20} 1·2366, n_D^{20} 1·4524, $[\alpha]^{23}$ −16·82°, are described. The optical homogeneity of (−)-chloromalic acid-I is established by its quantitative reconversion into (−)-*trans*-oxidoethylene-αβ-dicarboxylic acid. Reduction of (−)-chloromalic acid-I affords *d*-malic acid, whilst hydrolysis converts it into *d*-tartaric acid mixed with a little *meso*-acid, thus confirming the configurative relationship of *d*-malic and *d*-tartaric acids (cf. Freudenberg and Brauns, *loc. cit.*).

Chloromalic acid-II is conveniently resolved into its optical antipodes by fractional crystallisation of the morphine hydrogen salt from 96% alcohol. (+)-*Chloromalic acid*-II has m. p. 166—167° (decomp.), $[\alpha]_D$ +9·35±1·5° in water (*morphine hydrogen* salt, $[\alpha]_D$ −72·6° in water); it is slowly converted by boiling water into *meso*tartaric acid. (−)-*Chloromalic acid*, m. p. 166—167° (decomp.), is reduced to *l*-malic acid. H. WREN.

Properties of molybdomalic complexes. II. Action of bases. E. DARMOIS (Bull. Soc. chim., 1926, [iv], **39**, 1515—1527; cf. A., 1926, 559, 723).—The action of bases (ammonium, barium, and sodium hydroxides, aniline, etc.) on α-ammonium *d*-dimolybdomalate is studied by polarimetric and other methods. On progressive addition of a base to a dilute solution of the complex, the latter tends towards a feeble lævorotation; with concentrated solutions, however, this state is attained more rapidly, and the solution then becomes dextrorotatory again, passing through a maximum. The base probably combines with a part of the molybdic acid, forming, in the case of ammonia, the lævo-compound $MoO_3,2C_4H_4O_5(NH_4)_2$, which, in very dilute solution, hydrolyses to the less lævorotatory ammonium malate. In concentrated solutions, the complex *compound*,

$4MoO_3,5C_4H_6O_5,11NH_3,5H_2O$, exists, intermediate to $4MoO_3,2C_4H_6O_5$ (dextro) and $MoO_3,2C_4H_6O_5$ (lævo). It is formed together with basic molybdates. An explanation of the observed maximum dextrorotation is offered. Molybdomalates are considered to be derived from $[Mo_4O_{11}]H_4$, and structures are suggested for the compounds $4MoO_3,2C_4H_4O_5(NH_4)_2$ and $MoO_3,2C_4H_5O_5NH_4$ (cf. A., 1926, 457). The complex $MoO_3,2C_4H_4O_5K_2$ is decomposed by potassium hydroxide into the normal malate without the formation of an intermediate complex. The work of Gernez is explained with the aid of the results (cf. A., 1891, 291, 545). S. K. TWEEDY.

Sapogenins of quillaic acid. A. WINDAUS, F. HAMPE, and H. RABE (Z. physiol. Chem., 1926, **160**, 301—307).—Sthamer's saponin, when heated with dilute sulphuric acid, yields *prosapogenin*, probably a dibasic acid, $C_{35}H_{56}O_{12}$, m. p. 206—207° (decomp.) [*potassium* salt]. It gives an *oxime*, $C_{35}H_{57}O_{12}N$, m. p. 258°, and when treated with concentrated hydrochloric acid yields furfuraldehyde (1 mol.) and carbon dioxide (1 mol.), thus probably containing either glycuronic or galacturonic acid. The saponin, when heated with dilute sulphuric acid at 140—145°, yields *endsapogenin*, a monobasic acid, $C_{29}H_{46}O_5$, m. p. 294° (decomp.); the *potassium* salt, *monomethyl* ester, m. p. 225°, *monoxime*, m. p. 282°, *semicarbazone*, m. p. 288°, *diacetyl* derivative, m. p. 250°, and *methyl ester oxime*, m. p. 238°, are described. It does not contain a double linking, and on oxidation with nitric acid yields a trinitrodicarboxylic acid, $C_{25}H_{35}O_{10}N_3$, m. p. 240° (decomp.) [*dimethyl* ester, m. p. 197° (decomp.)]. Endsapogenin of quillaic acid, is, therefore, a dihydroxyketocarboxylic acid, and is not closely related to bile acid, as was supposed, and cannot, like bile acid, be a decomposition product of sterols. P. W. CLUTTERBUCK.

βγ-Dihydroxy-Δ$^{\beta}$-butene-αδ-dicarboxylic acid, the so-called "dihydroxymaleic acid." H. SCHMALFUSS and H. BARTHMEYER (Z. physiol. Chem., 1926, **160**, 196—213).—Dihydroxymaleic acid may be characterised as its dimercurous salt, which is, however, very unstable, 1 mol. yielding, on treatment with water at 70°, tartronic acid (1 mol.), carbon dioxide (1 mol.), and mercury (2 atoms). Dihydroxymaleic acid (1 mol.), on treatment with excess of mercurous nitrate, yields at 70° nitric acid (8 mols.), carbon dioxide (4 mols.) and mercury (8 atoms). Several methods for the determination of the acid are described, and its possible importance in the metabolism of *Glaucium luteum*, Scop., in which it is found, is discussed. The limits of the qualitative test with ferric chloride and potassium hydroxide are 0·05 mg., and of the titanium salt test 0·01 mg. of dihydroxymaleic acid. P. W. CLUTTERBUCK.

Double citrates of quadrivalent vanadium. G. CANNERI (Gazzetta, 1926, **56**, 637—642).—Addition of citric acid to the solution of a vanadyl salt and neutralisation of the liquid with ammonia gives a deep blue liquid, further addition of ammonia then giving a precipitate which partly redissolves to form a brown solution. In the dilute solutions, ammonia or an alkali hydroxide causes change in colour from blue to brown, but the alkali carbonates do not alter the colour. This behaviour differs sharply from that of the analogous solutions containing tartaric acid, which, with ammonia or an alkali carbonate, give a purplish-violet solution owing to the formation of complex ions corresponding with violet vanadyltartrates. Evaporation of the neutralised citric solutions of vanadyl salts yields turquoise-blue crystals of double citrates, which may be obtained also either by dissolving hydrated vanadium dioxide in citric acid and neutralising with alkali, or from vanadates and excess of citric acid. These salts dissolve readily in water and respond to all the characteristic reactions of ordinary vanadyl salts, and their constitution, unlike that of the vanadyltartrates, in which the appearance of the force of co-ordination is indicated by their colour reaction, seems to be $OH{\cdot}C(CH_2{\cdot}CO_2R)_2{\cdot}CO_2{\cdot}VO{\cdot}VO{\cdot}CO_2{\cdot}C(CH_2{\cdot}CO_2R)_2{\cdot}OH$. Thus, the presence in the citric acid molecule of a carboxyl and a hydroxyl group united to the same carbon atom is not a sufficient condition for the formation of internal complex salts. The double citrates of vanadyl and *ammonium*, $(NH_4)_4(VO)_2(C_6H_5O_7)_2$, *potassium* ($+6H_2O$), and *sodium* ($+12H_2O$) were analysed. T. H. POPE.

Products of the bromination of paracetaldehyde. II. A. STEPANOV, N. PREOBRASCHENSKI, and M. SCHTSCHUKINA (Ber., 1926, **59**, [*B*], 2533—2538; cf. A., 1925, i, 1240).—The action of bromine (1 mol.) on paracetaldehyde at −15° gives *bromoparacetaldehyde*, b. p. 77·5°/8 mm., 82·5°/10 mm., m. p. 27·5°, with dibromoparacetaldehyde and unchanged paracetaldehyde. The monobromo-compound decomposes smoothly at 130° into bromoacetaldehyde and acetaldehyde, from which it can be regenerated under the influence of hydrogen bromide. Paracetaldehyde and bromine (2 mols.) afford dibromoparacetaldehyde in 89—94% yield with very little tribromoparacetaldehyde. Complete action between paracetaldehyde and bromine (3 mols.) is very slow, and is complicated by the action of hydrogen bromide on the aldehyde, resulting in the production of tetrabromobutaldehyde. Attempts to remove the liberated hydrogen bromide by operating in the presence of calcium carbonate show the acid to have a very pronounced accelerating effect on the action.

The action of bromine on paracetaldehyde is accompanied by only slight evolution of hydrogen bromide. The course of the change is explained on the hypothesis that paracetaldehyde is in equilibrium with a small proportion of acetaldehyde which, under the influence of bromine, becomes enolised to vinyl alcohol; the latter substance combines with bromine, yielding the very unstable *αβ-dibromoethyl alcohol*, b. p. 31°/17 mm., d_4^{20} 2·1782, n_D^{20} 1·5492, which passes into tribromoparacetaldehyde and hydrogen bromide. The liberated acid combines with acetaldehyde or vinyl alcohol, yielding α-bromoethyl alcohol, which, with αβ-dibromoethyl alcohol, gives a mixture of mono- and di-bromoparacetaldehyde. H. WREN.

Ester condensation: replacement of functional groups under the action of aluminium ethoxide. R. DWORZAK (Monatsh., 1926, **47**, 11—16; cf. A., 1925, i, 783, 1239).—Chloral is converted by aluminium

ethoxide in benzene solution into trichloroethyl alcohol (33% yield) together with small quantities of acetaldehyde, paracetaldehyde, and ethyl and trichloroethyl trichloroacetates. The relation of the Tischtschenko reaction to this conversion of an aldehyde into its alcohol is discussed and a scheme of connected, reversible reactions is given in which the production of the two possible aldehydes and the four possible esters is accounted for. G. M. BENNETT.

Process of making aldols. C. J. HERRLY.—See B., 1926, 995.

Action of alkali hydroxide on the sodium salt of enolic glutacondialdehyde. Sorbaldehyde. P. BAUMGARTEN and G. GLATZEL (Ber., 1926, **59**, [*B*], 2658—2665; cf. A., 1926, 844).—Treatment of a solution of the enolic form of glutacondialdehyde in 7·5% sodium hydroxide with steam yields much resin, formic acid, acetaldehyde, crotonaldehyde, and two aldehydes, C_6H_8O and $C_8H_{10}O$. The former of these is identified as sorbaldehyde, b. p. 76°/30 mm. (*semicarbazone*, m. p. 203°), since it is oxidised by silver oxide to sorbic acid and adds 4 atoms of bromine; it is smoothly hydrogenated in aqueous suspension in the presence of palladium to a saturated aldehyde converted by silver oxide into *n*-hexoic acid. The aldehyde, $C_8H_{10}O$, b. p. 79°/1 mm., appears to be a cyclic compound, since it reacts with bromine with evolution of hydrogen bromide; its constitution could not be established. H. WREN.

Olefinic terpene ketones from volatile oil of flowering *Tagetes glandulifera*. II. T. G. H. JONES (J.C.S., 1926, 2767—2770).—Ethyl *iso*valerylacetate condensed with *sec.*-butyl iodide in presence of sodium ethoxide gives *ethyl* sec.-*butyl*isovalerylacetate, b. p. 133°/24 mm., which on hydrolysis with alcoholic potassium hydroxide yields *γη-dimethyloctan-ε-one*, b. p. 187°/760 mm., d^{25} 0·8190, n_D 1·4190. Under similar conditions, ethyl *iso*valerylacetate and ethyl α-iodopropionate give α-methyl-β-*iso*valerylpropionic acid, m. p. 166°, identical with the acid obtained by oxidising *γη*-dimethyl-Δ$^{\alpha}$-octen-ε-one. Hot 70% sulphuric acid converts *γη*-dimethyl-Δ$^{\alpha}$-octen-ε-one into *iso*valeric acid, methyl ethyl ketone, and methyl *iso*butyl ketone, the latter substance being produced also when tagetone is decomposed by boiling alcoholic potassium hydroxide. Tagetone is probably represented by the tautomeric systems ·CO·CH$_2$·C(:CH$_2$)·CH:CH$_2$ — ·C(OH):CH·C(:CH$_2$)·CH:CH$_2$ — ·CO·CH:CMe·CH:CH$_2$. The compound $C_{10}H_{18}O$ (see A., 1926, 72), obtained by the reduction of tagetone with sodium in moist ether or with zinc dust and acetic acid, is named *tagetol*. H. BURTON.

Interaction of amino-compounds and carbohydrates. III. Action of nitrous acid on certain nitrogenous sugar derivatives and related compounds. A. HYND and M. G. MACFARLANE (Biochem. J., 1926, **20**, 1264—1272).—Amino-compounds reacting with nitrous acid can be subdivided into three groups. Compounds such as glycine and glucosimine are representatives of one group in which the nitrogen is liberated readily on reaction with nitrous acid in the presence of a weak acid. In the second group, which is represented by substances like carbamide, glucose ureide, and glucosamine, the liberation of nitrogen proceeds slowly in presence of weak acid, but rapidly in presence of a strong acid. Urethane, guanidine, and creatine are typical of the third group of compounds, which require the presence of a strong acid for the above reaction. A number of compounds have been investigated on these lines, and structural formulæ are assigned to these substances in the light of the results obtained (cf. Plimmer, A., 1926, 156). S. S. ZILVA.

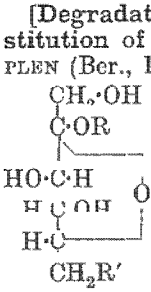
Carbohydrates. V. Bitter taste of sugar derivatives. P. BRIGL and W. SCHEYER (Z. physiol. Chem., 1926, **160**, 214—233).—Nineteen sugar derivatives of solubilities at the ordinary temperature varying between 4% and 0·00125% and of differing bitterness to taste (when compared with glucose penta-acetate as standard) are investigated stalagmometrically, and it is shown that there is no direct relationship between surface activity and degree of bitterness. Introducing groups which decrease the solubility in water and increase solubility in organic solvents tends to augment the bitterness, but no parallel could be drawn between solubility and bitterness. Sucrose octa-acetate possesses the greatest degree of bitterness, 34×10^{-6} g. being detectable by taste. There appears to be a relationship, however, between configuration and taste, since all the derivatives of β-glucose are more bitter than those of α-glucose. P. W. CLUTTERBUCK.

Oxygen bridges in the sugars. II. Position of the oxygen bridge in dextrose. F. MICHEEL and K. HESS (Annalen, 1926, **450**, 21—29; cf. A., 1926, 1230).—Methylation of *iso*propylideneglucose with methyl sulphate and sodium hydroxide yields the trimethyl ether, which by treatment with 0·5% aqueous methyl-alcoholic hydrochloric acid (40% water) is converted into 3 : 5 : 6-trimethylmethylglucoside. This is methylated further to 2 : 3 : 5 : 6-tetramethylmethylglucoside, b. p. 105—107°/2 mm., α_D^{20} −9·24° (in water), from which by hydrolysis with 0·3% hydrochloric acid 2 : 3 : 5 : 6-tetramethylglucose, m. p. a little above 0°, b. p. 117—120°/1 mm., α^{20} −11·1° (in water), n_D^2 1·4525, results. Since *iso*propylideneglucose is readily obtained from and converted into di*iso*propylideneglucose under very mild conditions and differs little from it in rotatory power, it contains the same oxygen bridge. The tetramethylglucose <1 : 4> obtained from it is identical with that prepared from γ-methylglucoside (Irvine, Fyfe, and Hogg, J.C.S., 1915, **107**, 524) and from 2 : 3 : 6-trimethyl-γ-methylglucoside (Schlubach and Bomhard, A., 1926, 600), and differs greatly from 2 : 3 : 4 : 6-tetramethylglucose <1 : 5> (Purdie and Irvine, J.C.S., 1904, **85**, 1049). It follows that γ-glucose has a 1 : 4-oxygen bridge, normal glucose a 1 : 5. The formation of di*iso*propylideneglucose only from β-glucose is explained as due to migration of the 1 : 5- to a 1 : 4-ring only in β-glucose under the conditions.

The *iso*propylidenedioxy-groups are shown to be partly hydrolysed during Zeisel determinations, causing an error of +2 to 3% in the methoxyl value. C. HOLLINS.

Occurrence of gentiobiose in the products of the commercial hydrolysis of corn [maize] starch. H. BERLIN.—See B., 1926, 992.

[Degradation of reducing bioses. IV. Constitution of turanose and melezitose.] G. ZEMPLEN (Ber., 1926, 59, [*B*], 2539—2540; cf. A., 1926, 1229).—In conformity with the observation of Haworth and Hirst that sucrose contains a butylene oxidic grouping, the amended constitution (I) is suggested for turanose (R=H, R′=glucose residue) and melizitose (R=R′=glucose residue). H. WREN.


(I.)

Syntheses of sugars. VI. 6-β-*d*-Galactosido-α-glucose. Constitution of melibiose. B. HELFERICH and H. RAUCH (Ber., 1926, 59, [*B*], 2655—2657).—1 : 2 : 3 : 4-Tetra-acetylglucose is converted by acetobromogalactose and silver oxide in chloroform solution into 6-β-d-*galactosido-α-glucose octa-acetate*, m. p. 166° (corr.), $[\alpha]_D^{20}$ 0°, which is hydrolysed to the non-crystalline 6-β-d-*galactosido-α-glucose*, $[\alpha]_D^{18}$ +36·4° in water, probably a mixture of isomerides. The corresponding *phenylosazone* has m. p. about 185° (corr.), $[\alpha]_D$ −69·6° to −23·9° in 4 hrs. The non-identity of the synthetic sugar with melibiose indicates that the accepted constitution or configuration of the latter substance is untenable. H. WREN.

Pentose of digitonin. H. KILIANI (Ber., 1926, 59, [*B*], 2462—2465).—Hydrolysis of digitonin with aqueous hydrochloric acid leads to the production of *d*-galactose, dextrose, and *l*-xylose, identified as strontium *l*-xylonate. Hydrolysis of glucosides such as digitonin is advantageously effected with alcoholic hydrogen chloride when the main purpose is the isolation of the corresponding genin; the use of alcohol should be avoided if the liberated sugars are to be identified, since ethyl glucosides are formed to a considerable extent. H. WREN.

Cellulose. XXII. Crystalline trimethylcellulose. K. HESS and H. PICHLMAYR (Annalen, 1926, 450, 29—40; cf. A., 1925, ii, 782).—Trimethylcellulose, prepared from natural cellulose, "viscose" silk, or "copper" silk, after one precipitation from benzene–light petroleum is readily obtained crystalline from chloroform–alcohol. If separation is too rapid, the product is amorphous, but may be rendered crystalline by moistening with chloroform–alcohol and keeping for a few days. The crystalline form is retained after removal of the solvent. Like crystalline cellulose triacetate, crystalline trimethylcellulose gradually undergoes association in glacial acetic acid solution, the mol. wt. (determined cryoscopically) increasing from about 300 to about 850 in 30 hrs. C. HOLLINS.

Cellulose. XXIII. Acetolysis of cellulose. II. K. HESS and H. FRIESE (Annalen, 1926, 450, 40—58; cf. Hess, Weltzien, and Singer, A., 1925, i, 641; Irvine and Robertson, *ibid.*, 1926, 823).—A product representing an intermediate stage in the acetolysis of cellulose to cellobiose and *iso*cellobiose is described. Cellulose is treated below −5° with a mixture of acetic acid and anhydride containing 2·5% of sulphuric acid; the temperature is raised slowly and maintained at 30° for 2·5 days. After filtering and pouring into water, a white precipitate is obtained which, after extraction with hot methyl alcohol, leaves pure *hexa-acetylbiosan*, $C_{24}H_{34}O_{16}$, m. p. 258—259°, $[\alpha]_D$ −12·61° (in chloroform). This is hydrolysed by methyl-alcoholic sodium hydroxide to *biosan*, decomp. about 270°, which reduces Fehling's solution, and may be re-acetylated to hexa-acetylbiosan by boiling acetic anhydride and pyridine, or acetolysed to cellobiose and *iso*cellobiose. Methylation of biosan with methyl sulphate and alkali gives *hexamethylbiosan*, m. p. 210—215°, $[\alpha]_D^{20}$ −10·18° (in water), which is converted by methyl-alcoholic hydrogen chloride into 2 : 3 : 6-trimethylglucose-αβ-methylglucoside, m. p. 118—120°, $[\alpha]_D^{20}$ +62·04° (in methyl alcohol), from which by the action of aqueous hydrochloric acid 2 : 3 : 6-trimethylglucose, identical with that from cellulose or cellobiose, is obtained. It is suggested that biosan is a true dimeride of the fundamental cellulose molecule as opposed to cellulose, which is an agglomerate of such molecules. It is shown that cellobiose formation is independent of the degree of association of cellulose or cellulose acetates. Hexa-acetyl- and hexamethyl-biosans do not exhibit the tendency to association shown by cellulose acetates. C. HOLLINS.

Cellulose. K. HESS. XXIV. Presence of a foreign substance in cellulose fibres. F. MICHEEL and W. REICH (Annalen, 1926, 450, 59—65).—Cellulose purified by the usual methods is found to contain a compound which is difficult to separate and shows itself as an insoluble, gelatinous substance when the completely acetolysed cellulose is re-acetylated with pyridine and acetic anhydride. After freeing from ash (35—45%, mainly calcium oxide), the substance has $[\alpha]_D$ about +20°, decomp. 230—240°. It shows no crystal structure under the microscope, but the *X*-ray diagram indicates the presence of crystals and has no relation to that of cellulose or mercerised cellulose. C. HOLLINS.

[Constitution of cellulose.] G. SCHULTZE and K. HESS (Annalen, 1926, 450, 65—74; cf. Pringsheim and others, A., 1926, 942).—Repetition fails to confirm the "de-association" of cellulose acetates when heated in boiling naphthalene, and "cellosan" is shown to have no relation to cellulose. C. HOLLINS.

Substituted amines. Preparation of substituted acetamides and the corresponding primary amines. J. L. E. ERICKSON (Ber., 1926, 59, [*B*], 2665—2668).—Acetamide is converted by benzyl bromide at 200° into acetbenzylamide, b. p. 157°/2 mm., m. p. 61° (yield 80%); ammonium bromide and diacetamide are also produced by the action of the liberated hydrogen bromide on a portion of the acetamide. *Acet-β-phenylethylamide*, b. p. 154°/2 mm., m. p. 45°, is prepared similarly in 388% yield. The following substituted acetamides are produced at 200—220°: acetethylamide, b. p. 206°; acet-*n*-propylamide, b. p. 225°; *acet*-n-*butylamide*, b. p. 229°; *acetisoamylamide*, b. p. 232°. The amides are hydrolysed by concentrated hydrochloric acid to the corresponding amines. H. WREN.

Simple synthesis of α-amino-acids. G. SCHROETER (Z. angew. Chem., 1926, **39**, 1460).—When *p*-tolylsulphonamides are treated with α-halogenocarboxylic acids in aqueous or alcoholic alkali solution *p*-tolylsulphonamido-acids result, which are converted into α-amino-acids by hydrochloric acid, acetyl or chloroacetyl chloride. E. HOLMES.

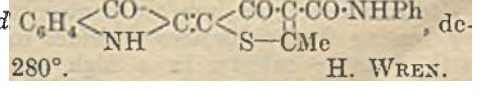
Action of Grignard reagents on amino-acids. Action of mineral acids on β-amino-αα-diphenylethanol. X. Experiments with acylamino-acids and peptides. F. BETTZIECHE [with R. MENGER and K. WOLF] (Z. physiol. Chem., 1926, **160**, 263—269; 270—300).—IX. β-Amino-αα-diphenylethanol when heated in a sealed tube with 40% sulphuric acid gives deoxybenzoin (yield 62%), obtained also from diphenylacetaldehyde and 4% sulphuric acid, the amount decreasing the stronger the acid. If the reaction is carried out with concentrated sulphuric acid in ice, however, the yield is 76%. Diphenylacetaldoxime when heated under reflux with 4% sulphuric acid also gives deoxybenzoin. Triphenylacetaldehyde yields triphenylethanone when heated with hydrochloric acid under reflux, the yield being greater with 40% sulphuric acid and being very good with ice-cooled sulphuric acid.

X. The following substances react with the appropriate Grignard reagent: ethyl benzoylphenylalanine, giving β-benzamido-β-benzyl-αα-diethylethanol, m. p. 135°, yield 69%; phenylglycine ester hydrochloride, giving an oil the benzoyl derivative of which has m. p. 136°; ethyl benzoylphenylglycine, giving β-*benzamido*-β-*phenyl*-αα-*dimethylethanol*, m. p. 136°; ethyl benzoyl-leucine, giving β-*benzamido*-αα-*diphenyl*-β-iso*butylethanol*, m. p. 184°, yield 52%; ethyl benzoylalanine, giving β-*benzamido*-αα-*dibenzylpropanol*, m. p. 122°, synthesised for comparison by benzoylation of the free amino-alcohol, the yield here being 66%; ethyl toluenesulphonylglycine with magnesium phenyl bromide, giving β-*toluenesulphonamido*-αα-*diphenylethanol*, m. p. 138° (*sodium* salt), yield 50%, identical with a sample obtained from toluenesulphonyl chloride and β-amino-αα-diphenylethanol; ethyl toluenesulphonylglycine, giving β-*toluenesulphonamido*-αα-*dibenzylethanol*, m. p. 150—151°, yield 35%, identical with a sample obtained from toluenesulphonyl chloride and β-amino-αα-dibenzylethanol; ethyl toluenesulphonalanine, giving β-*toluenesulphonamido*-αα-*dibenzylpropanol*, m. p. 161—162°, yield 39%, identical with a sample obtained by acylation of the amino-alcohol; ethyl benzenesulphonylglycine, giving β-*benzenesulphonamido*-αα-*diphenylethanol*, m. p. 139°, yield 51%; ethyl naphthalenesulphonylglycine, giving β-*naphthalenesulphonamido*-αα-*diphenylethanol*, m. p. 163—164°, yield 43%; ethyl glycylalanine hydrochloride, giving β-*glycylamido*-αα-*diphenyl*-β-*methylethanol*, m. p. 186·5—187°; ethyl glycylalanine hydrochloride, giving β-*glycylamido*-β-*methyl*-αα-*dibenzylethanol*, m. p. 107·5°; ethyl benzoylglycylalanine, giving β-*benzoylglycylamido*-αα-*diphenyl*-β-*methylethanol*, m. p. 187·5—188°, yield 61%; ethyl benzoylglycylalanine, giving β-*benzoylglycylamido*-β-*methyl*-αα-*dibenzylethanol*, m. p. 183°; ethyl benzoylglycylphenylaminoacetate, giving β-*benzoylglycylamido*-αaβ-*triphenylethanol*, m. p. 213·5—214°; ethyl benzoylglycylphenylaminoacetate, giving β-*benzoylglycylamido*-β-*phenyl*-αα-*dibenzylethanol*, which first melts at 147—148°, resolidifies at 175°, and then melts at 187·5—188°, the difference being probably due to intramolecular change; ethyl phthalamidoacetate, giving several products, of which the chief was *ethyl* o-*benzoylbenzoylglycine*, m. p. 143°, which on partial hydrolysis gave *o*-benzoylhippuric acid, m. p. 183°, and on more complete hydrolysis, benzoylbenzoic acid, m. p. 126—127°, and glycine ester hydrochloride.

P. W. CLUTTERBUCK.

Action of sodium hypochlorite on acid amides. III. I. J. RINKES (Rec. trav. chim., 1926, **45**, 819—824; cf. A., 1920, i, 322).—The urethanes formed from amides of unsaturated fatty acids are soluble in the aqueous methyl alcohol, and owing to their greater ease of hydrolysis the reaction must be carried out at 0°. Δ$^{\alpha}$-Nonenoamide (Harding and Weizmann, J.C.S., 1910, **97**, 301) thus treated yields Δ$^{\alpha}$-*octenylurethane*, m. p. 28·5°, b. p. 155—160°/10 mm., which on hydrolysis with dilute sulphuric acid yields octaldehyde (*p*-nitrophenylhydrazone, m. p. 75°). The monoamide of maleic acid, m. p. 172—173° (decomp.) (Anschutz, A., 1891, 176, gives 152—153°), yields β-*carboxyvinylurethane*, m. p. 126° (decomp.), whilst *cyclo*hexenecarboxylamide gives *cyclo*hexanone, isolated as its dibenzylidene derivative. Decomposition of the ozonide of *o*-allylphenol with zinc and acetic acid yields *o*-hydroxyphenylacetaldehyde, b. p. about 90°/vacuum (*semicarbazone*, m. p. 171°; p-*nitrophenylhydrazone*, m. p. 148°).

J. W. BAKER.

Acylation of β-aminocrotonanilide. E. BENARY and W. KERCKHOFF (Ber., 1926, **59**, [*B*], 2548—2551; cf. A., 1923, i, 37, 201).—Acylation of β-aminocrotonanilide differs from that of β-aminocrotonic ester in that there is little tendency towards the production of *N*-derivatives. Benzoyl chloride and β-aminocrotonanilide in pyridine afford β-*amino*-α-*benzoylcrotonanilide*, NH_2·CMe:CBz·CO·NHPh, m. p. 173°, converted by boiling dilute sulphuric acid into benzoylacetanilide and by phenylhydrazine into 1 : 5(3)-*diphenyl*-3(5)-*methylpyrazole*-4-*carboxyanilide*, m. p. 167°. β-*Amino*-α-*cinnamoylcrotonanilide*, m. p. 201°, prepared similarly, is hydrolysed to *cinnamoylacetanilide*, m. p. 107°, and converted by phenylhydrazine into 1-*phenyl*-3(5)-*methyl*-5(3)-*cinnamylpyrazole*-4-*carboxyanilide*, m. p. 224°. β-*Amino*-α-*chloroacetylcrotonanilide*, m. p. 155°, is converted by methyl-alcoholic potassium hydroxide into 3-*hydroxy*-5-*methylpyrrole*-4-*carboxyanilide*, m. p. 181°, and by potassium hydrogen sulphide into 3-*hydroxy*-5-*methylthiophen*-4-*carboxyanilide*, m. p. 125°. The latter substance is transformed by nitrous acid into 2-*oximino*-3-*keto*-5-*methyl*-2 : 3-*dihydrothiophen*-4-*carboxyanilide*, decomp. 235° after darkening at 150°, and by isatin and concentrated sulphuric acid into the *compound*  , decomp. above 280°.

H. WREN.

Sodium salts of cyanamide. W. TRAUBE, F. KEGEL, and H. E. P. SCHULZ (Z. angew. Chem., 1926, **39**, 1465—1469).—When an aqueous solution of

disodium cyanamide is kept at 0° for 20 hrs., it deposits 68% of *monosodium cyanamide dihydrate*. Calcium and disodium cyanamides give the stable dialkylcyanamides quite smoothly (Traube and Engelhardt, A., 1911, i, 955), but the monosodium salt gives mono- and dialkyl-derivatives, which are unstable and give polymerisation products. Among these is *guanylmethylcarbamide*, $C_3H_8ON_4$, which gives a *hydrochloride*, $C_3H_8ON_4,HCl,H_2O$, m. p. 155°, and is proved to have two free amino-groups by the production of a *copper* derivative, $Cu(C_3H_7ON_4)_2,4H_2O$, m. p. 208°. Monosodium cyanamide with the ethyl halides gives 19% of diethylcyanamide, b. p. 60—70°/12 mm., 186°/760 mm.; it does not condense in an analogous manner to the methyl compound, but 2 mols. together with 1 mol. of free cyanamide give ring closure with the production of *diethylmelamine*, $C(NH_2)-N\overset{C\cdot NHEt}{\underset{N:C(NHEt)\ N}{\|}}$, b. p. 200°/11 mm., 330°/atm. pressure, m. p. 155—156° (*hydrochloride*, m. p. 265°; *nitrate*, m. p. 169—170°). On heating disodium cyanamide with methyl sulphate, 19% of *isotrimethylmelamine*, m. p. 179°, is obtained with a little guanylmethylcarbamide. E. HOLMES.

Nitrosyl derivatives of bivalent sulphur. III. Nitrosyl thiocyanate. H. LECHER and F. GRAF (Ber., 1926, 59, [*B*], 2601—2602).—Ethyl nitrite reacts with thiocyanic acid in anhydrous ethereal solution at —78° with formation of nitrosyl thiocyanate (cf. Söderbäck, A., 1920, i, 219), which is too unstable to permit its isolation. H. WREN.

[Thiocyanogen chloride.] H. LECHER and G. JOSEPH (Ber., 1926, 59, [*B*], 2603—2606; cf. Kaufmann and Liepe, A., 1924, i, 839).—The properties of monothiocyanogen chloride are not in harmony with a unimolecular structure, and determinations of the mol. wt. in boiling benzene or chloroform indicate the composition $(CNClS)_6$. With diethylamine, it gives half the quantity of diethylrhodanamine (cf. A., 1923, i, 661) which is derivable theoretically from the unimolecular compound, but the fate of the remainder of the compound could not be ascertained. With dimethylaniline, it affords *p*-thiocyanodimethylaniline in quantitative yield. The constitution of the substance cannot yet be elucidated, but "unimolecular thiocyanogen chloride" should be deleted from the literature. H. WREN.

Reactions of sodium nitroprusside. N. TARUGI (Annali Chim. Appl., 1926, 16, 407—413).—Sodium nitroprusside and thiocyanate mixed in alkaline solution and acidified give a violet solution from which are obtained blue crystals of a *substance*, probably $Na_2Fe(CN)_5\cdot N(OH)\cdot SCN$, which further loses water to give a green substance. E. W. WIGNALL.

Rubidium and cæsium alkyls. A. VON GROSSE (Ber., 1926, 59, [*B*], 2646—2654; cf. A., 1926, 555).—Rubidium and cæsium are conveniently prepared by heating their respective chlorides to dull redness with metallic calcium in a high vacuum. When dissolved in mercury, the metals react readily with a solution of triphenylmethyl chloride in anhydrous ether, giving *rubidium triphenylmethyl* and *cæsium triphenylmethyl* as very reactive, dark red powders giving blood-red solutions in ether. *Lithium triphenylmethyl* is an orange-red powder which yields a stable *etherate*. Rubidium and zinc ethyl give the additive *compound*, $RbEt,ZnEt_2$, m. p. 70—75°; cæsium appears to yield a similar substance. H. WREN.

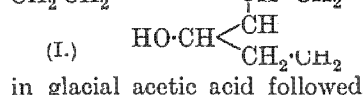
Reducing action of Grignard reagents. J. STAS (Bull. Soc. chim. Belg., 1926, 35, 379—386; cf. A., 1925, i, 1052).—Further attempts to synthesise tri*iso*propylcarbinol (βδ-dimethyl-γ-*iso*propylpentan-β-ol) by the action of magnesium *iso*propyl bromide or chloride on di*iso*propyl ketone at low temperatures were unsuccessful, the tertiary alcohol alone being obtained. A similar result was obtained with the cyanohydrin of the ketone; magnesium ethyl bromide yields exclusively βδ-dimethyl-γ-ethylpentan-β-ol. Examination of the behaviour of di*iso*propyl, dipropyl, ethyl *iso*propyl, methyl *iso*propyl, diethyl, and dimethyl ketones with magnesium alkyl bromides shows that the reducing action of magnesium *iso*propyl bromide increases with the substitution of methyl groups in the ketone. It appears that the nature of the ketone is a more important factor than the nature of the Grignard reagent in determining whether reduction takes place. The following are described: βγδ-*trimethylpentan-γ-ol*, b. p. 156·5°, d_4^{20} 0·8492, n_D^{20} 1·4353; βδ-*dimethyl-γ-ethylpentan-γ-ol*, b. p. 176—177°/755 mm., d_4^{20} 0·8610, n_D^{20} 1·4434; β-*methyl-γ-iso*propylhexan-γ-*ol*, b. p. 73—74°/14 mm., 184°/760 mm. (decomp.), d_4^{20} 0·8537, n_D^{20} 1·4427; δ-ethylheptan-δ-ol, d_4^{20} 0·8337, n_D^{20} 1·4332; δ-iso*propylheptan-δ-ol*, b. p. 79—81°/14 mm., 188—190°/760 mm. (slight decomp.), d_4^{20} 0·8436, n_D^{20} 1·4390; γ-iso*propylhexan-γ-ol*, b. p. 176·5—177·5°/755 mm., d_4^{20} 0·8506, n_D^{20} 1·4398; and β*γ-dimethylhexan-γ-ol*, b. p. 61—62°/18 mm., d_4^{20} 0·8371, n_D^{20} 1·43087. Di*iso*propyl ketone and magnesium phenyl bromide afford γ-*phenyl*-βδ-*dimethylpentan-γ-ol*, b. p. 118—119°/11 mm., d_4^{20} 0·9755, n_D^{20} 1·5239. R. BRIGHTMAN.

Coupling action of the Grignard reagent. III. Formation of αβγ-triphenylpropane and similar hydrocarbons in coupling reactions of benzyl halides. R. C. FUSON (J. Amer. Chem. Soc., 1926, 48, 2937—2942; cf. A., 1926, 1237).—Spath's supposed αβγ-triphenylpropane (A., 1914, i, 1) obtained in the reaction of Grignard reagents with benzyl halides, has been identified as α-*phenyl*-β-p-*benzylphenylethane*, b. p. 213—216°/5 mm., or 225—230°/10 mm., d_4^{18} 1·0394, n_D^{22} 1·5929, which is obtained by heating benzyl chloride with dibenzyl either alone or in presence of a little zinc dust. As Späth was probably operating with a deficiency of Grignard reagent, this reaction explains the presence of the above hydrocarbon in his reaction product. αβγ-*Triphenylpropane*, b. p. 179—181°/2 mm., or 225—230°/10 mm., d_4^{18} 1·0482, n_D^{22} 1·6042, was prepared by reducing phenyldibenzylcarbinol with hydriodic acid (cf. Klages and Heilmann, A., 1904, i, 487). p-*Benzyl*-n-*propylbenzene*, b. p. 152—155°/10 mm., d_4^{18} 0·9739, n_D^{18} 1·5552, is obtained similarly from *n*-propylbenzene and benzyl chloride, and is identical with Spath's supposed αβ-diphenylbutane. F. G. WILLSON.

Inactive 1 : 3-dimethyl*cyclo*pentane. G. CHAVANNE (Bull. Acad. roy. Belg., 1926, [v], 12, 105—122).—See A., 1926, 1130.

1 : 2-Dimethyl*cyclo*pentane compounds. M. VAN RYSSELBERGE (Bull. Acad. roy. Belg., 1926, [v], 12, 171—192).—See A., 1926, 1238.

Catalytic dehydrogenation; polycyclic hydrocarbons. N. D. ZELINSKI, I. TITZ, and L. FATEJEV (Ber., 1926, 59, [*B*], 2580—2590; cf. A., 1924, i, 665, 952).—Reduction of *cyclo*pentanone in moist ethereal solution by sodium affords *cyclo*pentanol, an *alcohol*, $C_{10}H_{18}O$, b. p. 107—108°/9 mm., d_4^{20} 0·9862, n_D^{20} 1·4903, and the *sub*-



(I.)

the alcohol, $C_{10}H_{18}O$, with hydrogen iodide in glacial acetic acid followed by hydrogenation of the product in the presence of platinised charcoal gives a hydrocarbon, $C_{10}H_{18}$, b. p. 190—191°, d_4^{20} 0·8780, n^{20} 1·4711, which is converted by platinised charcoal at 300° into hydrogen and naphthalene. *cyclo*Pentanol is converted by hydrogen bromide into the corresponding bromide, which, with sodium in the presence of ether, affords *cyclo*pentene with smaller amounts of di*cyclo*pentyl, b. p. 188—189°/753 mm., d_4^{20} 0·8604, n_D^{20} 1·4652. The latter hydrocarbon differs in physical properties from the product described above, and like the monocyclic *cyclo*pentane hydrocarbons does not suffer catalytic dehydrogenation. The hydrocarbon derived from *cyclo*pentyl*cyclo*pentanol is in all probability a mixture of *cis*- and *trans*-decahydronaphthalenes, and rearrangement of ring systems appears to occur under the influence of hydrogen iodide.

Reduction of 3-methyl*cyclo*pentanone with sodium gives 3-methyl*cyclo*pentanol and a saturated, dicyclic *alcohol*, $C_{12}H_{22}O$, b. p. 124—126°/13 mm., $d_4^{14\cdot5}$ 0·9483, $n_D^{14\cdot5}$ 1·4798. The latter substance is converted by potassium hydrogen sulphate into an unsaturated *hydrocarbon*, $C_{12}H_{20}$, b. p. 215—217°/760 mm., d_4^{17} 0·8676, which is reduced to the saturated *hydrocarbon*, $C_{12}H_{22}$, b. p. 215—216° (corr.), d_4^{20} 0·8451, n_D^{20} 1·4570. Since the latter hydrocarbon does not suffer dehydrogenation at 300° in presence of platinised charcoal, the series of compounds must contain the di*cyclo*pentyl arrangement. When, however, the unsaturated hydrocarbon is treated with zinc dust and hydrobromic acid and then reduced, the *product*, $C_{12}H_{22}$, b. p. 214—215°/750 mm., $d_4^{15\cdot5}$ 0·8548, d_4^{20} 0·8518, is readily dehydrogenated to a dimethylnaphthalene, m. p. 86—87° (picrate, m. p. 139°). Similarly, the saturated alcohol, $C_{12}H_{22}O$ (see above), when cautiously treated with zinc dust and hydriodic acid, gives a saturated hydrocarbon, $C_{12}H_{22}$, b. p. 218—219°, $d_4^{18\cdot5}$ 0·8751, $n_D^{18\cdot5}$ 1·4753, and when more drastically treated with the same reagents a hydrocarbon, $C_{12}H_{22}$, b. p. 217—219°, d_4^{18} 0·8622, n_D^{18} 1·4682; each of these hydrocarbons is dehydrogenated to a dimethylnaphthalene, m. p. 91° and 106·5—107° respectively (picrates, m. p. 130° and 143°). The alcohol, $C_{12}H_{22}O$, and an excess of zinc dust and fuming aqueous hydriodic acid yield a saturated hydrocarbon, b. p. 217·5—219°/760 mm., d_4^{20} 0·8594, dehydrogenated to a dimethylnaphthalene, m. p. 75—76° (picrate, m. p. 122°). Change in the ring system of the alcohol is therefore caused by hydriodic acid. A similar change is caused by zinc dust and hydrobromic acid, which give a saturated hydrocarbon, b. p. 216—218°/760 mm., d_4^{20} 0·8666, dehydrogenated to a dimethylnaphthalene, m. p. 86—87°. Final proof that 3 : 3′-*dimethyl*cyclo*pentyl* is incapable of catalytic dehydrogenation rests on the behaviour of the hydrocarbon, b. p. 213—215°, d_4^{20} 0·8483, n_D^{20} 1·4582, synthesised from 3-methyl*cyclo*pentyl iodide and sodium.

Di*cyclo*hexyl, b. p. 239·5—240°, d_4^{20} 0·8847, n_D^{20} 1·4800, prepared from *cyclo*hexyl bromide and sodium, is readily dehydrogenated to diphenyl. H. WREN.

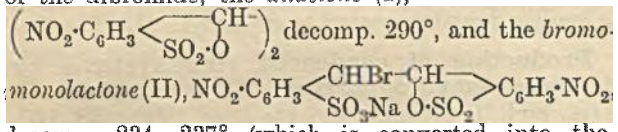
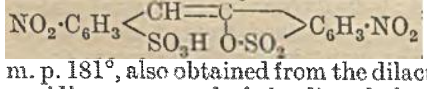
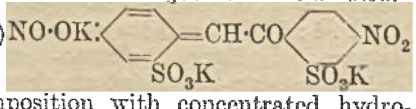
Production of condensed ring systems by catalytic dehydrogenation. N. D. ZELINSKI, I. TITZ, and M. GAVERDOWSKAJA (Ber., 1926, 59, [*B*], 2590—2593).—Fluorene is readily obtained by the passage of di*cyclo*hexylmethane, b. p. 250—252° (corr.), d_4^{20} 0·8750, n_D^{20} 1·4752, or diphenylmethane over platinised charcoal at 300°. Under similar conditions, dibenzyl gives phenanthrene. Fluorene is likewise obtained from di*cyclo*hexyl ketone or benzophenone. Carbazole is obtained from di*cyclo*hexylamine or diphenylamine. The yellow colour of solutions of carbazole in concentrated sulphuric acid appears peculiar to the compound isolated from anthracene oil. H. WREN.

Preparation and physical constants of γ-phenylpropinene. L. BERT and P. C. DORIER (Bull. Soc. chim., 1926, **39**, 1610—1612).—γ-Phenyl-Δ$^{\alpha}$-propinene is most economically prepared by the action of sodamide on γ-chloroallylbenzene (A., 1925, i, 803, 1373). A 75% yield is obtained after purification through the copper derivative. The substance has b. p. 68—69°/17 mm., d_4^0 0·917, d_4^{15} 0·910, d_4^{20} 0·899, $n_D^{8\cdot5}$ 1·514, n_D^{20} 1·509 (cf. Bourguel, A., 1923, i, 430; 1925, i, 770). M. CLARK.

Kekule formula for benzene and the existence of isomeric *o*-disubstitution products. H. H. HODGSON (J. Soc. Dyers and Col., 1926, **42**, 365—368).—The author claims that 3-*chloro*-1-*bromo*-4 : 6-*dinitrobenzene*, slender parallelograms (from alcohol), m. p. 101°, as prepared from 3-chloro-4 : 6-dinitroaniline by the diazo-reaction is isomeric with the 1-*chloro*-3-*bromo*-4 : 6-*dinitrobenzene*, hexagonal plates, m. p. 101°; similarly obtained from 3-bromo-4 : 6-dinitroaniline. The first "isomeride" appears to be the stable form, and is also obtained by the nitration of 1-chloro-3-bromobenzene. The "1-chloro-" is converted into the "1-bromo-" compound on fusion or repeated crystallisation from alcohol; from benzene, both separate in plates.

3-*Chloro*-4 : 6-*dinitroaniline*, m. p. 174°, and 3-*bromo*-4 : 6-*dinitroaniline*, m. p. 178°, are described. Diazotisation of the latter in the presence of hydrochloric acid and cuprous chlorides affords, according to the conditions, 1 : 6-*dichloro*-3-*bromo*-4-*nitrobenzene*, m. p. 70°, 1 : 4 : 6-*trichloro*-3-*bromobenzene*, m. p. 138°, or mixtures of these. 3-*Bromo*- and 3-*chloro*-4 : 6-*dinitrobenzeneazo*-β-*naphthol* are described. R. BRIGHTMAN.

Acetylene derivatives. VI. 2 : 2′-Disulphonic acids of the stilbene, tolane, and deoxybenzoin series. P. RUGGLI and E. PEYER (Helv. Chim. Acta, 1926, **9**, 929—950).—The action of halogens

and alkali on several derivatives of stilbene-2 : 2′-disulphonic acid in a manner analogous to that employed in the case of the corresponding dicarboxylic acids (Ruggli and Meyer, A., 1922, i, 343) has been studied. Although the sulphonic acids also show a great tendency to form lactonic compounds, it is not so pronounced as in the earlier case, so that it was possible to isolate derivatives of tolane-2 : 2′-disulphonic acid. Sodium 4 : 4′-dinitrostilbene-2 : 2′-disulphonate treated with bromine yields, instead of the dibromide, the *dilactone* (I),  decomp. 290°, and the *bromomonolactone* (II), decomp. 234—237° (which is converted into the dilactone when heated in aqueous solution above 65°), whilst the mother-liquors, on treatment with potassium acetate and methylation of the potassium salt with methyl sulphate, yield the *dibromide* of methyl 4 : 4′-dinitrostilbene-2 : 2′-disulphonate, m. p. 245—250° (decomp.), also obtained by the direct action of bromine on the disulphonate (*dipyridine* additive compound, m. p. 203—214°, which when treated with alkali yields the *potassium* salt of the dibromide). Chlorine similarly yields the dilactone and the *chloromonolactone*. When treated with methyl sulphate, the original disodium salt yields *methyl* 4 : 4′-*dinitrostilbene*-2 : 2′-*disulphonate* (*pyridine* compound, m. p. 259—261°; *phenylhydrazine* additive compound), which with chlorine gives the *dichloride*, decomp. 252° (*pyridine* compound, m. p. 247—250°, which on treatment with alkali behaves in a manner similar to the bromine compound). The bromomonolactone (II) on treatment with pyridine and methyl sulphate yields *methyl* 4 : 4′-*dinitro*-ω-*bromostilbene*-2 : 2′-*disulphonate*, m. p. 204°, and on treatment with alkali and potassium chloride yields the corresponding *dipotassium* salt. On treatment with a large excess of 50% potassium hydroxide solution, it yields *potassium* 4 : 4′-*dinitrotolane*-2 : 2′-*disulphonate*, from which is obtained the free *acid*, $+5H_2O$, which on rapid heating has m. p. 190—195° and is converted into the *lactone* of 4 : 4′-*dinitrodeoxybenzoin*-2 : 2′-*disulphonic acid*,  [*methyl* ester, m. p. 181°, also obtained from the dilactone (see below); *pyridine* compound of the dimethyl ester, m. p. 202—203°]. Methyl sulphate converts the dinitrotolanedisulphonic acid into its *methyl* ester, m. p. 234—235° (*pyridine* compound, m. p. 246—247°; *dibromide*, m. p. 242—253°), whilst treatment with phosphorus pentachloride and phenol yields the *phenyl* ester, m. p. 185—186°. The dilactone (I) on treatment with methyl-alcoholic potassium hydroxide solution yields *tripotassium* 4 : 4′-*dinitrodeoxybenzoin*-2 : 2′-*disulphonate* (*aci*-form)  which on decomposition with concentrated hydrochloric acid yields the corresponding *acid*, $+4H_2O$ (normal form), m. p. 185° (decomp.) (*methyl* ester, m. p. 231°). Pyridine converts the dilactone into an additive *compound*, m. p. 211—212°, which on treatment with methyl sulphate yields the methyl ester of the lactone of dinitrodeoxybenzoindisulphonic acid previously obtained. Reduction of the dinitrotolanedisulphonic acid with stannous chloride yields 4 : 4′-*diaminostilbene*-2 : 2′-*disulphonic acid* (*diacetyl* derivative). Phenyl *trans*-4 : 4′-dinitrostilbene-2 : 2′-disulphonic acid (Green, Marsden, and Scholefield, J.C.S., 1904, **85**, 1434) on treatment with chlorine yields a dichlorinated *compound*; the position of the chlorine atoms is not known. On reduction with stannous chloride in acetic–hydrochloric acid solution it yields *phenyl* 4 : 4′-*diaminostilbene*-2 : 2′-*disulphonate*, m. p. 245—250° (*diacetyl* derivative, m. p. 298—302°). Elimination of the amino-groups from 4 : 4′-diaminostilbene-2 : 2′-disulphonic acid by diazotisation and treatment of the product with phosphorus pentachloride and phenol yields *phenyl stilbene*-2 : 2′-*disulphonate*, m. p. 184·5—185°. J. W. Baker.

Electrochemical oxidation of benzene homologues. III. *p*-Xylene. F. Fichter and M. Rinderspacher (Helv. Chim. Acta, 1926, **9**, 1097—1101).—The electrochemical oxidation of *p*-xylene in 0·5*N*-sulphuric acid suspension with a lead oxide anode, a lead cathode, and using a diaphragm, yields *p*-tolualdehyde, *p*-toluic acid (in which the side-chain only has been attacked), *p*-xylenol, *p*-xyloquinol, *p*-xyloquinone, and (impure) 4 : 4′-dihydroxy-2 : 5 : 2′ : 5′-tetramethyldiphenyl (in which the nucleus is attacked). When no diaphragm is used, the products are αβ-dihydroxy-αβ-di-*p*-tolylethane (*p*-hydrotoluoin, 70%), *iso*-*p*-hydrotoluoin (10%), and some *p*-tolylmethyl alcohol. In a mixture of acetone and 2*N*-sulphuric acid the products are *p*-tolualdehyde, traces of terephthalic acid, and *ω′-acetylstyrene-p-carboxylic acid*, m. p. 143—145°, which is produced by condensation of the acetone with the terephthalaldehydic acid produced by the electrochemical oxidation. *p*-Xylenol by electrochemical oxidation in 2*N*-sulphuric acid suspension yields 4 : 4′-dihydroxy-2 : 5 : 2′ : 5′-tetramethyldiphenyl and *p*-xyloquinone. J. W. Baker.

Oxidations in the benzene series by gaseous oxygen. II. Alkylbenzenes with two or more carbon atoms in the side-chain. H. N. Stephens (J. Amer. Chem. Soc., 1926, **48**, 2920—2922; cf. A., 1926, 1028).—The action of gaseous oxygen at about 100° on aromatic hydrocarbons containing *n*-, *sec.*-, and *tert.*-alkyl groups causes oxidation only at the α-carbon atom of the side-chain. Thus ethylbenzene, *n*-propylbenzene, cumene, and *p*-cymene yielded, respectively, acetophenone, propiophenone, acetophenone, and *p*-tolyl methyl ketone. At least one hydrogen atom must be attached directly to the α-carbon atom for oxidation to take place, *tert.*-butylbenzene, for example, being unattacked after treatment with gaseous oxygen at 102—104° for 25 days. The presence of water inhibits the oxidation when at least two hydrogen atoms are attached to the α-carbon, but favours it when only one hydrogen atom occupies that position. It is suggested that in the latter case the elements of an alcohol are eliminated, *e.g.*, methyl alcohol from an *iso*propyl group, and that water, not being a product of reaction, is, consequently, without retarding effect. F. G. Willson.

Intermediate products in the Friedel and Crafts reactions. S. C. J. Oliver (Rec. trav. chim., 1926, **45**, 817—818).—Nitrobenzene forms a crystalline additive compound with aluminium chloride, which dissolves in, but does not itself react with, benzene, whilst the solution when treated with benzyl chloride gives a better yield of diphenylmethane than when aluminium chloride alone is used as the catalyst. This observation supports Boeseken's theory of catalysis (A., 1926, 806) as opposed to the view that the catalyst acts by virtue of the intermediate compounds formed, since neither benzene nor benzyl chloride forms an additive compound with aluminium chloride. J. W. Baker.

Preparation of 2 : 3- and 1 : 4-dinitronaphthalene. R. K. Chudozilov (Chem. Listy, 1926, **20**, 509—511).—6-Nitro-7-aminotetrahydronaphthalene is converted by means of the diazo-reaction into 6 : 7-*dinitrotetrahydronaphthalene*, m. p. 98—99°, which affords 2 : 3-*dinitronaphthalene*, m. p. 170·5—171°, and 6-*nitro*-7-*hydroxytetrahydronaphthalene*, m. p. 83—84°. Similarly, 1-nitro-4-aminotetralin is converted by the diazo-reaction into 5 : 8-*dinitrotetralin*, m. p. 87—88°, affording on dehydrogenation 1 : 4-dinitronaphthalene, m. p. 131—132°. The latter is also obtained from 1-nitro-4-aminonaphthalene by the diazo-reaction (cf. A., 1923, i, 550). R. Brightman.

Manufacture of primary and secondary aromatic amines. E. Merck, Assees. of W. W. Krauss.—See B., 1926, 964.

Derivatives of hydroxyphenylglycine. II. K. Shimo (Bull. Chem. Soc. Japan, 1926, **1**, 226—233; cf. A., 1925, i, 1423; Galatis, *ibid.*, 1921, i, 556; 1926, 1243).—The following derivatives of anilinoacetonitrile were prepared:

p-Acetoxy-*N*-acetyl-, m. p. 94—95°; p-*benzoyloxy*-*benzoyl*-, m. p. 129—130°; p-*acetoxy*-α-*methyl*-, m. p. 129—131°; p-*acetoxy*-αα-*dimethyl*-, m. p. 77—78°; p-*benzoyloxy*-α-*phenyl*-, m. p. about 200°; p-*acetoxy*-α-*phenyl*-, m. p. 119—120°; p-*acetoxy*-α-*phenyl*-α-*methyl*-, m. p. 142—143°; o-*hydroxy*-N-*acetyl*-, m. p. 167—168°; o-*acetoxy*-N-*acetyl*-, m. p. 105—106°; o-*benzoyloxy*-, m. p. 120—121°; m-*acetoxy*-α-*phenyl*-α-*methyl*-, m. p. 123—124°.

Schotten–Baumann benzoylation of the *p*-hydroxy-αα-dimethyl- or *p*-hydroxy-α-phenyl-α-methyl-derivatives gives *p*-benzoyloxybenzanilide.

From *p*-hydroxyphenylglycine the methyl ester, m. p. 97—98°, ethyl ester, m. p. 78—79°, the N-*acetyl* derivative, m. p. 174—175°, and p-*acetoxy*-N-*acetylphenylglycine*, m. p. 203—204°, were obtained. o-*Hydroxy*-N-*acetylphenylglycine*, m. p. 201—202° (decomp.), was also prepared. E. W. Wignall.

Reactions of thiocarbanilide. R. T. C. Loh and W. M. Dehn (J. Amer. Chem. Soc., 1926, **48**, 2956—2959).—Thiocarbanilide is oxidised quantitatively in alkaline solution by sodium peroxide to diphenylcarbamide; other alkaline oxidising agents give yields decreasing in the order: potassium permanganate, potassium chromate, potassium persulphate, bleaching powder, potassium hypobromite, and potassium hypoiodite. The conversion of the thion- into the keto-group by alkaline oxidising agents appears to be a general reaction. Treatment of a solution of thiocarbanilide in sulphuric acid (prepared cold) with fuming nitric acid at 75—85° affords *s*-tetranitrodiphenylcarbamide, m. p. 204°, which, when heated with mixed nitric and sulphuric acids, yields *s*-hexanitrodiphenylcarbamide, m. p. 209°. When heated with a freshly-prepared aqueous solution of the calculated quantity of mercurous nitrate, thiocarbanilide affords di-*p*-nitrothiocarbanilide, m. p. 161°. Thiocarbanilide forms an additive *compound*, m. p. 85°, with 1 mol. of mercuric chloride, when the two are mixed in alcoholic solution. Additive *compounds* with the following metallic halides were prepared by mixing the components in methyl ethyl ketone and precipitating with toluene: cupric bromide (0·5 mol.), m. p. 187°; cadmium bromide (0·5 mol.), yellow, m. p. 140°; mercuric iodide (0·5 mol.), m. p. 183°; zinc chloride (0·5 mol.), m. p. 172°; auric chloride (0·5 mol.), m. p. 194°; stannic chloride (0·5 mol.), m. p. 260°; arsenious bromide, (1 mol.), m. p. above 250°; arsenious iodide (1 mol.), yellow, m. p. similar; and mercuric iodide (1 mol.), yellow, m. p. 139°. F. G. Willson.

Catalytic preparation of amines. II. Preparation of the toluidines and *m*-phenylenediamine. E. Briner, A. Ferrero, and B. Paillard (Helv. Chim. Acta, 1926, **9**, 956—958; cf. Briner, Ferrero, and Luserna, A., 1924, i, 503).—The yields of *o*-, *m*-, and *p*-toluidines obtained by passing a mixture of the corresponding cresol and ammonia over freshly-prepared aluminium oxide at 420° are 43·1, 40·0, and 42·4%, respectively, which are increased to 55·1, 51·4, and 52·3%, respectively, when a catalyst which has been used once previously is employed. Further use of the catalyst decreases its activity. The corresponding yields of *m*-phenylenediamine obtained from resorcinol are 36·9 and 53·0%, respectively. J. W. Baker.

Free ammonium radicals. VII. The ammonium character of triarylamines. E. Weitz and H. W. Schwechten (Ber., 1926, **59**, [*B*], 2307—2314; cf. A., 1924, i, 425).—If it be assumed that an aryl group attached to nitrogen makes more demand on the latter than corresponds with a complete valency, the triarylamines must be regarded as ammonium radicals and hence capable of forming salts, not by addition of acids, but of acid residues. These salts, $[Ar_3N]\cdot X$, designated triarylaminium salts, are described. Triphenylamine is unsuitable, since it is readily converted by oxidising agents into *NN'*-tetraphenylbenzidine or its *meri*- or *holo*-quinonoid salts. *Tri*-p-*tolylaminium picrate* is produced by oxidation of the amine in strongly-cooled benzene and light petroleum with lead dioxide in presence of picric acid. *Tri*-p-*tolylaminium perchlorate*, m. p. 123°, is not formed by the oxidation of the amine in presence of perchloric acid, but is readily produced by the action of chlorine peroxide on the base in ethereal solution. The salts give intensely coloured solutions. They are readily transformed by reducing agents, even by ferrous salts, into tri-*p*-tolylamine. H. Wren.

Action of aminosulphonic acid on aromatic amines. A. Quilico (Gazzetta, 1926, **56**, 620—630; cf. Levi and Quilico, Giorn. Chim. Ind. Appl.,

1915, **7**, 127).—Further evidence is advanced to show the extreme instability of α-naphthylaminesulphonic acid and the identity of Paal and Janicke's sulphamic acid (A., 1896, i, 235) with α-naphthylamine-2-sulphonic acid. The general character of the reaction by which sulphamic derivatives are formed when amines are heated with aminosulphonic acid is verified, the reaction being extended to the cases of *m*-toluidine and β-naphthylamine. In all instances, this reaction yields first sulphamic derivatives, which at higher temperatures give sulphonic derivatives. The transposition takes place very readily with α-naphthylamine, but less so with β-naphthylamine. With amines of the benzene series, the *para*-position or, if this is occupied, the *ortho*-position is preferred by the migrating sulphonic group. α-Naphthylamine gives the 2-sulphonic, and β-naphthylamine the 6-sulphonic acid. T. H. POPE.

Ring-formation. A. C. SIRCAR and P. K. DE (J. Indian Chem. Soc., 1926, **3**, 245—252).—The hypothetical *p*-diphenylene is not produced in the action of copper on 4 : 4′-di-iododiphenyl or *p*-di-iodobenzene (cf. Turner, J.C.S., 1915, **107**, 1495). The formation of the following derivatives is advanced as evidence against the Kaufler type of formula for 4 : 4′-diaminoazobenzene: a *diphthalyl* derivative, m. p. above 300°, using phthalyl chloride, whilst phthalic anhydride does not react; an *oxalyl* derivative, m. p. above 300°; *di-o-hydroxybenzylidene* derivative, m. p. 265°; *di-3 : 4-dihydroxybenzylidene* derivative, darkening at 250°, but not melted at 270°, and 2 : 4 : 2′ : 4′-*tetramethylazoquinoline*, m. p. 193°, produced by the action of acetylacetone. The *di*-p-*anisylidene* derivative of benzidine, m. p. 246—248°, is also described. G. M. BENNETT.

Diphenylyl derivatives of ammonia, *p*-phenylenediamine, and benzidine. *meri*-Quinonic salts. J. PICCARD (J. Amer. Chem. Soc., 1926, **48**, 2878—2885).—An extension of the known series of *meri*-quinonoid salts derived from *p*-phenylenediamine and benzidine (cf. Piccard, A., 1911, i, 568). The colours of these *meri*-quinonoid salts from the respective bases are as follows: *p*-phenylenediamine, yellow; monomethyl-, orange; dimethyl-, red; phenyl-, violet-red; trimethyl-, violet; tetramethyl-, violet-blue; diphenyl-, blue; didiphenylyl-, bluish-green; tetraphenyl-, green; diphenyldidiphenylyl-, green; and tetradiphenylyl-*p*-phenylenediamine, yellowish-green; benzidine, blue; diethyl-, green; tetramethyl-, greenish-yellow; diphenyl-, yellow; didiphenylyl-, orange-yellow; tetraphenyl-, orange; diphenyldidiphenylyl-, red; and tetradiphenylyl-, violet-red. These series illustrate the regular succession of colours through those of the first order to those of the second. As the colour of the *meri*-quinonoid salt derived from benzidine itself is blue, the colours of the corresponding salts from its above derivatives are chiefly of the second order (cf. Piccard, A., 1926, 1079).

Phenyldiphenylylamine (*diphenylylaniline*), m. p. 112° (*acetyl* derivative, m. p. 110°), is obtained by heating together diphenylylacetamide, iodobenzene, potassium carbonate, nitrobenzene, and a trace of copper powder at 230—250° for 12 hrs., or alternatively from acetanilide and *p*-iododiphenyl by the same method, with subsequent hydrolysis. *Phenyldidiphenylylamine* (*didiphenylylaniline*), m. p. 160°, is prepared analogously from iodobenzene and aminodiphenyl, and from aniline (1 mol.) and iododiphenyl (2 mols.). Tridiphenylylamine, m. p. 257—259°, is obtained in the same way from didiphenylylamine and iododiphenyl. When pure, this substance gives a colourless solution in concentrated sulphuric acid, but the solution turns green rapidly in presence of air (cf. Bülow, A., 1924, i, 1183). Diphenyldiphenylylamine was also synthesised similarly from aminodiphenyl (1 mol.) and iodobenzene (2 mols.). Tetraphenylbenzidine (cf. Wieland, *ibid.*, 1913, i, 1386) was obtained as above from 4 : 4′-di-iododiphenyl and diphenylamine, and from benzidine and iodobenzene. *Didiphenylylbenzidine*, m. p. 300° (diacetyl derivative, m. p. 245—249°), was obtained similarly from diphenylylacetamide (2 mols.) and 4 : 4′-di-iododiphenyl (1 mol.), and from diacetylbenzidine (1 mol.) and iododiphenyl (2 mols.), and analogous methods were applied for the synthesis of diphenyldidiphenylylbenzidine (cf. Piccard, *ibid.*, 1924, i, 208) and *tetradiphenylylbenzidine*, m. p. 254—259°. The latter forms an orange-red additive *compound*, m. p. indefinite, with 2 mols. of nitrobenzene (cf. Ostromisslensky, *ibid.*, 1911, ii, 195), and a yellow additive *compound* with 1 mol. of toluene. Diphenyldidiphenylylbenzidine was also obtained by oxidation of diphenyldiphenylylamine to diphenyldidiphenylyldiphenoquinonedi-immonium acetate and subsequent reduction (cf. Piccard and Abouchy, *ibid.*, 1924, i, 316; Piccard, Helv. Chim. Acta, 1924, **7**, 789).

F. G. WILLSON.

Preparation and hydrolysis of isomeric azoxybenzyl bromides. J. B. SHOESMITH and W. E. TAYLOR (J.C.S., 1926, 2832—2834; cf. *ibid.*, 1922, **121**, 1391; A., 1923, i, 908; 1926, 389).—The rates of hydrolysis of the isomeric azoxybenzyl bromides with aqueous propyl alcohol are found to be in the order $o > p > m$. Since the azoxy-group directs *ortho-para* substitution, the results are in agreement with the rule that in a series of substituted benzyl halides, $R{\cdot}C_6H_4{\cdot}CH_2Hal$, the isomerides in which the $\cdot CH_2Hal$ group is attached to the carbon atom of the benzene nucleus which is attacked during substitution of the $R{\cdot}C_6H_5$ compound are the ones which are most readily hydrolysed.

o-*Azoxybenzyl bromide*, m. p. 105° (violent decomp. at 106°), and m-*azoxybenzyl bromide*, m. p. 119°, are prepared from the corresponding alcohols by the action of hydrogen bromide. A complex by-product is formed with the *ortho*-derivative. p-*Azoxybenzyl bromide*, m. p. 203°, is prepared from p-*azoxybenzyl alcohol*, m. p. 167°, by treatment with phosphorus pentabromide in bromoform solution.

H. BURTON.

Stability of benzenediazonium chloride solutions. II. Reaction of benzenediazonium chloride with certain organic hydroxy-substances. H. A. H. PRAY.—See this vol., 26.

Relationship between quinonehydrazones and *p*-hydroxyazo-compounds. V. *p*-Arylsulphonazophenols. W. BORSCHE and R. FRANK (Annalen,

1926, 450, 75—84; cf. Borsche and Ockinga, A., 1905, i, 719).—Benzenesulphonhydrazide reacts with *p*-benzoquinone below 0° in the presence of dilute hydrochloric acid to give 4-*benzenesulphonazophenol*, $PhSO_2 \cdot N_2 \cdot C_6H_4 \cdot OH$, m. p. 101° [*benzoate*, m. p. 149° (decomp.)], decomposed slowly by water, quickly by acids, into benzenesulphinic acid and a *p*-hydroxybenzenediazonium salt. At ordinary temperatures the azo-compound decomposes as it is formed, and the sulphinic acid produced combines with the quinone to give 2 : 5-dihydroxydiphenylsulphone. This provides a preparative method for *p*-hydroxybenzenediazonium salts. 2 : 4 : 4′-*Trihydroxyazobenzene* melts at 226°. Attempts to reduce *p*-benzenesulphonazophenol with phenylhydrazine gave benzenesulphonphenylhydrazide, m. p. 164·5°. 4-p-*Toluenesulphonazophenol*, m. p. 95° (decomp.; *benzoate*, decomp. 137°; NN′-*di*-p-*toluenesulphonyl*-p-*benzoyloxyphenylhydrazine*, m. p. 174°, from the benzoate and *p*-toluenesulphinic acid), prepared from *p*-benzoquinone and *p*-toluenesulphonhydrazide (m. p. 115°; acetone derivative, m. p. 159—160°), behaves similarly. 2 : 5-Dihydroxyphenyl-*p*-tolylsulphone, m. p. 211° (p-*toluenesulphonate*, m. p. 162°), and p-*toluenesulphonphenylhydrazide*, m. p. 171—172°, are described. *Quinol di*-p-*toluenesulphonate*, m. p. 159°, and p-*hydroxyphenyl* p-*toluenesulphonate*, m. p. 98—99°, are prepared from quinol and *p*-toluenesulphonyl chloride in pyridine. C. Hollins.

Etherification of hydroaromatic alcohols. J. B. Senderens and J. Aboulenc (Compt. rend., 1926, 183, 830—832).—*cyclo*Hexyl ethers cannot be prepared by the catalytic method (cf. A., 1926, 46) from *cyclo*hexanol or its mixtures with aliphatic alcohols, the *cyclo*hexanol being always dehydrated to *cyclo*hexene and $\Delta^{1:1'}$-di*cyclo*hexene. When, however, a mixture of *cyclo*hexanol and benzyl alcohol with 2% of sulphuric acid trihydrate is refluxed at 130—135°, benzyl ether and cyclo*hexyl benzyl ether*, b. p. 182—183°/50 mm., d_4^{15} 1·008, are obtained. The latter is decomposed on warming with sulphuric acid dihydrate into *cyclo*hexene and resinous matter. The following derivatives were prepared similarly: 3-*methyl*-, b. p. 186·5—187·5° (corr.)/50 mm., d^{15} 1·006; 4-*methyl*-, b. p. 190·5—191·5°/50 mm., d_4^{15} 1·004; 3 : 4-*dimethyl*-, b. p. 192—193°/50 mm., d_4^{15} 1·005; and 3-*methyl*-6-iso*propyl*-cyclo*hexyl benzyl ether*, b. p. 198—200°/50 mm., d_4^{15} 1·001. H. E. F. Notton.

Catalytic action of Japanese acid earth. IV. Action on *cyclo*hexanol and its derivatives. H. Inoue (Bull. Chem. Soc. Japan, 1926, 1, 219—226; cf. A., 1926, 1110, 1132).—The dehydrogenation of *cyclo*hexanol in presence of Japanese acid earth yields at 200° mainly *cyclo*hexene, but at 330° mainly methyl*cyclo*pentane, which can also be obtained by using *cyclo*hexene, but not from *cyclo*hexane. Methyl*cyclo*hexanol yields, at 250°, methyl*cyclo*hexenes; at 350°, a dimethyl*cyclo*pentane is formed, with other products. E. W. Wignall.

Bromophenols. XX. Behaviour of pentahalogenophenols towards aluminium chloride in benzene. M. Kohn and G. Dömötör (Monatsh 1926, 47, 207—240; cf. A., 1926, 832).—When chlorophenols are gently warmed with excess of bromine and a little iron powder, in absence of moisture (cf. *ibid.*, 521), good yields of pentahalogenophenols are obtained. These are oxidised by nitric acid (*d* 1·5) to the corresponding tetrahalogeno-*p*-benzoquinones, whilst, when they are treated with aluminium chloride in presence of benzene, the *o*- and *p*-bromine atoms are replaced by hydrogen, chlorine and *m*-bromine atoms remaining unattacked. In spite of their high mol. wt., many of these phenols can be distilled without decomposition at atmospheric pressure. 2 : 4 : 6-*Trichloro*-3 : 5-*dibromophenol*, m. p. 204°. (all m. p. corr.), monoclinic (*methyl ether*, m. p. 127°, b. p. 336—340°/747 mm.; *benzoate*, m. p. 196°), is oxidised to 2 : 6-*dichloro*-3 : 5-*dibromobenzoquinone*, m. p. above 280°. The crystallographic and optical properties of the compounds the crystalline form of which is indicated are fully described. 2 : 4-*Dichloro*-3 : 5 : 6-*tribromophenol*, m. p. 209°, triclinic (*methyl ether*, m. p. 143—144°, b. p. 350—355°/752 mm.; *benzoate*, m. p. 202°), obtained by the general method from 2 : 4-dichlorophenol, is oxidised to *chlorotribromo*-p-*benzoquinone*, m. p. above 275°, which affords, on reduction by Kohn and Grün's method (A., 1925, i, 1265), *chlorotribromoquinol dimethyl ether*, m. p. 185—186°. The dichlorotribromophenol reacts with aluminium chloride in presence of benzene, giving 2 : 4-*dichloro*-3 : 5-*dibromophenol*, m. p. 122°, rhombic pyramidal (*methyl ether*, m. p. 114°, b. p. 329—331°/757 mm.), from which 2 : 4-*dichloro*-3 : 5-*dibromo*-6-*nitrophenol*, m. p. 141° (*methyl ether*, m. p. 86°); 2 : 4-*dichloro*-3 : 5-*dibromo*-6-*iodophenol*, m. p. 187° (*methyl ether*, m. p. 148°), and 2-*chloro*-3 : 5-*dibromo*-6-*iodobenzoquinone*, m. p. above 280°, are obtained. 2 : 6-Dichloro-4-bromophenol, prepared by chlorinating *p*-bromophenol, is successively converted by similar methods into 2 : 6-*dichloro*-3 : 4 : 5-*tribromophenol*, m. p. 223·5°, monoclinic (*methyl ether*, m. p. 145°, b. p. 335—345°/765 mm.; *benzoate*, m. p. 175°); 2 : 6-*dichloro*-3 : 5-*dibromobenzoquinone*, m. p. above 292°; 2 : 6-*dichloro*-3 : ɔ-*dibromophenol*, m. p. 128°, monoclinic (*methyl ether*, m. p. 109·5°, b. p. 309—311°/740 mm.); 2 : 6-*dichloro*-3 : ɔ-*dibromo*-4-*nitrophenol*, m. p. 179·5° (*methyl ether*, m. p. 131°); 2 : 6-*dichloro*-3 : 5-*dibromo*-4-*iodophenol*, m. p. 210—212° (*methyl ether*, m. p. 167°). *p*-Chlorophenol is brominated to 4-*chloro*-2 : 3 : 5 : 6-*tetrabromophenol*, m. p. 215°, monoclinic (*methyl ether*, m. p. 161°, b. p. 353—355°/756 mm.; *benzoate*, m. p. 203°), from which tetrabromobenzoquinone; 4-*chloro*-3 : 5-*dibromophenol*, m. p. 121°, b. p. 320—321°/743 mm., monoclinic (*methyl ether*, m. p. 82·5°, b. p. 300°/745 mm.); 4-*chloro*-3 : 5-*dibromo*-2 : 6-*dinitrophenol*, m. p. 149° (*methyl ether*, m. p. 128—129°); 4-*chloro*-3 : ɔ-*dibromo*-2 : 6-*di*-*iodophenol*, m. p. 203° (decomp.) (*methyl ether*, m. p. 173°); and 3 : ɔ-*dibromo*-2 : 6-*diiodobenzoquinone* are obtained. Similarly, *o*-chlorophenol affords 2-*chloro*-3 : 4 : 5 : 6-*tetrabromophenol*, m. p. 224° (*methyl ether*, m. p. 158·5°, b. p. 346—350°/765 mm.; *benzoate*, m. p. 178°); chlorotribromobenzoquinone; 2-*chloro*-3 : 5-*dibromophenol*, m. p. 68°, b. p. 285—287°/754 mm. (*methyl ether*, m. p. 102·5°, b. p. 291—293°/754 mm.); 2-*chloro*-3 : 5-*dibromo*-4 : 6-*dinitrophenol*, m. p. 155—157° (*methyl ether*, m. p. 125°); 2-*chloro*-3 : 5-*dibromo*-4 : 6-*di*-*iodophenol*, m. p. 177° (decomp.) (*methyl ether*,

m. p. 172°), and 2-chloro-3 : 5-dibromo-6-iodobenzoquinone. H. E. F. NOTTON.

Bromophenols. XXI. New halogenated phenols from *m*-chlorophenol. M. KOHN and A. ZANDMAN (Monatsh., 1926, **47**, 357—377).—Bromination of *m*-chlorophenol in aqueous solution yields 3-*chloro*-2 : 4 : 6-*tribromophenol*, m. p. 106°, of which the *methyl ether*, m. p. 96°, b. p. 323—325°/766 mm., is converted by nitration into 3-*chloro*-2 : 4 : 6-*tribromo*-5-*nitroanisole*, m. p. 116°, demethylated to the corresponding phenol, m. p. 146·5°. Fuming nitric acid oxidises the free chlorotribromophenol to 3-*chloro*-2 : 6-*dibromobenzoquinone*, m. p. 165°, reduced by sulphurous acid to 3-*chloro*-2 : 6-*dibromoquinol*, m. p. 144° (*dimethyl ether*, m. p. 90°, b. p. 317—319°/756 mm.; *dibenzoate*, m. p. 165°). The action of iodine on *m*-chlorophenol in alkaline solution yields 3-*chloro*-2 : 4 : 6-*tri-iodophenol*, m. p. 140° (*methyl ether*, m. p. 115·5°), converted by fuming nitric acid into 3-*chloro*-2 : 6-*di-iodobenzoquinone*, m. p. 175°. Bromination of *m*-chlorophenol with bromine and iron powder gives 3-*chloro*-2 : 4 : 5 : 6-*tetrabromophenol*, m. p. 210°, which is debrominated by the action of aluminium chloride and benzene with production of 3-*chloro*-*o*-*bromophenol*, m. p. 68—69° (*methyl ether*, m. p. 31·5°, b. p. 238—240°/746 mm.). Nitration of this phenol produces 3-*chloro*-5-*bromo*-2 : 4 : 6-*trinitrophenol*, m. p. 165·5°, of which the *methyl ether*, m. p. 106—107°, results from the nitration of 3-chloro-5-bromoanisole with nitric and sulphuric acids, whilst nitration with cold fuming nitric acid alone yields 3-*chloro*-*o*-*bromo*-2 : 4-*dinitroanisole*, m. p. 165°, demethylated to 3-*chloro*-*o*-*bromo*-2 : 4-*dinitrophenol*, m. p. 97°.

The direct iodination of 3-chloro-5-bromophenol furnishes 3-*chloro*-5-*bromo*-2 : 4 : 6-*tri-iodophenol*, m. p. 207° (*methyl ether*, m. p. 199°), which is oxidised by fuming nitric acid to 3-*chloro*-*o*-*bromo*-2 : 6-*di-iodobenzoquinone*, m. p. 253—255°. Chlorination of 3-chloro-5-bromophenol in glacial acetic acid solution yields 2 : 3 : 4 : 6-tetrachloro-5-bromophenol, m. p. 197° (cf. McCombie and Ward, J.C.S., 1913, **103**, 1995) (*methyl ether*, m. p. 115·5°, b. p. 310—313°/745 mm.). In a similar way, 3 : 4 : 5-tribromophenol gives 2 : 6-dichloro-3 : 4 : 5-tribromophenol (cf. preceding abstract) (methyl ether, m. p. 145°). Bromination of 3-chloro-5-bromophenol in glacial acetic acid solution furnishes 3-*chloro*-4 : 5-*dibromophenol*, m. p. 116—117°, of which the *methyl ether*, m. p. 72—75°, b. p. 296—300°/746 mm., yields on nitration 3-*chloro*-4 : *o*-*dibromo*-2 : 6-*dinitroanisole*, m. p. 100—101°. 3-Chloro-4 : 5-dibromophenol is converted by chlorine in glacial acetic acid into 2 : 3 : 6-*trichloro*-4 : 5-*dibromophenol*, m. p. 204—205°, from which 2 : 3 : 5-*trichloro*-5-*bromobenzoquinone*, not melted at 260°, is obtained by oxidation. The same chlorodibromophenol yields by direct iodination 3-*chloro*-4 : 5-*dibromo*-2 : 6-*di-iodophenol*, m. p. 191—192°. G. M. BENNETT.

Benzoquinonethiolimines. E. GEBAUER-FULNEGG and E. RIESZ (Monatsh., 1926, **47**, 57—61).—*p*-Aminophenol reacts in ether solution with 4-chloro-2-nitro-1-chlorothiolbenzene to yield 4-*chloro*-2-*nitrophenylthiol*-*p*-*hydroxyanilide*, $C_6H_3(NO_2)Cl\cdot S\cdot NH\cdot C_6H_4\cdot OH$, red, m. p. 119°, which is oxidised by dichromate in acetic acid solution to *benzoquinone*-4-*chloro*-2-*nitrophenylthiolimine*, $C_6H_3(NO_2)Cl\cdot S\cdot N{:}C_6H_4{:}O$, orange, m. p. 194°. The latter gave neither an oxime nor a phenylhydrazone. Simultaneous acetylation and reduction of either substance with zinc and acetic anhydride yields 4-*chloro*-1-*methylbenzthiazole*, m. p. 68°, through the intermediate formation of the *o*-acetamidothiophenol. G. M. BENNETT.

Constitution of australol. J. C. EARL and M. T. TRIKOJUS (J. Proc. Roy. Soc. N.S.W., 1925, **59**, 301—305).—The essential oil from *Eucalyptus polybractea* (d^{15} 0·970, saponification number 50—51; after acetylation, 121) yielded 10% of phenols, from which the solid, m. p. 60°, was separated which had been given the name "australol" by Smith ("Research on the Eucalypts," 2nd ed., 395) when obtained from a similar source (Robinson and Smith, A., 1915, i, 978). This is now identified as *p*-*iso*propylphenol (*p*-hydroxycumene) (m. p. 60°, benzoate, m. p. 71·5°). G. M. BENNETT.

Co-ordination valency of two hydroxyl groups in the *ortho*-position. III. Polyphenolic complexes of the rare earths. L. FERNANDES (Gazzetta, 1926, **56**, 682—688; cf. A., 1926, 1036).—When pyrocatechol (or pyrogallol) is added to the solution of a salt of a rare-earth metal and the liquid is then rendered alkaline by means of an alkali hydroxide or ammonia, a flocculent or pulverulent precipitate is formed, $[OH\cdot R(\cdot O\cdot C_6H_4\cdot OH)_2]$ (1). This compound is electrolytically almost neutral and exhibits amphoteric behaviour. In a weak acid such as acetic acid it dissolves to a solution which deposits a white crystalline compound, $(OAc)[\cdot R<\begin{smallmatrix}O\\O\end{smallmatrix}>C_6H_4]$ (2), on cooling, but if it is dissolved in alkali hydroxide (or ammonia) solution, the complex radical acts as an acid and the compound $[R(\cdot O\cdot C_6H_4\cdot OH)_3]R'_3$ (3) is formed: R=Ce, La, Pr, Nd; R'=K, Na, NH_4.

When the complex molecule contains only one phenolic radical, in acid solution, the grouping exerts a basic function, the alkalinity of the metal being only partly neutralised; thus, compounds of type (2) are formed. When, however, two phenol residues enter the complex radical, this becomes neutral and, hence, undissociated; and when three phenolic radicals enter, the compound exhibits acid properties. Compounds of types (2) and (3) are usually moderately stable, whilst the neutral compounds decompose so easily that they explode violently at 90° and oxidise with liberation of heat in the air even at the ordinary temperature.

The compounds of praseodymium, neodymium, and lanthanum are similar in properties, but the cerium compounds are different, the cerium salts, with both pyrocatechol and pyrogallol, being deep violet instead of white. The hydroxide of the pyrocatechol–cerium compound, unlike its analogues, dissolves in concentrated ammonia solution to a deep violet liquid, which, when boiled, deposits a deep violet, crystalline compound, $[Ce(C_6H_4O_2)_3](NH_4)_2H,H_2O$.

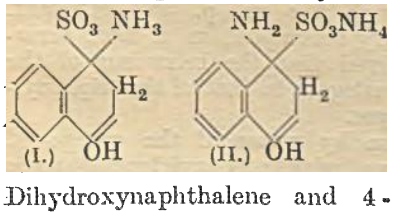
Seventeen of these complex compounds were prepared and analysed. T. H. POPE.

5-Halogenoresorcinols. H. H. HODGSON and J. S. WIGNALL (J.C.S., 1926, 2826—2827).—The three 5-halogenoresorcinols are prepared by converting the

5-halogeno-*m*-anisidines (A., 1926, 1034) into the 5-halogeno-3-hydroxyanisoles and hydrolysing these with aqueous hydriodic acid. *5-Chloro-3-hydroxyanisole*, m. p. 99°; *5-bromo-3-hydroxyanisole*, m. p. 102°; and *5-iodo-3-hydroxyanisole*, m. p. 90°, on bromination are converted into *5-chloro-2 : 4 : 6-tribromo-3-hydroxyanisole*, m. p. 110°; *2 : 4 : 5 : 6-tetrabromo-3-hydroxyanisole*, m. p. 120°; and *2 : 4 : 6-tribromo-5-iodo-3-hydroxyanisole*, m. p. 125°. *5-Chlororesorcinol* and *5-iodoresorcinol* form *monohydrates* having m. p. 67° and m. p. 92·3°, respectively. The anhydrous chloro-compound has m. p. 117°; the iodo-compound could not be dehydrated completely. *5-Bromoresorcinol*, m. p. 87°, crystallises from water as the *monohydrate*, m. p. about 79°. The halogenoresorcinols on bromination yield *5-chloro-2 : 4 : 6-tribromoresorcinol*, m. p. 143°; 2 : 4 : 5 : 6-tetrabromoresorcinol, m. p. 212° (Claassen, A., 1878, 868, gives m. p. 163°; Benedikt, Monatsh., 1880, **1**, 366, gives m. p. 167°), and *2 : 4 : 6-tribromo-5-iodoresorcinol*, m. p. 214°. H. BURTON.

Derivatives of stilbene. J. N. ASHLEY (J.C.S., 1926, 2804—2807).—*2-Nitro-4-amino-3′ : 4′-dimethoxystilbene*, m. p. 186—187° (*hydrochloride*, m. p. 223° after darkening at 200°; *acetyl* derivative, m. p. 183—184°), obtained by reduction of the 2 : 4-dinitro-compound with ammonium sulphide, is converted into *4-chloro-2-nitro-3′ : 4′-dimethoxystilbene*, m. p. 124—125°, and then into *4-chloro-2-amino-3′ : 4′-dimethoxystilbene*, m. p. 147—148° (*acetyl* derivative, m. p. 180°). A suspension of the diazonium sulphate of this chloroamine on treatment with copper powder yielded an amorphous nitrogen compound, with no trace of a phenanthrene derivative. Nitration of 4-chloro-2-nitro-3′ : 4′-dimethoxystilbene in glacial acetic acid yields *4-chloro-2 : 6′-dinitro-3′ : 4′-dimethoxystilbene*, m. p. 175°, which on reduction and acetylation gives *4-chloro-2 : 6′-diacetamido-3′ : 4′-dimethoxystilbene*, m. p. 275° (decomp.). Phosphoryl chloride does not convert this diacetamido-compound into a 2 : 6-naphthyridine (cf. Gulland and Robinson, A., 1925, i, 1188), but into a *compound*, $C_{20}H_{19}O_3N_2Cl$, m. p. about 230° (decomp.) after darkening at 160°, probably a quinoline derivative. H. BURTON.

Tautomerism of phenols. VII. 1 : 4-Dihydroxynaphthalene and 4-amino-α-naphthol. VIII. 1 : 2-Dihydroxynaphthalene. W. FUCHS and H. PIRAK (Ber., 1926, 59, [*B*], 2454—2458, 2458—2461; cf. A., 1924, i, 960).—VII. 4-Amino-α-naphthol is prepared by coupling α-naphthol with diazotised aniline and reductive fission of the azo-derivative with tin and hydrochloric acid. Its oxidation to α-naphthaquinone and subsequent reduction affords 1 : 4-dihydroxynaphthalene in poor yield. Treatment of 1 : 4-dihydroxynaphthalene or 4-amino-α-naphthol or its hydrochloride with ammonium sulphite or hydrogen sulphite affords the *substances* (I) and (II), which are readily transformed into 4-amino-α-naphthol. Dihydroxynaphthalene and 4-amino-α-naphthol give additive products, soluble in water, with sodium hydrogen sulphite. The product from dihydroxynaphthalene is converted by ammonia into 4-amino-α-naphthol, whereas that from aminonaphthol yields dihydroxynaphthalene when decomposed by alkali hydroxide; the ratio Na : S in the additive compound is variable and never 1 : 1.



VIII. 1 : 2-Dihydroxynaphthalene is prepared by coupling β-naphthol with diazotised aniline, reductive fission of the azo-dye to 2-amino-α-naphthol, and oxidation of the latter substance to the corresponding quinone, which is subsequently reduced. 1 : 2-Dihydroxynaphthalene and sodium hydrogen sulphite afford *sodium* 1 : 2-*dihydroxy*-1 : 2-*dihydronaphthalene*-1-*sulphonate*. Ammonium hydrogen sulphite gives *ammonium* 1-*amino*-2-*hydroxy*-1 : 2-*dihydronaphthalene*-1-*sulphonate*. The additive products are converted by alkali hydroxide into 1 : 2-dihydroxynaphthalene and 1-amino-β-naphthol, respectively. With phenylhydrazine, they yield the *compound*, $C_{22}H_{18}N_4$, m. p. 211—212°, regarded as the diphenylhydrazone of β-naphthaquinone. H. WREN.

Distillation of cholesterol with zinc dust. P. FANTL and M. KABOS (Monatsh., 1926, **47**, 251—258).—The mixture of hydrocarbons obtained by distilling cholesterol with zinc dust in a stream of hydrogen at atmospheric pressure (cf. van der Haar, A., 1922, i, 565) is separated by distillation into four fractions, b. p./7 mm., (*a*), 50—60°, (*b*), 95—97° (n_D 1·5060), (*c*), 162—168° (n_D 1·5301), (*d*), 185—187°. These approximate in composition and mol. wt. to the formula $(C_5H_8)_n$, where n—1, 2, 3, and 4, respectively. The mol. refractions indicate that both (*b*) and (*c*) are doubly unsaturated, but the double linkings cannot be detected by titration with bromine. When cholesterol is distilled with zinc dust at 10 mm. pressure, the hydrocarbon skeleton is retained unchanged, cholesterilene, m. p. 73°, $[\alpha]_D^{\infty}$ —53·37° (cf. Tschugaeff and Fomin, A., 1910, i, 734), being formed in 50—60% yield. This substance is not reduced by sodium and boiling amyl alcohol, but catalytic hydrogenation in presence of palladium-black converts it into a mixture of cholestane and ψ-cholestane (cf. Windaus, *ibid.*, 1919, i, 204). When cholesterilene dissolved in benzene is shaken with aqueous acetic and sulphuric acids, a small amount of cholesterol, identified as the digitonide, is regenerated.
H. E. F. NOTTON.

Substitution by halogen of the hydroxyl group of secondary alcohols. P. A. LEVENE and L. A. MIKESKA (J. Biol. Chem., 1926, **70**, 355—364).—By the general method of resolution of Pickard and Kenyon (J.C.S., 1907, **91**, 2058) there were obtained l-*phenylmethylcarbinol*, $[\alpha]_D^{\infty}$ —54·86°, l-*phenylethylcarbinol*, $[\alpha]_D^{\infty}$ —55·54°, l-*phenylpropylcarbinol*, $[\alpha]^{\infty}$ —57·21°, d-*phenylisopropylcarbinol*, $[\alpha]_D^{\infty}$ +47·66°, and d-*phenylbutylcarbinol*, $[\alpha]_D^{\infty}$ +40·83°. *d*-Phenylmethylcarbinol, $[\alpha]_D^{\infty}$ +16·36°, when heated with thionyl chloride gives d-α-*phenylethyl chloride*, $[\alpha]_D^{\infty}$ +11·89°; *l*-phenylethylcarbinol, $[\alpha]_D^{\infty}$ —54·53° gave similarly l-α-*phenylpropyl chloride*, $[\alpha]_D^{\infty}$ —50·34°; with hydrogen bromide at 0° *d*-phenylethylcarbinol, $[\alpha]_D^{\infty}$ +34·83°, gave l-α-*phenylpropyl bromide*, $[\alpha]_D^{\infty}$ —1·51°. *d*-Phenylpropylcarbinol, $[\alpha]_D^{\infty}$ +23·39°, with thionyl

chloride gives d-α-*phenyl*-n-*butyl chloride*, $[\alpha]_D^{20}$ +26·88°, and with hydrogen bromide d-α-*phenyl*-n-*butyl bromide*, $[\alpha]_D^{20}$ +4·62° *l*-Phenyl*iso*propylcarbinol, $[\alpha]_D^{20}$ −25·19°, with thionyl chloride gives l-α-*phenyl*-β-*methyl*-n-*propyl chloride*, $[\alpha]_D^{20}$ −28·34°; *d*-phenyl*iso*propylcarbinol, $[\alpha]_D^{20}$ +47·03°, with hydrogen bromide gives d-α-*phenyl*-β-*methyl*-n-*propyl bromide*, $[\alpha]_D$ +27·02°. *l*-Phenyl-*n*-butylcarbinol, $[\alpha]_D^{20}$ −4·01°, with thionyl chloride gives l-α-*phenyl*-n-*amyl chloride*, $[\alpha]_D^{0}$ −13·43°; another sample, $[\alpha]_D^{20}$ −12·83°, gave, with phosphorus pentachloride, a product $[\alpha]_D^{20}$ −5·12°. The absence of Walden inversion in some cases is ascribed to differences in the distortion of the asymmetric carbon atom by the halogenating agent employed. C. R. HARINGTON.

Ability of enolic ethers to undergo catalytic hydrogenation. Constitution of thebaine. H. WIELAND and P. GARBSCH (Ber., 1926, **59**, [*B*], 2490—2493).—α-Ethoxystyrene is readily hydrogenated in alcoholic solution in the presence of palladium-black to α-phenylethyl ethyl ether, b. p. 69°/12 mm. *cyclo*Hexanone dimethylacetal is transformed by benzoyl chloride and quinoline into Δ¹-*methoxy*cyclo*hexene*, b. p. 36°/12 mm., which is smoothly hydrogenated in the absence of moisture to hexahydroanisole, b. p. 130—131°/720 mm. The ready hydrogenation of the substances indicates that the group ·C(OMe):C· is not present in thebaine and renders necessary revision of the formula ascribed to this substance by Knorr and Horlein (cf. Wieland and Kotake, A., 1925, i, 1448). H. WREN.

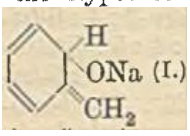
Aryl ethers of triphenyl-, diphenyl-, and naphthyl-carbinols and the corresponding cryptophenols. Tautomerism of toluene. P. SCHORIGIN (Ber., 1926, **59**, [*B*], 2502—2509).—*o*-Cresol is converted by the successive action of sodium and triphenylmethyl chloride in boiling ethereal solution into o-*tolyl triphenylmethyl ether*, m. p. 112—113°, which is also prepared from triphenylmethyl chloride and *o*-cresol in anhydrous pyridine. o-ββ*β-Triphenylethylphenol*, m. p. 183°, is obtained as by-product (yield 33%) in the first method of preparing the ether described above; it becomes the main product when triphenylmethyl chloride is heated at 120° with a solution of sodium in an excess of *o*-cresol. Its constitution is established by its oxidation to triphenylcarbinol and conversion into triphenylmethane by distillation with zinc dust.

Diphenylmethyl bromide and sodium phenoxide in presence of anhydrous ether yield *phenyl diphenylmethyl ether*, m. p. 54°, b. p. 233—243°/23 mm., and *o*-diphenylmethylphenol, m. p. 125°, b. p. 245—250°/13 mm.; these substances with diphenylketazine are also obtained from diphenyldiazomethane and phenol.

Phenol and α-naphthylmethyl bromide in the presence of alcoholic potassium hydroxide afford *phenyl α-naphthylmethyl ether*, m. p. 76—77°, b. p. 238—240°/19 mm.; o-*tolyl α-naphthylmethyl ether*, b. p. 230°/11 mm., m. p. 60°, is similarly prepared. Under like conditions, β-naphthylmethyl bromide yields *phenyl β-naphthylmethyl ether*, m. p. 115—116°, and o-*tolyl β-naphthylmethyl ether*, m. p. 94—95°. With these compounds, the formation of cryptophenols is not observed.

α-Naphthylmethyl bromide has b. p. 167°/10 mm., m. p. 53·5—54·5°.

The unusual phenomenon of the entry of the alkyl group into the side-chain of *o*-cresol is explained by the hypothesis that this substance reacts in its tautomeric form (I). Similarly, substitution in the side-chain of toluene is simply explained by the assumption that it is transformed by addition of energy (action of heat or radiation) into methylenedihydrobenzene. Addition then occurs at the double linking of the methylene group, and is followed by elimination from the adduct in such a manner as to restore the normal arrangement of double linkings in the benzene nucleus. H. WREN.



(I.)

Decomposition of ethers by metallic sodium. P. SCHORIGIN (Ber., 1926, **59**, [*B*], 2510—2514; cf. A., 1923, i, 207; 1924, i, 1185, 1188; 1925, i, 1404).—Under the influence of sodium at 100°, *o*-tolyl triphenylmethyl ether undergoes normal fission into triphenylmethane and *o*-cresol and phenolic transformation into *o*-ββ*β*-triphenylethylphenol. Phenyl diphenylmethyl ether is similarly converted into a mixture of diphenylmethane, *s*-tetraphenylethane, phenol, and triphenylcarbinol. Phenyl α-naphthylmethyl ether yields αβ-di-1-naphthylethane, m. p. 162—163°, 1-methylnaphthalene, and phenol; *o*-tolyl 1-naphthylmethyl ether behaves similarly. Phenyl 2-naphthylmethyl ether affords phenol, 2-methylnaphthalene, αβ-di-2-naphthylethane, and phenyl-2-naphthylcarbinol, whereas 2-methylnaphthalene, αβ-di-2-naphthylethane, and (?)*o*-β-2-naphthylethylphenol, m. p. 129—130°, are derived from *o*-tolyl 2-naphthylmethyl ether. H. WREN.

Coloured salts of the di- and tri-phenylmethane series. II. W. MADELUNG (J. pr. Chem., 1926, **114**, [ii], 1—55).—The theoretical discussion of the various theories of the constitution of coloured salts of the di- and tri-phenylmethane series is continued (cf. A., 1925, i, 1459), experiments being described supporting the view that these salts are best represented by formulæ containing organic complex positive ions.

[With F. VOLKER.]—When a mixture of aniline, aniline hydrochloride, and *pp'*-diaminobenzophenone is heated, it yields pp'-*diaminobenzophenoneanil*, m. p. 206°. Ammonia converts the orange-yellow *hydrochloride* of this alkyl-free analogue of auramine into pp'-*diaminobenzophenoneimine*, m. p. 170°, which with alkali cyanides yields pp'-*diaminodiphenylaminoacetonitrile*, m. p. 197°, a colourless leuco-cyanide which dissolves in acetic acid to a green solution, and with hydrogen sulphide yields pp'-*diaminothiobenzophenone*, red needles, m. p. 238° (*diacetyl* derivative, green crystals, m. p. 237°). The sulphur content of different samples of the thioketone varied considerably, although the m. p. was constant. Apart from the ready decomposition of some derivatives, it is considered that the behaviour of the auramine series is analogous to that of the triphenylmethane series of dyes.

The decomposition by water of the orange-red methiodide of *p*-dimethylaminobenzylideneaniline is explained by the formulation [CHR·NMePh]I+

$H_2O \rightleftharpoons HI + CHR(OH)\cdot NMePh \longrightarrow RHC{:}NPh + MeOH$. This structure for the methiodide is supported by the fact that *p*-dimethylaminobenzaldehyde yields a *methiodide*, m. p. 148—149°, which reacts with aniline, yielding a colourless *methiodide*, m. p. 172—173°, of *p*-dimethylaminobenzylideneaniline. The aldehyde combines with methylamine, yielding *p-dimethylaminobenzylidenemethylamine*, m. p. 60°, which yields a yellow *hydrochloride* and *methiodide*, both unstable towards water, and a *perchlorate*.

The complex formula demands that just as $R_2C{:}NH \xrightarrow{HX} [R_2C\cdot NH_2]X$, so $R_2C{:}O \xrightarrow{HX} [R_2C\cdot OH]X$, and this suggests that a mono-salt of Michler's ketone should be a dye salt. *pp'*-Tetramethyldiaminobenzophenone (*diperchlorate* described) yields a yellow *perchlorate* having an absorption curve corresponding with that of auramine; this dissolves in acetic anhydride to a deep violet solution, which deposits green crystals of an *acetyl* derivative corresponding with equivalent proportions of acetylated and unacetylated perchlorate. The presence of the hydroxyl group makes possible the indirect preparation of alkyl derivatives. With sodium methoxide, the keto-chloride of Michler's ketone (cf. Staudinger, A., 1909, i, 905) yields the yellow *dimethylacetal*, m. p. 130°, which is the methyl ether of the *O*-methylated carbinol base; but although it gives carmine-coloured solutions with acids, the corresponding dye salt cannot be isolated. With sodium ethoxide, the keto-chloride yields the *diethylacetal*, m. p. 118°, and with sodium cyanide it yields pp'-*tetramethyldiaminodiphenylmalononitrile*, m. p. 191°, a yellow substance of which the acetic acid solution develops an intense green colour by the action of sunlight or heat, suggesting an equilibrium between the leuco-cyanide and the ionised complex cyanide. With sodium ethyl sulphide, the keto-chloride yields the *diethylthiol*, m. p. 122°, which with acetic acid gives a stable, green dye salt (*perchlorate*, green needles).

With sodium ethoxide, *pp'*-tetramethyldiaminothiobenzophenone ethiodide yields pp'-*tetramethyldiaminodiphenyl-α-ethoxy-α-ethylthiolmethane*, m. p. 130°, which with acids gives the carmine colour of the *O*-ethyl dye salt with evolution of mercaptan, showing that the tenacity of the ethylthiol is less than that of the ethoxy-radical. With sodium cyanide, the thioketone yields pp'-*tetramethyldiaminodiphenyl-α-ethylthiolacetonitrile*, m. p. 158°, which with acids gives a green dye salt with evolution of mercaptan. Oxidation of the thioketone with ferric chloride solution yields a violet-coloured *substance* (*perchlorate*, $C_{34}H_{40}O_8N_4S_2Cl_2$, described):

$$2[R_2C\,SH]X \longrightarrow [R_2C\cdot S\cdot S\cdot CR_2]X_2.$$

The reactions of phenolic aldehydes and ketones and the relationship between colour and structure are discussed from the point of view of complex formulæ.

R. W. West.

Halochromy of triphenylmethane derivatives. J. S. P. Blumberger (Chem. Weekblad, 1926, 23, 534—546).—A summary of the literature.

Esters of chaulmoogric acid. P. P. Herrera-Batteke and A. P. West (Philippine J. Sci., 1926, 31, 161—168).—The following esters are described: *α-methyl-n-heptyl*, b. p. 214·6°/0 mm.; *allyl*, b. p. 222·3°/5 mm.; *phenyl*, b. p. 233° (in a vacuum), m. p. 40°; *o-tolyl*, b. p. 218·8°/0 mm.; *m-tolyl*, b. p. 207·4°/0 mm.; *p-tolyl*, b. p. 207·1°/0 mm. J. M. Gulland.

Reactivity and stability of linking of organic radicals. I. Addition of hydrogen sulphide to nitriles, and hydrolysis of esters. K. Kindler (Annalen, 1926, 450, 1—20; cf. A., 1923, i, 568).—In the conversion of nitriles, R·CN, into thioamides and in the hydrolysis of ethyl esters, $R\cdot CO_2Et$, the rate of reaction is found to be a direct function of the stability of the linking between R and the ·CN or $\cdot CO_2Et$. Substituents which loosen this linking diminish the rate of addition or hydrolysis, whilst "positive" substituents greatly increase it. The rate of reaction of benzonitriles and benzoic esters increases with varying substituent groups in the order: *p*-NO_2, *m*-NO_2, *m*-I, *p*-I, *m*-Br, *p*-Br, *m*-Cl, *p*-Cl, H, *m*-Me, *p*-Me, *p*-MeO, *m*-NH_2, *p*-NH_2. This observation suggests a simpler means for determining the relative stability of linking of radicals than the dissociation, oxazole, and carbinol methods (Walden, "Chemie der freien Radikale," Leipzig, 1924; Skraup and Moser, A., 1922, i, 574; Skraup and Freundlich, *ibid.*, 539). The effect of substituents in a benzene ring on the stability of linking of each of the remaining hydrogen atoms is correlated with Korner's rules. As the dissociation constants of substituted benzoic acids, $X\cdot C_6H_4\cdot CO_2H$, increase with increased negativity of X, so the rate of hydrolysis of esters, $X\cdot C_6H_4\cdot CO_2Et$, and the firmness with which the NH_2 group is held in arylamines, $X\cdot C_6H_4\cdot NH_2$ (measured by their weakness as bases), decreases.

For the determination of thioamides an alcoholic solution is treated with alcoholic silver nitrate, and excess of silver is titrated with 0·1*N*-potassium thiocyanate. Aromatic thioamides are not decomposed by evaporation of their alcoholic solutions at 25—30° under reduced pressure. The m. p. of halogenated thiobenzamides are: p-*chloro*-, 124°; p-*bromo*-, 141·5°; m-*bromo*-, 120°; p-*iodo*-, 153°. Velocity constants are determined for the formation of these thiobenzamides from halogenated benzonitriles by the action of hydrogen sulphide under 1·75 atm. pressure at 60·6° in absolute alcohol in the presence of sodium ethoxide.

Velocity constants are also given for the hydrolysis of the following ethyl esters by a solution of sodium in 87·83% aqueous alcohol: benzoate, *m*- and *p*-chloro-, *m*- and *p*-bromo-, *p*-iodo-, *m*- and *p*-nitrobenzoates, *m*- and *p*-toluates, anisate, and *m*- and *p*-aminobenzoates. C. Hollins.

Alkaline hydrolysis of *d*-lysuric acid [dibenzoyl-lysine]. P. Karrer and M. Ehrenstein (Helv. Chim. Acta, 1926, 9, 1063—1066; cf. A., 1926, 603).—Hydrolysis of *d*-dibenzoyl-lysine with baryta under the given conditions yields in addition to *d*-ε-benzoyl-lysine, m. p. 253°, and not 235° as previously given (*loc. cit.*), which is the main product, a small quantity of (?)α-monobenzoyl-lysine, m. p. 227—228°, isolated after conversion of the ε-compound into α-bromo-ε-benzamidohexoic acid, by the action of nitrosyl bromide, the α-compound being unattacked. The observation of Passoth (Z. physiol. Chem., 1926, 155, 294) that the alkaline hydrolysis of dibenzoyl-

lysine yields α-benzoyl-lysine may be correct under the different experimental conditions employed. α-Benzoylornithine is also unattacked by nitrosyl bromide. J. W. Baker.

Compounds of titanium halides with oxygenated organic substances. G. Scagliarini and G. Tartarini (Atti R. Accad. Lincei, 1926, [vi], 4, 318—324).—With oxygenated organic compounds which do not contain hydroxyl and cannot pass into enolic modifications, titanium halides form in the cold additive compounds analogous to those formed by stannic halides. The following compounds are described: with benzophenone, $TiCl_4,COPh_2$; with methyl phthalate, $TiCl_4,C_6H_4(CO_2Me)_2$; with piperonal, $TiCl_4,2CHO{\cdot}C_6H_3{\cdot}O_2CH_2$.

With hydroxylated compounds such as salicylic acid, it is not possible to obtain at the ordinary temperature true additive compounds with titanium halides, but the following substituted compounds (cf. Dilthey, A., 1904, i, 290) were prepared: with salicylaldehyde, $TiCl_2(O{\cdot}C_6H_4{\cdot}CHO)_2,HCl$, a violet-red crystalline powder, slowly decomposing in the air, and $TiBr_2(O{\cdot}C_6H_4{\cdot}CHO)_2,HBr$, a brown compound; with salicylic acid, $Ti(O{\cdot}C_6H_4{\cdot}CO_2H)_2TiCl_6$, a red powder, turning first orange and then red; with methyl salicylate, $Ti(O{\cdot}C_6H_4{\cdot}CO_2Me)_2TiCl_6$, red crystals, altering rapidly in the air; with phenyl salicylate, $Ti(O{\cdot}C_6H_4{\cdot}CO_2Ph)_2TiCl_6$, dark red powder, readily alterable. T. H. Pope.

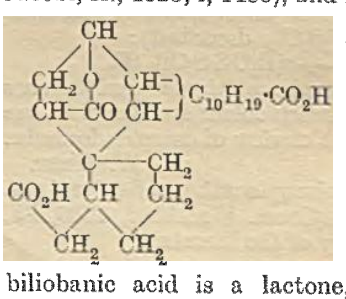
Synthesis of *dl*-2 : 4-dihydroxyphenylalanine (*dl*-resorcylalanine). K. Hirai (Biochem. Z., 1926, 177, 449—452).—Condensation of resorcylaldehyde with glycine anhydride gave a non-crystalline product, whilst condensation with hydantoin yielded no result. The aldehyde was therefore methylated and then condensed with glycine anhydride by Sasaki's method. *Di*-2 : 4-*dimethoxybenzylidineglycine anhydride* crystallises from hot acetic acid, m. p. 286—287°, and on treatment with hydrogen iodide and red phosphorus gives dl-2 : 4-*dihydroxyphenylalanine*, m. p. 223–224° (decomp.). It gives a dark greenish-violet colour with ferric chloride. P. W. Clutterbuck.

Decomposition of organic compounds [alkyl phthalates] by heat. W. Nagel and R. H. Abelsdorff (Wiss. Veroff. Siemens-Konz., 1926, 5, 193—210).—With the exception of dimethyl phthalate all the dialkyl esters of phthalic acid decompose on prolonged boiling, yielding phthalic anhydride and the corresponding alcohol and olefine, thus: $C_6H_4(CO_2{\cdot}C_nH_{2n+1})_2 = C_6H_4(CO)_2O + C_nH_{2n+1}{\cdot}OH + C_nH_{2n}$. The mixed esters containing a methyl radical yield methyl alcohol and the olefine derived from the other ester radical. The velocity of the reaction increases with the length of the carbon chain of the alcohol, and is greater with tertiary alcohols than with secondary. The following new esters have been prepared by heating the acid chloride of monomethyl phthalate with the appropriate alcohol: *methyl* n-*propyl phthalate*, b. p. 294—296°; *methyl* iso*propyl phthalate*, a yellow oil decomposed on heating; *methyl* n-*butyl phthalate*, and *methyl* iso*butyl phthalate*, b. p. 303—304°. *Methyl* tert.-*butyl phthalate* is formed by the interaction of the acid chloride of monomethyl phthalate with the reaction product of magnesium ethyl iodide and *tert.*-butyl alcohol; it is a brown oil which cannot be distilled. A. R. Powell.

Synthesis of derivatives of methylenedioxybenzene. W. H. Perkin and V. M. Trikojus (J.C.S., 1926, 2925—2932).—Meconinecarboxylic acid on hydrolysis with hydriodic acid gives 3-*hydroxy*-4-*methoxyphthalidecarboxylic acid*, m. p. 203°, and finally 3 : 4-*dihydroxyphthalidecarboxylic acid* (*normeconinecarboxylic acid*), m. p. 215° [*methyl* ester separates from dilute methyl alcohol with $1H_2O$, m. p. 104°; m. p. (anhydrous) 150°]. Attempts to methylenate this acid under various conditions were unsuccessful.

2 : 3-Dihydroxybenzoic acid (*o*-protocatechuic acid), prepared by oxidising *o*-veratraldehyde with potassium permanganate to *o*-veratric acid, followed by demethylation with hydriodic acid, is converted into 2 : 3-*methylenedioxybenzoic acid* (*o*-*piperonylic acid*), m. p. 227° (*ethyl* ester, m. p. 35·5°), by methylene iodide and aqueous-alcoholic potassium hydroxide. This acid condenses with formaldehyde in presence of acetic–hydrochloric acid, forming 3 : 4-*methylenedioxyphthalide*, m. p. 226°, which could not be converted into the corresponding methylenedioxyphthalaldehydic acid by oxidation. *o*-Piperonylic acid on treatment with thionyl chloride gives 2 : 3-*methylenedioxybenzoyl chloride*, m. p. 116°, which is converted by ammonia into 2 : 3-*methylenedioxybenzamide*, m. p. 176°. Treatment of the amide with thionyl chloride yields 2 : 3-*methylenedioxybenzonitrile* (*o*-*piperonylonitrile*), m. p. 80°, which is converted by hydroxylamine into 2 : 3-*methylenedioxybenzenylamino-oxime*, m. p. 139°. Reduction of *o*-piperonylonitrile with anhydrous stannous chloride in ether–hydrogen chloride solution yields 2 : 3-*methylenedioxybenzaldehyde* (*o*-*piperonal*), m. p. 34° (*p*-*nitrophenylhydrazone*, m. p. 258°), which condenses with malonic acid in presence of pyridine and piperidine, giving 2 : 3-*methylenedioxycinnamic acid*, m. p. 194°. *o*-Piperonal when treated with hydroxylamine gives at first an *α*-*oxime*, m. p. 127°, which on keeping passes into the β-*oxime*, m. p. 138—139°. When the latter is melted, it reverts to the α-modification. H. Burton.

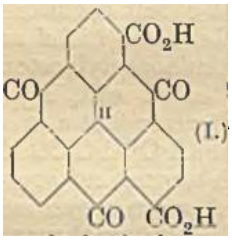
Chenodeoxycholic acid. III. A. Windaus and A. van Schoor (Z. physiol. Chem., 1926, **157**, 177—185; cf. A., 1925, i, 405).—Chenodeoxybilianic acid is best prepared from chenodehydrodeoxycholic acid by the action of cold dilute alkaline potassium permanganate solution, is oxidised by fuming nitric acid, yielding chenocholoidanic acid (cf. Wieland and Jacobi, A., 1925, i, 1488), and is readily hydrogenated to deoxybiliobanic acid. This when kept with potassium hydroxide solution yields a *tricarboxylic acid*, $C_{24}H_{38}O_7$, which on heating loses water with regeneration of deoxybiliobanic acid. It follows that deoxybiliobanic acid is a lactone, probably represented by the annexed formula, and that cheno(anthropo)-deoxycholic acid is a 3 : 12-dihydroxycholanic acid.



The tetracarboxylic acid, $C_{23}H_{36}O_8$, obtained by

heating chenocholoidanic acid, is also formed when the keto-dicarboxylic acid, $C_{23}H_{36}O_5$, obtained from hyodeoxycholic acid, is oxidised with fuming nitric acid. R. W. WEST.

Triphenylmethane compounds with linked benzene nuclei. II. Triketotrimethylenetriphenylmethanedicarboxylic acids. R. WEISS, A. SPITZER, and J. L. MELZER (Monatsh., 1926, **47**, 307—312; cf. A., 1925, i, 560).—Phthalyl chloride condenses with *p*-xylene in presence of aluminium chloride to give 1 : 4-dimethylanthraquinone and *di*-p-*xylylphthalide*, m. p. 180—184°, reduced by sodium amalgam to o-2 : 5 : 2′ : 5′-*tetramethylbenzhydrylbenzoic acid*, m. p. 236°, which is oxidised by alkaline permanganate to *triphenylmethane*-2 : 2′ : 2″ : 5 : 5′-*pentacarboxylic acid*, an amorphous powder (*pentamethyl* ester, m. p. 138—143°, made by means of diazomethane). The action of boiling concentrated sulphuric acid converts this substance into *triketotrimethylenetriphenylmethane*-3 : 3′-*dicarboxylic acid* (I), an insoluble amorphous powder, decomp. above 250° (*trisodium* salt, $+3{\cdot}5H_2O$), soluble in sulphuric acid or alkalis with a blue colour.



(I.)

Di-m-*xylylphthalide*, m. p. 159—162°, prepared in an analogous manner, is converted successively into o-2 : 4 : 2′ : 4′-*tetramethylbenzhydrylbenzoic acid*, m. p. 234—240°, *triphenylmethane*-2 : 2′ : 2″ : 4 : 4′-*pentacarboxylic acid* (*pentamethyl* ester, m. p. 160—162°), and *triketotrimethylenetriphenylmethane*-4 : 4′-*dicarboxylic acid*, decomp. above 250° (*trisodium* salt, $+1{\cdot}5H_2O$, one of the keto-groups being assumed to develop acidic properties).

G. M. BENNETT.

2-Mercaptoanthracene-3-carboxylic acid and anthracene-2-thioglycol-3-carboxylic acid. SOC. OF CHEM. IND. BASLE.—See B., 1926, 942.

Negative catalysis in the oxidation of benzaldehyde. O. M. REIFF (J. Amer. Chem. Soc., 1926, **48**, 2893—2899).—The rate of oxidation of benzaldehyde by gaseous oxygen is increased by addition of silica sand or broken glass and by shaking or stirring. Removal of water vapour inhibits the reaction, the chief factor in the promotion of which appears to be the formation of an active surface by the adsorption of a polar water layer on the wall of the reaction vessel, or other surface present. Stirring promotes the diffusion of oxygen to the active surface. The abnormal decrease in the rate of oxidation of benzaldehyde, as the reaction continues, is regarded as due to a poisoning action on the polar water layer by the condensation and oxidation products of benzaldehyde, the reaction being thus auto-inhibited. Negative catalysis caused by the addition of various inhibitors is explained by a similar poisoning action on the active surface by the inhibitor (cf. Taylor, A., 1925, ii, 562). F. G. WILLSON.

Chloro- and chloronitro-derivatives of *m*-hydroxybenzaldehyde. BRIT. DYESTUFFS CORPN., and H. H. HODGSON.—See B., 1926, 973.

Terpenes and related compounds. II. Preparation of piperonal from *iso*safrole using potassium dichromate. N. HIRAO (J. Soc. Chem. Ind. Japan, 1926, **29**, 504—508).—The optimum temperature for the oxidation of *iso*safrole to piperonal by means of chromic acid is 46—58°. The oxidising solution containing 45·4 g. of potassium dichromate, 60·4 g. of sulphuric acid, and 400 g. of water is added drop by drop to 25 g. of *iso*safrole during 2 hrs. with stirring, and piperonal (m. p. 35°) is obtained in a yield of 54% of theory. By increasing the amount of oxidising agent, the yield was raised to about 61%. The yield is markedly increased by the presence of salts of iron, cobalt, and manganese, the maximum yield being about 72%. K. KASHIMA.

Isomerisation of safrole under pressure. S. NAGAI (J. Soc. Chem. Ind. Japan, 1926, **29**, 364—370; cf. *ibid.*, 1924, **27**, 631).—High yields of *iso*safrole, up to 90—95% of theory, are obtained by heating safrole with alcoholic sodium or potassium ethoxide for 5—6 hrs. under 6—8 atm. pressure (cf. Hirao, A., 1926, 1135). K. KASHIMA.

Carbon rings. VIII. Constitution of muscone. L. RUZICKA (Helv. Chim. Acta, 1926, **9**, 1008—1117; cf. A., 1926, 1143).—Muscone on reduction by Clemmensen's method yields a *methyl*cyclo*pentadecane*, m. p. −19°, b. p. 150°/12 mm., d_4° 0·8626, 1·4776, which gives no m.-p. depression when mixed with a synthetic methyl*cyclo*pentadecane,* m. p. −19·5°, d_4° 0·8608, 1·4753 (the syntheses of substances marked with an asterisk are the subject of later communications). By the reduction of the corresponding ketones with sodium and boiling alcohol, 3- and 4-*methyl*cyclo*pentadecanol*, m. p. 55° and 50°, respectively, are prepared, but give no m.-p. depression when mixed with each other or with muscol (*loc. cit.*). Synthetic α-, β-, γ-, and δ-*methyltridecane-αν-dicarboxylic acids* * have m. p. 94°, 76° or 70°, 69° or 63°, and 55°, respectively, whilst β-, γ-, and δ-*methyldodecane-αι-dicarboxylic acids* * have m. p. 75°, 77°, and 74°, respectively. Repeated crystallisation of the mixture of dibasic acids, $C_{16}H_{30}O_4$, obtained by the oxidation of muscone (*loc. cit.*), however, yields an acid, m. p. 78°, which is higher than that of any of these except α-methyltridecane-αν-dicarboxylic acid. Since a mixture of this acid and the β-methyl isomeride would be obtained from 2-methyl*cyclo*pentadecanone, muscone is probably identical with the latter. In confirmation of this view, muscone forms a *benzylidene* derivative, b. p. 200—220°, which on oxidation with ozone and chromic acid yields an *acid*, m. p. 68—69° (58—60° on remelting), α_D +5°, which is very probably d-β-*methyltridecane-αν-dicarboxylic acid*,* since it gives no depression with a synthetic specimen of this acid, m. p. 70—73° (61—62·5° on remelting) (*anilide*, m. p. 139—140°; anilide of synthetic acid, m. p. 132—133°, mixed m. p. 133°). Heating with 50% potassium hydroxide solution, esterification (*methyl* ester, α_D +4°), and hydrolysis of the ester does not racemise the acid, so that the optical inactivity of the oxidation mixture, $C_{16}H_{30}O_4$, is probably due to compensation of equal *d* and *l* components. Muscone is therefore very probably *l*-2-methyl*cyclo*pentadecanone. J. W. BAKER.

Catalytic reduction of hydroxymethylenehydrindone and its condensation with phenyl-

hydroxylamine. H. RUPE and H. WIELAND (Helv. Chim. Acta, 1926, 9, 1001—1008).—Catalytic reduction of hydroxymethylenehydrindone yields *hydrindolylmethyl alcohol*, m. p. 56·5° (*acetate*, m. p. 63°; *benzoate*, m. p. 82°), which can be isolated only if all the operations are carried out at the ordinary temperature, since it readily loses 1 mol. of water to yield *methylenehydrindone*, which shows a great tendency to polymerise, and was obtained either as a gelatinous product or a white powder, decomp. above 360°, which is a polymeride of 12 mols. Hydroxymethylenehydrindone condenses with phenylhydroxylamine to yield *phenylhydroxylaminomethylenehydrindone*, m. p. 185° [*sodium* salt; *oxime*, decomp. 160°; *methyl ether*, m. p. 123° (decomp.)], which, hydrolysed with 5% sodium hydroxide solution, yielded azobenzene. On reduction with zinc dust and acetic acid, it yields *anilinomethylenehydrindone*, m. p. 215–217° (decomp.) (*hydrochloride*; *dibromide*, decomp. 250°; *oxime*, decomp. 170°), which is also obtained by the direct condensation of aniline with hydroxymethylenehydrindone. J. W. BAKER.

Synthesis of a higher homologue of curcumone and a ketodimethyltetrahydronaphthalene. H. RUPE and F. SCHÜTZ (Helv. Chim. Acta, 1926, 9, 992—1000).—The synthesis of γ-*p*-tolylbutyl methyl ketone has been effected and this ketone shown not to be identical with curcumone, thus confirming the structure already assigned (Rupe and Wiederkehr, A., 1924, i, 1066). Ethyl β-*p*-toluylpropionate is converted by magnesium methyl bromide into γ-*p*-tolyl-Δ^{β}-pentenoic acid, together with 2-p-*tolyl*-2 : 5 : 5-*trimethyltetrahydrofuran*, b. p. 118—120°/10 mm., which is the main product (43% yield) if a large excess of the Grignard reagent is employed. When treated with hydrogen bromide, it yields a *hydrocarbon*, $(C_{14}H_{18})_2$, m. p. 53°. Reduction of the pentenoic acid to γ-*p*-tolylvaleric acid is best effected by hydrogenation with a nickel catalyst (cf. Rupe and Steinbach, *ibid.*, 1911, i, 293) (*ethyl* γ-p-*tolylvalerate* has b. p. 142—143°/9 mm.). Thionyl chloride converts the reduced acid into its *chloride*, b. p. 134—135°/9 mm., which with zinc methyl yields γ-p-*tolylbutylmethyl ketone*, b. p. 141—141·5°/11·5 mm. (*semicarbazone*, m. p. 142°; *oxime*, b. p. 167°/8 mm.; *benzylidene* derivative, m. p. 67°). The acid chloride treated with aluminium chloride yields 4-*keto*-1 : 6-*dimethyltetrahydronaphthalene*, b. p. 146·5—147°/11·5 mm. (*semicarbazone*, m. p. 194—195°; *oxime*, m. p. 78·5°), which with magnesium methyl iodide yields 1 : 4 : 6-*trimethyl*-1 : 2-*dihydronaphthalene*, b. p. 122—123°/12 mm., but under certain experimental conditions (especially low temperature) the intermediate 1 : 4 : 7-*trimethyl*-1 : 2 : 3 : 4-*tetrahydro*-α-*naphthol*, b. p. 138·5—139°/11 mm., can be isolated. Ozonolysis of 1 : 4 : 6-trimethyl-1 : 2-dihydronaphthalene yields β-2-*acetyl*-4-*methylphenylbutyric acid*, m. p. 124° (*semicarbazone*, m. p. 176·5°), together with a small quantity of an *aldehyde*, b. p. 151—153°/9 mm. (*semicarbazone*, m. p. 22[illegible] 228°), probably possessing the structure:  . J. W. BAKER.

Stereoisomerism and isomorphism of the phenyl styryl ketones. C. DUFRAISSE and A. GILLET (Compt. rend., 1926, **183**, 746—748).—Two stereoisomeric forms of phenyl β-methoxystyryl ketone exist, *A*, m. p. 66°, and *B*, obtained in isomorphous forms, m. p. 78° and 81°, respectively. Phenyl α-bromo-β-methoxystyryl ketone exists in isomeric forms, m. p. 72° and 102°, respectively. *Phenyl* β-*ethoxystyryl ketone* exists in two stable isomorphous forms, m. p. 75° and 78°. Dibenzoylmethane has two isomorphous forms, m. p. 71° and 78°, respectively. When insolated, one form of α-phenyl α-bromo-β-methoxystyryl ketone, m. p. 72°, is changed into the other, m. p. 102°, and after further insolation this form is changed back to the first, m. p. 72°. L. F. HEWITT.

Metallic compounds of monoximes and the structure of oximes. T. W. J. TAYLOR and (MISS) E. K. EWBANK (J.C.S., 1926, 2818—2825; cf. *ibid.*, 1903, **83**, 24; A., 1922, i, 661).—The investigation of 11 monoximes of different types, and the possibility of obtaining from them co-ordinated complexes with iron, nickel, cobalt, and copper, gave the following results. (In the following formulæ R=1 mol. of oxime −1H). Oximinoacetone, Me·CO·CH:N·OH, gives with solutions of nickel and cobalt acetates in presence of sodium hydroxide, ill-defined *nickel* and *cobalt* salts, R_2Ni and R_2Co. Oximinoacetylacetone, Me·CO·C(:N·OH)·COMe, yields a *cobalt* salt, R_3Co; with ammoniacal nickel acetate, it gives first a green *compound*, CMe(:NH)·C(CO·Me):N·O·Ni·O·CO·Me, changing rapidly to a reddish-brown *compound*, $[CMe(:NH)\cdot C(CO\cdot Me):N\cdot O\cdot]_2Ni$. A green *copper* salt, $R\cdot Cu\cdot O\cdot CO\cdot Me,H_2O$, is described. Oximinobenzoylacetone, Ph·CO·C(:N·OH)·COMe, gives a *cobalt* salt, R_3Co, and a *copper* derivative, R·CuOH. Ethyl oximinoacetoacetate, Me·CO·C(:N·OH)·CO_2Et, gives a *cobalt* salt, R_3Co, a *nickel* complex of the same type as that obtained from oximinoacetylacetone, and a *copper* derivative, $R\cdot CuOH,H_2O$ (anhydrous salt explodes at 100—110°). Oximinoacetophenone forms *iron*, *cobalt*, and *nickel* salts of the formulæ R_2Fe, R_3Co, and R·NiO·CO·Me(?). Oximinomalonanilide, $OH\cdot N:C(CO\cdot NHPh)_2$, yields iron, *cobalt*, *nickel*, and *copper* derivatives, R_2M (M=1 atom of metal). α-Benzilmonoxime, Ph·CO·CPh:N·OH(α), forms a *copper* derivative, R·CuOH (see also Tschugaev, A., 1907, i, 830).

No complex salts could be prepared from β-benzilmonoxime, ethyl oximinomalonate, ethyl oximinobenzoylacetate, and methyl α-oximinoethyl ketone. The necessary conditions for metallic complex formation appear to be (i) the presence of a reactive carbonyl group in the oxime, (ii) co-ordination between the carbonyl group and the metallic salt, (iii) ring closure through elimination of a hydrogen ion or a molecule of the acid originally united with the metal. These views indicate that α-benzilmonoxime contains a reactive carbonyl group, whereas the β-oxime does not. This is explained by assigning to the β-oxime the co-ordinated structure . The structure of other oximes is discussed in view of the results. H. BURTON.

Unsaturated 1 4-diketones. I. Synthesis and structure of αβ-di-(2 : 4 : 6-trimethylbenzoyl)-

vinyl alcohol. R. E. LUTZ (J. Amer. Chem. Soc., 1926, **48**, 2905—2915; cf. A., 1925, i, 681).—Further investigation has shown that the addition of halogens to dibenzoylethylene and its analogues leads generally to two stereoisomeric dihalides, the lower-melting (α-) isomeride being separable from the higher-melting (β-) isomeride by differences in solubility, the latter generally separating directly from the reaction mixture. The following were prepared: αβ-*dibromo*-αβ-*dibenzoylethane*, m. p. 107—107·5° (α-) and m. p. 179° (decomp.) (β-); αβ-*dichloro*-αβ-*dibenzoylethane*, m. p. 86° (α-) and m. p. 167° (decomp.) (β-) (*loc. cit.*); αβ-*dibromo*-αβ-*di*-p-*bromobenzoylethane*, m. p. 138° (α-) and m. p. 208·5° (decomp.) (β-); αβ-*dichloro*-αβ-*di*-p-*bromobenzoylethane*, m. p. 129—129·5° (α-) and m. p. 215·5° (decomp.) (β-); αβ-*dibromo*-αβ-*di*-(2 : 4 : 6-*trimethylbenzoyl*)*ethane*, m. p. 161·5° (α-) and m. p. 207° (decomp.) (β-); and αβ-*dichloro*-αβ-*di*-(2 : 4 : 6-*trimethylbenzoyl*)*ethane*, m. p. 215° (decomp.), only the β-isomeride being obtained in this case. The pairs of isomerides gave the same dibenzoylethanes when reduced with zinc and acetic acid. Conversion of the α- into the β-isomeride was effected to some extent by boiling in alcoholic solution. Treatment of either modification of αβ-dibromo-αβ-di-*p*-bromobenzoylethane with methyl-alcoholic sodium methoxide affords *α-methoxy*-αβ-*di*-p-*bromobenzoylethylene*, m. p. 155°. *α-Bromo*-αβ-*di*-(2 : 4 : 6-*trimethylbenzoyl*)*ethylene*, yellow, m. p. 110°, is obtained when αβ-dibromo-αβ-di-(2 : 4 : 6-trimethylbenzoyl)ethane is boiled in alcohol. Treatment of αβ-dibromo-αβ-di-*p*-bromobenzoylethane with alcoholic sodium acetate affords *α-hydroxy*-αβ-*di*-p-*bromobenzoylethylene*, orange, m. p. 101·5—102·5° (*copper* salt), whilst αβ-dibromo-αβ-di-(2 : 4 : 6-trimethylbenzoyl)ethane affords similarly *di*-(2 : 4 : 6-*trimethylbenzoyl*)*ethanone*, $Me_3C_6H_2{\cdot}CO{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}C_6H_2Me_3$, yellow, m. p. 145—145·5°, a small proportion of the *enolic* modification, *α-hydroxy*-αβ-*di*-(2 : 4 : 6-*trimethylbenzoyl*)*ethylene*, yellow, m. p. 103·5—104·5° (*copper* salt), being formed at the same time. The latter modification was always obtained by the application of excess of alcoholic sodium acetate, either to the original dibromo-derivative or to the ketonic form. Treatment of the above enolic derivative with ethereal diazomethane affords a yellow *isomeride*, m. p. 107·5—108°, of the α-methoxy-αβ-di-(2 : 4 : 6-trimethybenzoyl)-ethylene previously described (*loc. cit.*), the preparation of which, it is now found, leads also to a trace of the yellow modification. Dibenzoylacetylene is obtained by treating αβ-dibromo-αβ-dibenzoylethane with a trace of sodium acetate in acetone–alcohol in presence of sodium carbonate. Treatment of αβ-dibromo-αβ-dibenzoylethane with alcoholic methylamine affords α-methylamino-αβ-dibenzoylethylene, yellow, m. p. 164°, whilst dimethylamine yields similarly a yellow *compound*, $C_{19}H_{22}O_2N_2$, m. p. 96·5°. Trimethylamine affords, in the same way, a *substance*, m. p. above 230°, together with α-bromo-αβ-dibenzoylethylene and dibenzoylacetylene.

F. G. WILLSON.

Alkylation of hydroxynaphthaquinone. I. Oxygen Ethers. L. F. FIESER (J. Amer. Chem. Soc., 1926, **48**, 2922—2937).—The methoxynaphthaquinone obtained by Sachs, Berthold, and Zaar (A., 1907, i, 426) from the silver salt of hydroxynaphthaquinone ("naphthalenic acid") can be separated by fractional crystallisation into two isomerides, *4-methoxy-β-naphthaquinone* (I), orange-yellow, m. p. 190°, and *2-methoxy-α-naphthaquinone* (II), pale yellow, m. p. 183·5°; (I) is readily hydrolysed by dilute aqueous alkali, and is transformed quantitatively into (II) when treated with boiling methyl-alcoholic hydrogen chloride. When treated with boiling aqueous sodium hyposulphite, (I) affords *4-methoxy*-1 : 2-*naphthaquinol*, decomp. 130° (*diacetate*, m. p. 135°), whilst boiling alcoholic *o*-phenylenediamine affords 6-methoxynaphthaphenazine, m. p. 180° (cf. Kehrmann and Messinger, A., 1891, 1213). (I) yields a *semicarbazone*, m. p. 246° (decomp.) (cf. Sachs, *loc. cit.*), whilst warm aqueous *p*-toluidine affords 4-*p*-toluidino-β-naphthaquinone, m. p. 250° (decomp.) (cf. Elsbach, A., 1882, 853), and toluidinonaphthaquinonetoluidide, m. p. 177° (cf. Fuchs, A., 1876, i, 247). Toluidino-β-naphthaquinone methyl ether has m. p. 147° (cf. Zincke and Brauns, A., 1883, 209). (II) is less readily hydrolysed by acids than (I). It is obtained by esterification of hydroxynaphthaquinone by methyl alcohol and hydrogen chloride, or by the action of diazomethane. On reduction as above, it yields *2-methoxy*-1 : 4-*naphthaquinol*, decomp. 107° (*diacetate*, m. p. 129—130°). It does not react with aqueous or alcoholic *p*-toluidine, but in acetic acid solution yields *p*-toluidino-α-naphthaquinone, m. p. 200° (cf. Elsbach, *loc. cit.*). Treatment of the silver salt of hydroxynaphthaquinone with ethyl iodide also yields a mixture (m. p. 96—97°; cf. Miller, A., 1911, i, 308; 1916, ii, 19), which can be separated by crystallisation from benzene or by means of aqueous sodium hydrogen sulphite, in which the *p*-quinone derivative is less soluble, into 4-ethoxy-β-naphthaquinone, m. p. 126° (cf. Baltzer, A., 1882, 204) (corresponding *ethoxynaphthaquinol diacetate*, m. p. 108—109°; *6-ethoxynaphthaphenazine*, m. p. 158·5°), and *2-ethoxy-α-naphthaquinone*, m. p. 120° (*quinol diacetate*, m. p. 81·5°). The following alkoxynaphthaquinones were prepared by the action of the appropriate alkyl bromide on the above silver salt: 4-n-*butoxy*-β-*naphthaquinone*, orange-yellow, m. p. 98°; 2-n-*butoxy*-α-*naphthaquinone*, brownish-yellow, m. p. 104°, and 4-iso*propoxy*-β-*naphthaquinone*, orange-yellow, m. p. 126°. Treatment of the silver salt of 2-chloro-3-hydroxy-α-naphthaquinone with ethyl iodide yields *3-chloro-2-ethoxy-α-naphthaquinone*, yellow, m. p. 97—98° (cf. Zincke, A., 1888, 708). It is concluded that, in solution, hydroxynaphthaquinone exists as a mixture of tautomerides, in which the *p*-quinonoid form greatly preponderates.

F. G. WILLSON.

Anthraquinone-2-glycine-3-carboxylic acid. SOC. OF CHEM. IND. BASLE.—See B., 1926, 942.

Wool dyes. [Sulphonic acids of 1 : 1′-dianthraquinonylamine and their halogen derivatives.] FARBENFABR. VORM. F. BAYER UND CO.—See B., 1926, 973.

Phytochemistry. III. Betulin. II. O. DISCHENDORFER and H. GRILLMAYER (Monatsh., 1926, **47**, 241—249; cf. A., 1924, i, 65).—With the object of definitely establishing the formula of betulin (cf. Schulze and Pieroh, A., 1922, i, 1045), some new

derivatives have been prepared. *Betulin dianisate*, m. p. 192—193° (uncorr.), $[\alpha]_D^{17}$ +49·13° (all rotations observed in chloroform), and *di*-m-*nitrobenzoate*, m. p. 267—268°, $[\alpha]_I^{15}$ +38·37°, and allo*betulin* p-*bromobenzoate*, m. p. 276° after sintering, $[\alpha]_I^{16}$ +66·24°; *anisate*, m. p. 295°, $[\alpha]_D^{16\cdot5}$ +77·32°, and m-*nitrobenzoate*, m. p. 277—278°, $[\alpha]_D^{21}$ +69·24°, are described. When *allo*betulone is heated at 150° with benzoyl chloride, enolisation takes place and allo*betulenol dibenzoate*, $C_{30}H_{46}(OBz)_2$, m. p. 228—230°, $[\alpha]_D^{15\cdot5}$ +33·16°, is formed, thus showing the presence of a ·CH_2·CO· grouping in *allo*betulone. allo*Betulenol di*-p-*bromobenzoate* has m. p. 225°, $[\alpha]_D^{13}$ +37·18°. The following additional data are recorded: monobromobetulin diacetate, $[\alpha]_D^{14}$ +6·18°; betulin dibenzoate, $[\alpha]_{D\cdot5}$ +43·28°; betulin di-*p*-bromobenzoate, $[\alpha]_D^{8}$ +44·19°. Bromination of *allo*betulone in chloroform solution at the ordinary temperature yields *dibromo*allo*betulone*, m. p. 220° (decomp.) after darkening at 218°. Analyses of these compounds, especially the last-named, leave no doubt that the composition of betulin is represented by the formula $C_{30}H_{50}O_2$ or $C_{30}H_{48}O_2$. H. E. F. Notton.

Higher terpene compounds. XXIX. L. Ruzicka, R. Steiger, and H. Schinz (Helv. Chim. Acta, 1926, 9, 962—978).—Manila copal is separated into (1) an acid portion, 80%, (2) a neutral, ether-soluble portion, 10%, and (3) a portion insoluble in sodium hydroxide and ether, 10%. The lower-boiling fraction of the neutral portion contains pinene and other terpenes (cf. Brooks, A., 1910, i, 691), whilst from the highest-boiling portion a primary sesquiterpene alcohol, b. p. 120—130°/0·3 mm., was isolated by means of its phthalic ester. The acid portion contains (*a*) soluble in ether 33·3%, (*b*) soluble in acetone 33·3%, (*c*) insoluble in acetone 33·3%. The combined acids in fractions (*a*) and (*b*) were converted into their methyl esters through their silver salts (OMe in mixture, 12·3%) and distilled in a high vacuum. The b. p. of the mixture rises continuously, but the lower fraction, b. p. 120—160°/0·3 mm., corresponds approximately with the ester of a monobasic *acid* $C_{15}H_{24}O_2$ or $C_{16}H_{26}O_2$, and the higher fraction, b. p. 207—208/9·5 mm., with that of a dibasic *acid*, $C_{23}H_{34}O_4$ (cf. Richmond, *ibid.*, 690, who obtained an acid, $C_{22}H_{34}O_4$). On hydrolysis, only amorphous acids could be obtained. The fraction (c) consists essentially of a dibasic *acid*, $C_{40}H_{60}O_4$, which decomposes when heated in a high vacuum, yielding a neutral distillate containing a *hydrocarbon*, $C_{38}H_{56}$, b. p. 230—250/0·3 mm. Dry distillation of the whole acid portion (1) at 330° in a vacuum yields acidic (not investigated) and neutral products; the latter on distillation boiled continuously from 100°/12 mm. to 250°/0·3 mm., the low fraction containing a dicyclic *hydrocarbon*, $C_{14}H_{22}$, b. p. 115°/12 mm., d_4^{17} 0·9371, n_D^{17} 1·5201, which on catalytic reduction yields the *hydrocarbon*, $C_{14}H_{26}$, b. p. 115°/12 mm., 0·9010, 1·4860, whilst the composition of the high fraction corresponds with the formula $C_{38}H_{56}$. The fraction b. p. 100—150°/12 mm. on dehydrogenation with sulphur yields a methylethylnaphthalene, $C_{13}H_{14}$, b. p. 140°/12 mm., d_4^{18} 1·011, n_D^{18} 1·6082 (*picrate*, m. p. 138°; *styphnate*, m. p. 131°), which on oxidation with alkaline potassium ferricyanide solution yields a new *naphthalenedicarboxylic acid*, m. p. 310° (probably the 1 : 3-, 1 : 5-, 2 : 6-, or 2 : 7-isomeride). Dehydrogenation of the fraction b. p. 130—150°/0·3 mm. yields a small quantity of the dimethylphenanthrene, m. p. 86°, previously obtained from *d*-pimaric acid (Ruzicka and Balas, A., 1923, i, 818). The methyl esters of the acid products obtained by the dry distillation of the acetone-soluble (ether-insoluble) acids (*b*) yielded, on distillation, two fractions, corresponding with the *methyl* esters of the acids $C_{15}H_{24}O_2$ and $C_{19}H_{30}O_2$, d_4^{18} 1·028, n_D^{18} 1·5071, and d_4^{22} 1·010, 1·5113, respectively, which on dehydrogenation yielded respectively the methylethylnaphthalene and the dimethylphenanthrene. A scheme by which the hydrocarbons are derived is suggested, and the relationships of the results to the preparation of copal varnish are discussed. J. W. Baker.

Synthesis of *l*-α-pinene from nopinene. G. Austerweil (Bull. Soc. chim., 1926, **39**, 1643—1646; cf. A., 1926, 619).—Pure nopinene, rectified over calcium, is heated with 3 parts of colophony at 160°—→ 100°. Rectification of the terpene product gives more than 70% of pure *l*-α-pinene. A similar result is obtained by heating nopinene with commercial stearin at 145°. *l*-α-Pinene shows remarkable stability towards organic acids. Heated at 125—130° with 1 part of benzoic acid, it gives only 3—5% of bornyl benzoate and scarcely a trace of limonene, whilst 90% is unattacked. Nopinene, under similar treatment, gives 14% of bornyl benzoate and the remainder of the nopinene is almost quantitatively converted into *l*-α-pinene. M. Clark.

Production of *iso*borneol from a mixture of camphene and associated oils. H. Gammay.—See B., 1926, 995.

Production of camphor from *iso*borneol. H. Gammay.—See B., 1926, 995.

Manufacture of esters of *iso*borneols and borneols. Chem. Fabr. vorm. Schering.—See B., 1926, 995.

Ring fission with coumaranone derivatives. K. von Auwers and H. Lorenz (Ber., 1926, **59**, [*B*], 2628—2635; cf. A., 1919, i, 217).—Introduction of a basic residue in the 2-position of 2-alkylcoumaranones does not increase the stability of the furan ring; since halogen, hydroxyl, or methoxyl also fails to produce a stabilising effect, the remarkable stability of 2 : 2-dialkylcoumaranones remains unexplained.

2-Bromo-2 : 5-dimethylcoumaranone is converted by aniline in benzene into 2-*anilino*-2 : 5-*dimethylcoumaranone*, m. p. 140°, which with semicarbazide slowly yields the *semicarbazone* of *p-hydroxyphenyl α-anilino-α-semicarbazidoethyl ketone*, $OH{\cdot}C_6H_4{\cdot}C(:N{\cdot}NH{\cdot}CO{\cdot}NH_2){\cdot}CMe(NHPh){\cdot}NH{\cdot}NH{\cdot}CO{\cdot}NH_2$, m. p. 216°, whereas with *p*-nitrophenylhydrazine it rapidly affords the *p*-nitrophenylosazone of *p*-hydroxyphenyl methyl diketone, m. p. 264°. 2-o-*Toluidino*-2 : 5-*dimethylcoumaranone*, m. p. 126°, similarly gives the *semicarbazone* of p-*hydroxyphenyl* α-o-*toluidino*-α-*semicarbazidoethyl ketone*, m. p. 219°. 2-α-Naphthylamino-2 : 5-*dimethylcoumaranone*, m. p. 103—105°, appears stable to semicarbazide, but with

p-nitrophenylhydrazine it yields the *p*-nitrophenylosazone of *p*-hydroxyphenyl methyl diketone, decomp. 261°. 2-β-*Naphthylamino*-2 : 5-*dimethylcoumaranone* is unaffected by semicarbazide. 2-Bromo-2 : 5-dimethylcoumaranone is transformed by ethyl sodiomalonate into *ethyl* 2 : 5-*dimethylcoumaranylmalonate*, m. p. 42—45° (corresponding *acid*, m. p. 178°), which, although stable towards semicarbazide, suffers fission with *p*-nitrophenylhydrazine. 2-*Thiocyano*-2 : 5-*dimethylcoumaranone*, m. p. 102°, from 2-bromo-2 : 5-dimethylcoumaranone and potassium thiocyanate in ether, is readily converted by semicarbazide into the disemicarbazone of *p*-hydroxyphenyl methyl diketone.

2-*Bromo*-2 : 4 : 6-*trimethylcoumaranone*, m. p. 51°, is prepared from bromine and the coumaranone in dry carbon disulphide. 2-*Anilino*-2 : 4 : 6-*trimethylcoumaranone*, m. p. 136—137°, is decomposed by *p*-nitrophenylhydrazine, but is stable towards semicarbazide. 2-α-*Naphthylamino*-2 : 4 : 6-*trimethylcoumaranone*, m. p. 167—168°, behaves similarly. 2-*Thiocyano*-2 : 4 : 6-*trimethylcoumaranone*, m. p. 78°, is stable towards semicarbazide. H. WREN.

Unsaturated 1 : 4-diketones. II. Formation of certain derivatives of furan. R. E. LUTZ (J. Amer. Chem. Soc., 1926, **48**, 2916—2919; cf. this vol., 58).—When treated with acetic anhydride in presence of a trace of concentrated sulphuric acid, *trans*.-dibenzoylethylene yields 2 : 5-*diphenyl*-3-*acetoxyfuran*, m. p. 95°. 2 : 5-*Di*-p-*tolyl*-3-*aceloxyfuran*, m. p. 100·5°, is obtained analogously, whilst substitution of acetyl chloride for the anhydride yields 3-*chloro*-2 : 5-*diphenylfuran*, m. p. 76°, and 3-*chloro*-2 : 5-*di*-p-*tolylfuran*, m. p. 85°, respectively. The above 3-chloro-2 : 5-di-*p*-tolyl derivative was also prepared by dehydration of the additive product from di-*p*-toluylethylene and hydrogen chloride. Whilst both the isomeric *s*-dichlorodibenzoylethanes are readily converted into furans (cf. Conant and Lutz, A., 1925, i, 681), only the α-isomeride of the corresponding dibromodibenzoylethane could be converted, by the combined action of acetic anhydride, acetyl chloride, and sulphuric acid, into 3 : 4-*dibromo*-2 : 5-*diphenylfuran*, m. p. 88·5—89°. Furans could not be obtained similarly from " β "-α-chloro-αβ-dibenzoylethylene or from dibenzoylacetylene.

F. G. WILLSON.

5-Hydroxyfurfuraldehyde. T. REICHSTEIN (Helv. Chim. Acta, 1926, **9**, 1066—1068).—Pure 5-hydroxyfurfuraldehyde is an exceedingly hygroscopic, crystalline solid, m. p. 35—35·5°, b. p. 115—120°/0·5 mm. [α-naphthylamide, m. p. 135—135·5°; semicarbazone, m. p. 194—195° (decomp.)]. On oxidation, it gives hydroxymethylpyromucic acid in 84% yield. J. W. BAKER.

Derivatives of furfuraldehyde. III. Transitory coloration of furyl ketones. I. KASIWAGI (Bull. Chem. Soc. Japan, 1926, **1**, 233—236).—The red colour produced by the action of alkali on saturated furyl ketones, or by keeping these, is changed irreversibly to yellow on heating or acidifying. The effect is ascribed to the formation of labile polymerides. E. W. WIGNALL.

Grape pigments. IV. Anthocyans of Isabella grapes. R. J. ANDERSON and F. P. NABENHAUER (J. Amer. Chem. Soc., 1926, **48**, 2997—3003; cf. A., 1924, i, 1390).—The pigment of the skins of Isabella grapes was isolated as the picrate and converted into the *chloride*, $C_{21}H_{19}O_{10}(OMe)_2Cl,4H_2O$, which, on hydrolysis, yielded dextrose and the anthocyanidin chloride (œnidin), $C_{15}H_9O_5(OMe)_2Cl,1{\cdot}5H_2O$, identical with that previously described (*loc. cit.*). The latter yielded a *tetra-acetate*, which, on oxidation with permanganate in acetone, afforded *acetylsyringic acid*, m. p. 190° after sintering at 187°, a synthesis of which is described. The pigment thus appears to be identical with that of the European grape, *Vitis vinifera* (cf. Willstatter and Zollinger, A., 1915, i, 285).

F. G. WILLSON.

Catalytic reduction of cyanogen compounds. H. RUPE and A. HECKENDORN (Helv. Chim. Acta, 1926, **9**, 980—991).—The catalytic reduction using a nickel catalyst at the ordinary temperature and pressure, of various unsaturated cyano-keto-derivatives has been studied. Ethyl benzylidenecyanoacetate yields the *aldehyde* of ethyl benzylmalonate (yield 80%; *semicarbazone*, m. p. 121°), which with phenylhydrazine and *p*-nitrophenylhydrazine yields, respectively, 1-*phenyl*-4-*benzylpyrazolone*, m. p. 143°, and 1-p-*nitrophenyl*-4-*benzylpyrazolone*, m. p. 176°, together with a secondary base isolated as its *oxalate*, m. p. 210°, and to which the constitution $[CH_2Ph{\cdot}CH(CO_2Et){\cdot}CH_2]_2NH$ is assigned. Similar reduction of ethyl benzylcyanoacetate yields the same aldehyde, showing that the double linking is reduced in the former case. In the reduction of ethyl *o*-nitrobenzylidenecyanoacetate, only the nitro-group is reduced, the product being *ethyl* 2-*aminoquinoline*-3-*carboxylate*, m. p. 135° (*hydrochloride*; *picrate*, m. p. 177°; *benzoyl* derivative, m. p. 160°), which on hydrolysis yields the free *acid*, m. p. 290°, purified by means of its *magnesium* salt, $+7H_2O$. The ester does not react with cold nitrous acid, but when warmed with sodium nitrite in hydrochloric acid solution it yields 2-hydroxyquinoline-3-carboxylic acid, which on heating yields carbostyril. The main product of the reduction of ethyl β-phenyl-γ-benzyl-α-cyanobutyrate [*nitrosoamine*, m. p. 148° or 153°, yielding the corresponding *diphenylhexahydronicotinic acid*, m. p. 196° (*silver* salt), on hydrolysis] is ethyl 1 : 3-diphenylpiperidine-4-carboxylate, formed by the reduction of the tetrahydropyridine derivative obtained by the elimination of water from ethyl α-methylamino-γ-benzoyl-β-phenylbutyrate, m. p. 104° (*hydrochloride*; *picrate*, m. p. 185°; *picrolonate*, m. p. 183°), which is also obtained in small yield. On hydrolysis it yields the free *acid*, m. p. 300—301°, isolated as its *hydrochloride*, from which it is obtained by conversion into its *copper* salt, which is decomposed by hydrogen sulphide. J. W. BAKER.

Derivatives of isatin and 4-nitroisatin. H. RUPE and K. APOTHEKER (Helv. Chim. Acta, 1926, **9**, 1049—1059).—Reduction of isatinphenylhydroxylamine (Rupe and Stocklin, A., 1924, i, 764) with zinc dust and acetic acid, or, better, catalytically with a nickel catalyst, yields the lactim form of *isatin-α-anil*, $C_6H_4\langle{}^{CO}_{N}\rangle C{\cdot}NHPh$, m. p. 176°, which on treatment with semicarbazide, hydroxylamine, or

phenylhydrazine yields, respectively, isatin-β-semicarbazone, -oxime, or -phenylhydrazone. The constitution of the product is confirmed by its non-identity with the dihydro-compound, β-anilinoindoxyl (isatin leuco-2-anil) (Pummerer and Gottler, A., 1910, i, 511), with which, however, the analytical data more closely agree, and the fact that the previously supposed lactam and lactim forms of isatin-α-anilide (Meyer-Jacobson, "Lehrbuch," II. 3, 274) are both represented by the lactam formula, since they are interconvertible on crystallisation, are both hydrolysed by hydrochloric acid with equal ease, and with semicarbazide, hydroxylamine, and phenylhydrazine both yield, respectively, *isatin-α-semicarbazone*, m. p. 226—228°, phenylhydrazone, and oxime, a mechanism for this reaction being suggested. Catalytic reduction of 4-nitroisatin (Rupe and Kersten, A., 1926, 843) yields *4-aminodioxindole* (isatin itself, under the same conditions being reduced to dioxindole), which with phenylhydrazine yields *4-aminoisatin-β-phenylhydrazone*, m. p. 243—245° (also obtained by the reduction of *4-nitroisatin-β-phenylhydrazone*, m. p. 286°), and with hydroxylamine and semicarbazide yields *4-aminoisatin-β-oxime*, m. p. 258°, and *4-aminoisatin-β-semicarbazone*, decomp. above 300°, respectively. Catalytic reduction of 4-nitroisatinphenylhydroxylamine (Rupe and Stocklin, *loc. cit.*, there designated as the 6-compound; cf. Rupe and Kersten, *loc. cit.*) yields *4-aminoisatinanil*, $NH_2 \cdot C_6H_3 < \overset{CO}{\underset{N}{>}} C \cdot NHPh$, m. p. 96° (*hydrochloride*), which with semicarbazide and phenylhydrazine yields, respectively, 4-aminoisatin-β-semicarbazone and -β-phenylhydrazone. J. W. BAKER.

[Constitution of the dyes from 2-methylated indolenium salts and phenylhydrazine.] E. ROSENHAUER and A. FEILNER (Ber., 1926, 59, [*B*], 2682; cf. A., 1926, 1257).—A correction. H. WREN.

Thioamides. VI. Some amino-acid derivatives containing sulphur in thioamide combination. E. S. GATEWOOD and T. B. JOHNSON (J. Amer. Chem. Soc., 1926, 48, 2900—2905).—2 : 5-Dithionpiperazine (cf. Johnson, A., 1912, i, 304) is obtained, together with a light brown *powder*, m. p. not below 280°, by adding aminoacetonitrile sulphate to aqueous-alcoholic ammonia and passing ammonium sulphide through the resulting solution at below 0°. It decomposes rapidly in alkaline solution, and affords hydrogen sulphide and glycine on hydrolysis. Treatment of ethyl hippurate with phosphorus pentasulphide in dry benzene affords *ethyl thionhippurate*, m. p. 38—40°, which, on hydrolysis, yields *thionhippuric acid*, m. p. 148—150°. The action of phosphorus pentasulphide on ethyl acetoaminoacetate (cf. Radenhausen, A., 1896, i, 137) or ethyl phenylacetamidoacetate (cf. Klages and Haack, A., 1903, i, 560) did not lead to purifiable products, whilst this reagent was without action on ethyl aminoacetamidoacetate (cf. Fischer and Fourneau, A., 1901, i, 675). F. G. WILLSON.

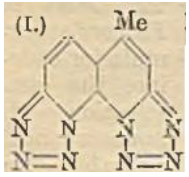
Action of phenylthiocarbimide and phenylcarbimide on isatic acid. A. REISSERT and H. SCHAAF (Ber., 1926, 59, [*B*], 2494—2502).—Isatin is converted by phenylthiocarbimide and sodium hydroxide in boiling aqueous-alcoholic solution into *4-hydroxy-2-thio-3-phenyl-1 : 2 : 3 : 4-tetrahydroquinazoline-4-carboxylic acid*, $C_6H_4 < \overset{C(OH)(CO_2H)\cdot NPh}{\underset{NH}{\quad}} \overset{|}{\underset{|}{\quad}} \underset{\quad CS}{\quad}$, m. p. 159—160° (decomp.) after becoming red at 140—145°; the *alkali*, *alkaline-earth*, *copper*, and *lead* salts are described. The *ethyl* ester, prepared by means of cold ethyl alcohol and hydrogen chloride, has m. p. 184°, the *methyl* ester, m. p. 166—167°. Treatment of the acid with ethyl sulphate in alkaline solution affords *ethyl 4-ethoxy-2-thio-3-phenyl-1 : 2 : 3 : 4-tetrahydroquinazoline-4-carboxylate*, m. p. 192—194°; *methyl 4-methoxy-2-thio-3-phenyl-1 : 2 : 3 : 4-tetrahydroquinazoline-4-carboxylate* has m. p. 179—180°. The esters do not dissolve in cold alkali hydroxide, but are transformed by the boiling reagent into the hydroxy-acid. Protracted treatment of the hydroxy-acid with boiling ethyl alcohol leads to loss of carbon dioxide and production of *4-ethoxy-2-thio-3-phenyl-1 : 2 : 3 : 4-tetrahydroquinazoline*, m. p. 194—196°; *4-methoxy-2-thio-3-phenyl-1 : 2 : 3 : 4-tetrahydroquinazoline* has m. p. 190—192°. The reaction appears to be due to initial formation of 2-thio-3-phenyl-2 : 3-dihydroquinazoline, which subsequently adds methyl or ethyl alcohol. In support of this view, it is found that the hydroxy-acid is converted when heated in neutral media of sufficiently high b. p. into *bimolecular 4-hydroxy-2-thio-3-phenyl-1 : 2 : 3 : 4-tetrahydroquinazoline*, m. p. 215°, converted by boiling glacial acetic acid into *unimolecular 4-hydroxy-2-thio-3-phenyl-1 : 2 : 3 : 4-tetrahydroquinazoline*, m. p. 172°, which with the requisite boiling alcohol gives the methoxy- and ethoxy-compounds described above. The hydroquinazoline loses water at 245° and yields *2-thio-3-phenyl-2 : 3-dihydroquinazoline*, m. p. 252—255°, which with boiling ethyl alcohol affords 4-ethoxy-2-thio-3-phenyl-1 : 2 : 3 : 4-tetrahydroquinazoline. The latter substance is converted by boiling 2*N*-hydrochloric acid into *di-4-ethoxy-3-phenyl-3 : 4-dihydro-2-quinazolyl sulphide*, m. p. above 345°.

4-Hydroxy-2-keto-3-phenyl-1 : 2 : 3 : 4-tetrahydroquinazoline-4-carboxylic acid, m. p. 174° (decomp.), is obtained from the corresponding thio-acid and mercuric oxide, or from sodium isatate and phenylcarbimide in the presence of anhydrous ether; the *hydrochloride* is described. It is converted by boiling ethyl alcohol into *4-ethoxy-2-keto-3-phenyl-1 : 2 : 3 : 4-tetrahydroquinazoline*, m. p. 185—186° (corresponding *methoxy*-compound, m. p. 199—201°). *Bimolecular 4-hydroxy-2-keto-3-phenyl-1 : 2 : 3 : 4-tetrahydroquinazoline*, m. p. 210—212°, is transformed by glacial acetic acid into the unimolecular *variety*, m. p. 182—184°, which readily becomes polymerised. *2 : 4-Diketo-3-phenyl-1 : 2 : 3 : 4-tetrahydroquinazoline*, m. p. 272°, is prepared by oxidation of 4-hydroxy-2-thio-3-phenyl-1 : 2 : 3 : 4-tetrahydroquinazoline-4-carboxylic acid or its sulphur-free analogue with hydrogen peroxide in alkaline solution. H. WREN.

[Quinoxaline.] O. HINSBERG (Ber., 1926, 59, [*B*], 2560).—A question of priority (cf. Korner Memorial notice, *ibid.*, [4], 102). H. WREN.

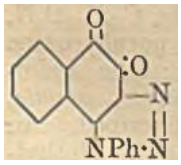
Syntheses of derivatives of 1 : 8-naphthyridine. O. SEIDE (Ber., 1926, 59, [*B*], 2465—2473).—

2 : 6-Diaminopyridine is converted by ethyl acetoacetate at 145—150° into 7-*amino*-2-*hydroxy*-4-*methyl*-1 : 8-*naphthyridine*, decomp. about 405° after darkening at 340° (*hydrochloride*). The base is converted by sodium nitrite in 33% sulphuric acid solution into 2 : 7-*dihydroxy*-4-*methyl*-1 : 8-*naphthyridine*, m. p. 337° (decomp.) (*sodium* salt), which with phosphorus pentachloride affords 2 : 7-*dichloro*-4-*methyl*-1 : 8-*naphthyridine*, m. p. 193°. Hydrazine hydrate at 150° converts the dichloro-compound into 2 : 7-dihydrazino-4-methyl-1 : 8-naphthyridine, isolated as the *dihydrochloride dihydrate* and characterised further as the *dibenzylidene* derivative, m. p. 263°. The constitution of the series of compounds is established by the transformation of the dihydrazino-derivative by nitrous acid into 1 : 2 : 7 : 8-*ditetrazole*-4-*methyl*-1 : 2 : 7 : 8-*tetrahydro*-1 : 8-*naphthyridine* (I), m. p. about 190° (decomp.), and its oxidation by permanganate to tetrazole, identified as the silver salt and in substance. 2 : 7-Dichloro-4-methyl-1 : 8-naphthyridine is converted by boiling hydriodic acid (b. p. 127°) into 2 : 7-dihydroxy-4-methyl-1 : 8-naphthyridine and by the acid (*d* 1·96) and red phosphorus at 170—180° into 4-*methyltetrahydronaphthyridine*, m. p. 103° [*picrate*, m. p. 248° (decomp.) after blackening at 235°; *chloroplatinate*, m. p. 215° (decomp.); *acetyl* derivative, m. p. 94°].

(I.) 

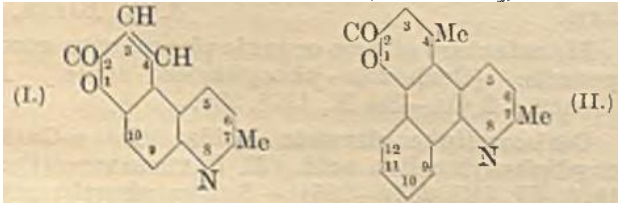
H. WREN.

1-Phenyl-αβ-naphthatriazolequinone. G. CHARRIER (Atti R. Accad. Lincei, 1926, [vi], 4, 312—315).—Like its 3-phenyl isomeride (A., 1926, 848), 1-phenyl-αβ-naphthatriazole is oxidised by chromic acid in acetic acid solution to 1-*phenyl*-αβ-*naphthatriazolequinone* (annexed formula) (yellow, decomp. about 212°), which forms a phenylhydroxyazo-derivative and a phenazine, to be described later, and gives 3-phenyl-4-*o*-carboxyphenyl-1 : 2 : 3-triazole-5-carboxylic acid when oxidised by alkaline permanganate.



T. H. POPE.

Quinolino-6 : 5-α-pyrones. : 8-*iso*Naphthoxazones. B. B. DEY, I. SARKAR, and T. R. SESHADRI (J. Indian Chem. Soc., 1926, **3**, 187—196; cf. Dey and Goswami, J.C.S., 1919, **115**, 531).—6-Aminocoumarin condenses with paracetaldehyde in presence of hydrochloric acid to yield 2-*methylquinolino*-6 : 5-α-*pyrone* [7-*methyl*-ψ-1 : 8-iso*naphthoxazone*, (I)], m. p. 220° [*hydrochloride*, *mercurichloride*, *mercuri-iodide*, *dichromate* ($3\frac{1}{2}H_2O$), *picrate*, *chloroplatinate*, *methiodide*, m. p. 245° (decomp.), *benzylidene* derivative, m. p. 205° (*hydrochloride*) described], which is

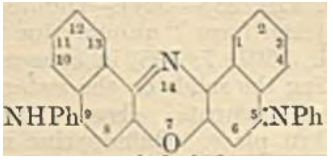


reduced by tin and hydrochloric acid to the *tetrahydro*-derivative, m. p. 179° [*hydrochloride*, *picrate*, *chloroplatinate*, *nitroso*-compound, m. p. 161°, *acetyl* derivative, m. p. 139°, methiodide, m. p. 202° (decomp.) described]. In the same way, 6-amino-4-methyl-αβ-naphthapyrone yields 2-*methyl*-7 : 8-*benzoquinolino*-6 : 5-α-4'-*methylpyrone* [4 : 7-*dimethyl*-ψ-*benzo*-1 : 8-iso*naphthoxazone* (II)], m. p. 248° (*hydrochloride*, *picrate*, *dichromate*, *chloroplatinate*, *mercurichloride*, and *mercuri-iodide* described), reduced to the *tetrahydro*-derivative, m. p. 204° [*acetyl* derivative, m. p. 202°, *chloroplatinate*, *nitroso*-derivative, m. p. 168° (decomp.), described]. 6-Aminocoumarin condensed with acetone and paraldehyde gives 2 : 4-*dimethylquinolino*-6 : 5-α-*pyrone* [5 : 7-*dimethyl*-ψ-1 : 8-iso*naphthoxazone*], m. p. 265° (*hydrochloride*, *dichromate*, *chloroplatinate*, *picrate*, *mercurichloride* described), reduced to the *tetrahydro*-derivative, m. p. 121° (*nitroso*-derivative, m. p. 177°, *benzoyl* derivative, m. p. 171°, described).

(I.) (II.)

G. M. BENNETT.

Azoxines. III. H. GOLDSTEIN and H. RADOVANOVITCH (Helv. Chim. Acta, 1926, **9**, 959—961).—Oxidation of 1-amino-4-anilino-β-naphthol yields 9-*anilino*-N-*phenyl*-αα-*dinaphthoxaz*-5-*ime* (annexed formula), m. p. 259°, a molecule of the quinonedi-imine first formed condensing with an unoxidised molecule.



The same substance is obtained by the condensation of anilino-β-naphthaquinone with 1-amino-4-anilino-8-naphthol, and it is the chief product when hydroxy- or amino-β-naphthaquinone is condensed with 1-amino-4-anilino-β-naphthol, traces only of 9-*anilino*-αα'-*dinaphthazox*-5-*one*, m. p. 328—330°, and 9-*anilino*-αα-*dinaphthoxaz*-5-*ime*, respectively, being formed.

J. W. BAKER.

Thiodiazines. IV. P. K. BOSE (J. Indian Chem. Soc., 1926, **3**, 197—210; cf. A., 1926, 1159).—Condensation of alkyl phenyldithiocarbazinates with phenacyl bromide under various conditions yields their phenacyl derivatives in *cis* and *trans* isomeric forms, which are distinguished by the fact that the *cis*-compound is the more readily converted into the corresponding thiodiazine derivative (cf. Busch, A., 1901, i, 430; 1911, i, 811). The *trans*-compound results when the condensation is carried out by the addition of alkali or calcium carbonate to the mixture of the reagents in alcoholic solution, whilst the *cis*-isomeride is formed when the dithiocarbazinate is previously dissolved in the alkali or the reaction conducted in cold pyridine solution. The following pairs of isomerides were obtained in this way from the requisite esters and phenacyl bromides: *methyl* trans-*phenacylphenyldithiocarbazinate*, , m. p. 100° (*phenylhydrazone*, m. p. 127°), and the cis-*isomeride*, , m. p. 93°, both of which were converted by heating at 100° in alcoholic solution into 2-*methylthiol*-4 : 5-*diphenyl*-1 : 3 : 4-*thiodiazine*, m. p. 180°; *ethyl* trans-*phenacylphenyldithiocarbazinate*, m. p. 82° (*phenylhydrazone*, m. p. 136°), and the cis-*isomeride*, m. p. 86°, converted into 2-*ethylthiol*-4 : 5-*diphenyl*-1 : 3 : 4-

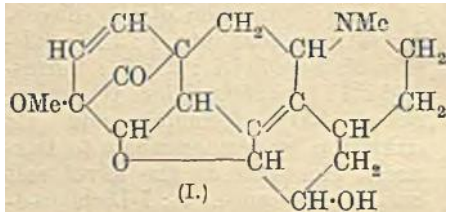
thiodiazine, m. p. 150°, this and the other thiodiazine derivatives being also obtained in the original condensation if the pyridine solution is boiled; n-*propyl* trans-*phenacylphenyldithiocarbazinate*, m. p. 56° (from the n-*propyl phenyldithiocarbazinate*, m. p. 125°), and its cis-*isomeride*, m. p. 61°, converted into 2-n-*propylthiol*-4 : 5-*diphenyl*-1 : 3 : 4-*thiodiazine*, m. p. 151°; *methyl* trans-p-*methylphenacylphenyldithiocarbazinate*, m. p. 110° (*phenylhydrazone*, m. p. 124·5°), and its cis-*isomeride*, m. p. 54°, of which the *trans*-compound was converted by heating at 100° in alcoholic solution into 2-*methylthiol*-4-*phenyl*-5-p-*tolyl*-1 : 3 : 4-*thiodiazine*, m. p. 187°, whilst the *cis*-compound was converted only into its isomeride; *ethyl* trans-p-*methylphenacylphenyldithiocarbazinate*, m. p. 95°, and its cis-*isomeride*, m. p. 77°, converted at 120—130° in alcoholic solution into 2-*ethylthiol*-4-*phenyl*-5-p-*tolyl*-1 : 3 : 4-*thiodiazine*, m. p. 148°. *Benzyl phenacylphenyldithiocarbazinate*, m. p. 75°, was obtained in only one form. G. M. Bennett.

Additive compounds. C. G. Santesson (Arch. exp. Path. Pharm., 1926, **118**, 313—324).—Quinine hydrochloride and antipyrine form "quinopyrine" (cf. Skand. Arch. Physiol., 1897, **7**, 385) in concentrated solution or on heating the solids on the water-bath. Conductivity measurements show that chemical reaction has taken place. Quinopyrine is much more soluble in water than quinine hydrochloride, gives the antipyrine reaction with ferric chloride, but gives the thalleioquin reaction only on considerable dilution, by which it is decomposed.

Pyramidone and veronal (2 : 1) form "veramone," which is not homogeneous, but react in molecular equivalents to yield a definite substance (Pfeiffer, A., 1925, i, 1318; 1926, 739), which the author considers to be a co-ordinated compound.

Cocaine hydrochloride and phenylurethane form a similar compound ("albromine"). J. M. Gulland.

Constitution of porphyroxine. J. N. Rakshit (Ber., 1926, **59**, [*B*], 2473—2486; cf. J.C.S., 1919, **115**, 456).—Porphyroxine is converted by distillation with zinc dust mainly into phenanthrene with small amounts of ammonia and trimethylamine and traces of other bases. It contains one methoxyl group. As a tertiary base, it is readily converted into the corresponding *methosulphate*, m. p. 205° (decomp.) after softening at about 180°, $[\alpha]^{25}$ —74·6° in methyl alcohol, and *methiodide*, m. p. 150—152°, $[\alpha]^{25}$ —82·5° in methyl alcohol, from which the *methochloride*, m. p. 171° (slight decomp.) after softening at 145°, $[\alpha]^{34}$ —90·4° in water, and *methohydroxide*, m. p. 112—115° (decomp.), $[\alpha]^{34}$ —71·8° in alcohol, are derived. Treatment of porphyroxine with acetic anhydride or acetyl chloride affords the *monoacetate*, $C_{21}H_{25}O_5N$, m. p. 125° after softening at 110°, $[\alpha]^{31}$ —187·2° in alcohol; since the alkaloid is insoluble in alkali hydroxide, the presence of a secondary alcoholic group is established. Porphyroxine acetate yields a *sulphate*, decomp. about 190° after softening at 170°, $[\alpha]^{30}$ —150·2° in water, *hydrochloride*, m. p. 126°, $[\alpha]^{30}$ —123·4° in water, *chloroplatinate*, m. p. 230° (decomp.) after darkening at 225°, *hydrobromide*, m. p. 155° (decomp.) after softening at 150°, $[\alpha]^{35}$ —98·8° in water, and *hydriodide*, m. p. 105—107° (decomp.). The presence of the ketonic group in porphyroxine is established by the isolation of the corresponding *oxime*, $C_{19}H_{24}O_4N_2$, m. p. about 198° (decomp.), *semicarbazone*, incipient decomp. 244°, and *phenylhydrazone*, m. p. 150° (slight decomp.). Insight into the constitution of porphyroxine is mainly afforded by the observation that it is converted by hydrogen peroxide in boiling weakly alkaline solution into codeine and formic acid. Porphyroxine differs from codeine in containing two additional atoms of hydrogen and a carbonyl group, and since these are readily and simultaneously removed (as water and formic acid) in a single reaction, it is very probable that they are attached to the same ring



(I.)

Pschorr's formula for codeine, the constitution (I) appears most probable for porphyroxine. Attempts to hydrogenate the base were unsuccessful.

Methylporphyroxine, m. p. 125—126°, $[\alpha]^{28}$ —131·8° in chloroform, is prepared by the action of sodium methoxide on porphyroxine methiodide, or, preferably, from porphyroxine methosulphate and methyl-alcoholic potassium hydroxide. The *hydrochloride*, *hydrobromide*, *sulphate*, *oxalate*, *hydriodide*, *acetate*, *phosphate*, and *chloroplatinate* have been prepared. The substance does not yield an acetate. It gives an *oxime*, m. p. 185—186°, *semicarbazone*, m. p. 217° (decomp.), and *phenylhydrazone*, m. p. 189° (slight decomp.). *Methyltetrahydroporphyroxine*, $C_{20}H_{29}O_4N$, m. p. 150°, is prepared by reducing porphyroxine methosulphate with sodium amalgam; the *hydrochloride*, *hydrobromide*, *hydriodide*, *nitrate*, *acetate*, *chloroplatinate*, and *chloroaurate* are described. An acetyl derivative could not be prepared. Methyltetrahydroporphyroxine yields an *oxime*, m. p. 234—235°, *semicarbazone*, incipient decomp. 210°, and *phenylhydrazone*, m. p. 126°. H. Wren.

Two new alkaloids from Yohimba bark. P. Karrer and H. Salomon (Helv. Chim. Acta, 1926, **9**, 1059—1062).—Two new alkaloids have been isolated from Yohimba bark. *ψ-Yohombine*, $C_{21}H_{26}O_3N_2$, differing only from yohombine in its crystalline form and its m. p., 264—265°, $[\alpha]_D^{15}$ +26·6° (*hydrochloride*, m. p. 258°), is obtained in only 0·01—0·015% yield. The second alkaloid, *corynanthine*, $C_{20}H_{22}O_2N_2(OMe)_2$, is isolated as its *hydrochloride*, m. p. 205°, $[\alpha]_D$ +12·15°, which, in distinction from the hydrochloride of ψ-yohimbine, is soluble in chloroform. J. W. Baker.

Manufacture of new organic phosphorus compounds. [Carbazole-phosphinous acids.] L. Cassella & Co.—See B., 1926, 996.

Carboxydiphenylarsinic acids. I. *o*-Carboxydiphenylarsinic acid. E. Sakellarios (Ber., 1926, **59**, [*B*], 2552—2554).—Sodium phenylarsinite couples with diazotised anthranilic acid in alkaline solution, yielding *o*-carboxydiphenylarsinic acid, m. p.

166° (decomp.) when rapidly heated (Aeschlimann and McCleland record m. p. above 300°; cf. A., 1924, i, 1358), benzoic acid and azobenzene-*oo'*-dicarboxylic acid, m. p. 237° (decomp.). *o*-Carboxydiphenylarsenious oxide, prepared from the acid and sodium hydrogen sulphite, has m. p. 133°. Attempts to convert these substances into compounds containing arsenic in a heterocyclic ring were unsuccessful.

H. WREN.

Compound of pyrocatechol and arsinoacetic acid. B. ENGLAND (Ber., 1926, 59, [*B*], 2669—2671).—The *compound*, $CO_2H{\cdot}CH_2{\cdot}As(C_6H_4O_2)_2$,AcOH, m. p. 146°, crystallises from solutions of arsinoacetic acid and pyrocatechol in glacial acetic acid; an analogous *compound*, m. p. 137°, is formed when the components are heated together. The *methyl* ester, $CO_2Me{\cdot}CH_2{\cdot}As(C_6H_4O_2)_2$, m. p. 117°, is described.

H. WREN.

Azo-dyes containing antimony. F. DUNNING and E. E. REID (J. Amer. Chem. Soc., 1926, 48, 2959—2963).—*p*-Aminophenylstibinic acid is obtainable (yield 35—60%) by diazotising *p*-aminoacetanilide, dissolved with the calculated amount of antimony trioxide in just sufficient 15% hydrochloric acid, filtering off the precipitated double salt (cf. May, J.C.S., 1912, **101**, 1037), suspending this in water, and adding gradually aqueous 10% sodium hydroxide at 3—5°, neutralising, precipitating impurities with carbon dioxide, and finally adding dilute acetic acid (cf. Schmidt, A., 1920, i, 900), the acetyl group then being removed by Schmidt's method (*ibid.*, 1922, i, 1203). The following dyes, mostly of brown shades, were prepared from the above stibinic acid: 4-*hydroxyazobenzene*-4'-*stibinic acid* (impure); 4-*hydroxy*-2-*chloro*-, 4-*hydroxy*-3-*nitro*-, 4-*hydroxy*-3-*amino*-, 4-*hydroxy*-3-*methyl*-, and 4-*hydroxy*-3-*carboxy-azobenzene*-4'-*stibinic acid*. Diazotised *p*-aminophenylstibinic acid and pyrocatechol gave a *product* other than the expected dye. *Disodium* salts of the above are described. They are stable in aqueous solution.

F. G. WILLSON.

Halogenated proteins. VI. Chlorocasein. A. J. J. VANDEVELDE (Rec. trav. chim., 1926, 45, 825—829).—The action of a saturated solution of chlorine in carbon tetrachloride on casein yields a *chlorocasein* (N, 10·5; Cl, 32%) soluble in potassium hydroxide solution, the amounts of chlorine in this compound and of bromine in the corresponding bromocasein (A., 1925, i, 1477) not being proportional to the mass of the two atoms. The action of water at 18° and 61°, potassium hydroxide and acetic acid, alcohol and ether on this chlorocasein has been investigated in detail, in each case a product containing a smaller percentage of chlorine being obtained. In all the compounds examined, correct results for the determination of chlorine could be obtained only by the method of ter Meulen and Heslinga (*ibid.*, 1924, ii, 55).

J. W. BAKER.

Chemical nature of hæmochromogen and its carbon monoxide compound. R. HILL (Proc. Roy. Soc., 1926, B, **100**, 419—430; cf. A., 1925, i, 994).—The spectra of nickel and copper hæmatoporphyrins are not appreciably altered by the addition of denatured globin or excess of pyridine or ammonia —a behaviour similar to that of free hæmatoporphyrin. Artificial iron hæmatoporphyrin, however, gives hæmochromogen, behaving exactly as hæmin prepared from blood, and on reduction does not show the hæmochromogen spectrum of other metallic hæmatoporphyrins except in presence of a nitrogeneous substance. Hence the hæmochromogen is the ferrous compound of the porphyrin. The iron atom alone confers on the reduced pigment the property of forming additive compounds.

Quantitative experiments on the combination of pyridine with reduced hæmatin show that in carbon monoxide–hæmochromogen one nitrogenous mol. is replaced by carbon monoxide. On addition of pyridine to carbon monoxide–reduced hæmatin, 1 mol. of the former is taken up, whilst an excess displaces carbon monoxide, and hæmochromogen results. These changes have been observed spectroscopically and occur with any nitrogenous compound, including denatured globin. The author proposes general formulæ in which the nitrogen and the carbon monoxide are co-ordinated with the iron, which has a co-ordination number of 6, and represents a carbon monoxide–hæmochromogen as $Hph{:}Fe{<}^{CO}_{N:}$, a hæmochromogen as $Hph{:}Fe{<}^{N:}_{N:}$, and the carbon monoxide compound of reduced hæmatin as $Hph{:}Fe{<}^{CO}_{X}$, where Hph is a porphyrin and X another molecule of the complex or a molecule of water.

J. M. GULLAND.

Constitution of sponges. I. The common bath sponge, *Hippospongia equina*. V. J. CLANCEY (Biochem. J., 1926, **20**, 1186—1189).—Spongin yields on hydrolysis mainly glutamic acid and glycine, with smaller quantities of leucine, aspartic acid, arginine, proline, lysine, tryptophan, and iodogorgonic acid.

S. S. ZILVA.

Denaturation of egg-albumin by weak acids in the presence of salts. H. MASTIN and S. B. SCHRYVER (Biochem. J., 1926, **20**, 1177—1185).—A well-defined acidic denaturated product of albumin can be obtained by the action of acid on or by electrolysis of egg-white in the presence of ammonium sulphate and other salts. The formation of this compound is characterised by an increase in the number of free acid groups without a corresponding increase in the amino-groups and by the appearance of free thiol groups.

These changes are probably due to hydrolysis of the protein at a thiodepside (C·CO·S·C·) grouping in the molecule.

S. S. ZILVA.

Preparation and physico-chemical properties of sericin. K. KODAMA (Biochem. J., 1926, **20**, 1208—1222).—Some physico-chemical properties of sericin and sericin-peptone dissolved in hydrochloric acid and sodium hydroxide solutions are given. The isoelectric points of sericin and sericin-peptone exist near p_H 3·9 and 4·4, respectively. The sericin in this investigation was prepared by a modification of Bondi's method (A., 1902, i, 579). The extraction of sericin in the autoclave deprives the protein of its precipitability by dilute acids. The glyoxylic acid

reaction for tryptophan also disappears after this treatment. S. S. Zilva.

Micro-determination of the Hausmann numbers of proteins. K. V. Thimann (Biochem. J., 1926, 20, 1190—1195).—The method requires only 3—6 mg. of total nitrogen in each determination. The various sources of error of the macro-method are avoided. S. S. Zilva.

[Rapid, dry method for the determination of carbon and hydrogen.] E. Berl and H. Burkhardt (Ber., 1926, 59, [*B*], 2682; cf. A., 1926, 749).—A method is described whereby the total content of the combustion tube can be heated to dull redness in a simple manner. H. Wren.

Sources of error in organic elementary analysis. I. Lead peroxide. J. Lindner (Ber., 1926, 59, [*B*], 2561—2573).—The adsorption of carbon dioxide by lead peroxide is appreciable at temperatures at which elementary analyses are performed. The carbon dioxide is removed more rapidly by a moist than by a dry current of air. The effect on the analytical values for carbon falls generally within the limits of normal variation, but in certain circumstances may contribute to the production of error. Large charges of finely-divided lead peroxide and low temperatures (about 150°) should be avoided as far as possible. Protracted heating at 200° does not cause any disturbance. Reception of carbon dioxide by peroxide which has been heated at a higher temperature appears to depend on the formation of carbonate; the carbon dioxide is completely evolved from the peroxide at normal, lower temperatures, whereas this is not the case with lead oxide containing lead carbonate. The action of nitric oxide causes absorption of carbon dioxide and the peroxide suffers protracted damage. The carbon dioxide is as loosely retained by such charges as by superheated peroxide. H. Wren.

Determination of phosphorus or arsenic in organic substances. R. Poggi and A. Polverini (Atti R. Accad. Lincei, 1926, [vi], 4, 315—318).—A solution of the material (0·35 g. of cacodylic acid or 0·2 g. of triphenylphosphine) in sulphuric acid (10 c.c.) is mixed with 5 g. of powdered potassium persulphate, and heated gently during about an hour, with further additions of persulphate (about 6 g. in all) until the liquid is colourless. The arsenic is then determined as magnesium ammonium arsenate or the phosphorus as ammonium phosphomolybdate. T. H. Pope.

Detection of methyl alcohol by use of potassium guaiacolsulphonate. R. Bauer (Pharm. Ztg., 1926, 71, 1543).—In applying the test, the oxidation with permanganate and dilute sulphuric acid must be very cautiously effected, as traces of formaldehyde are readily destroyed. S. I. Levy.

Detection of methyl alcohol; replacement of guaiacol by potassium guaiacolsulphonate to avoid errors. H. Matthes (Pharm. Ztg., 1926, 71, 1508—1509).—Since acetaldehyde reacts readily with guaiacol in presence of sulphuric acid with development of a red coloration, it is preferable to use potassium guaiacolsulphonate, which does not so react, but gives the formaldehyde reaction equally readily. If much methyl alcohol is present, the colour obtained is a strong violet-red. S. I. Levy.

Identification of amines. III. Toluene-ω-sulphonamides. C. S. Marvel and H. B. Gillespie (J. Amer. Chem. Soc., 1926, 48, 2943—2944).—Toluene-ω-sulphonyl chloride (1 mol.) and an amine (2 mols.) react in benzene solution to give a precipitate of the amine hydrochloride, and the corresponding toluene-ω-sulphonamide, which is recovered by evaporation, and is readily purified by recrystallisation from dilute alcohol. The following substituted sulphonamides are described: *allyl-*, m. p. 79°; *diethyl-*, oil; *piperidyl-*, m. p. 131·5°; n-*heptyl-*, m. p. 76°; *di*-n-*butyl-*, oil; o-*tolyl-*, m. p. 83°; m-*tolyl-*, m. p. 75°; o-*chlorophenyl-*, m. p. 91°; p-*chlorophenyl-*, m. p. 110°; m-*bromophenyl-*, m. p. 99·5°; p-*bromophenyl-*, m. p. 133·5°; *phenylmethyl-*, m. p. 101°; *phenylethyl-*, m. p. 118·5°; *phenyl*-n-*propyl-*, m. p. 135°; *phenyl*-n-*butyl-*, m. p. 108°; o-*anisyl-*, m. p. 72°; p-*anisyl-*, m. p. 103°; and *toluene-ω-sulphon*-p-*phenetidide*, m. p. 117·5°. Toluene-ω-sulphon-*o*-phenetidide has m. p. 74°, and not 85° as given by Fromm and Palma (A., 1906, i, 819). *Ditoluene-ω-sulphonanilide* has m. p. 71·5°, and *ditoluene-ω-sulphon*-p-*toluidide*, m. p. 74·5°. F. G. Willson.

Crystallographic constants. G. Gilta (Bull. Soc. chim. Belg., 1926, 35, 365—371).—Crystallographic methods are of value in determining the degree of purity of organic compounds and in detecting the formation of hydrates. For example, acetylsalicylic acid is monoclinic, $a:b:c$—1·7075 : 1 : 0·8528 $\beta=95°\,24'$. When the pure substance is recrystallised, leaflets flattened parallel to {100} are obtained, but in presence of acetic or salicylic acid needles elongated along the *c*-axis separate (cf. A., 1919, i, 124; 1920, i, 841). Sodium *m*-xylene-4-sulphonate crystallises from water ($+1H_2O$) at the ordinary temperature in monoclinic plates, $a:b:c$—1·7739 : 1 : 0·8558, $\beta=99°\,30'$, but below about 8° orthorhombic leaflets ($+4$ or $5H_2O$) are produced. H. E. F. Notton.

Biochemistry.

Aerobic and anaerobic metabolism of the common cockroach (*Periplaneta orientalis*). I. J. G. Davis and W. K. Slater (Biochem. J., 1926, 20, 1167—1172).—The cockroach while living in nitrogen goes into debt for oxygen, and when it is returned to air it consumes oxygen in excess of the normal uptake until the debt has been discharged. The rate of metabolism of the insect is influenced by its weight. The respiratory quotient, as in the case of higher animals, is depressed by starvation. S. S. Zilva.

Regulation of respiration. III. Continuous method of recording changes in acidity applied

to the circulating blood and other body fluids. IV. Tissue acidity, blood acidity, and pulmonary ventilation. Effects of semipermeability of membranes and the buffering action of tissues. R. GESELL and A. B. HERTZMAN (Amer. J. Physiol., 1926, **78**, 206—223, 610—629).—III. A manganese dioxide electrode is placed directly in the blood-stream of a dog, the *E.M.F.* balanced at a potentiometer, and a continuous record made graphically. Whereas electrodes did not give reproducible results in different fluids, they were found to give faithful records of the acid–base changes in any one fluid. Results were controlled by periodical determinations of blood samples by the hydrogen and quinhydrone electrodes. The effects of anoxæmia, asphyxia, and hæmorrhage and of the administration of carbon dioxide, carbonate, lactic acid, and ammonium chloride were studied. When large doses of sodium cyanide were given, the manganese dioxide electrode was at fault. Precautions against the appearance of reducing substances in the blood are emphasised.

IV. Synchronous records were taken of the changes in acidity of the arterial and venous bloods, the tissues, and the cerebrospinal fluid of dogs by means of manganese dioxide electrodes placed in the blood, fluid, and muscles. The increased acidity following administration of carbon dioxide and the increased alkalinity following sodium carbonate were found to be greater and to be more rapidly attained in the arterial than in the venous blood. In both cases, the tissues acted as buffers. Injection of sodium hydrogen carbonate increased the alkalinity of the blood, whilst the cerebrospinal fluid and the muscles became more acid. The buffering due to the tissues appeared to be minimal. These results suggest an impermeability of cell membranes for base and confirm the conclusion that it is the hydrogen-ion concentration of the respiratory centre itself which controls respiration. R. K. CANNAN.

Preparation and properties of the globin of oxyhæmoglobin. R. HILL and H. F. HOLDEN (Biochem. J., 1926, **20**, 1326—1339).—Oxyhæmoglobin is decomposed with a minimum amount of hydrochloric acid at a low temperature, and after the addition of ether and kieselguhr is filtered. The globin is precipitated from the filtrate with ammonia. It is soluble in presence or absence of salts over the range p_H 5—10. On treatment with hæmin dissolved in alkali carbonate, it yields methæmoglobin, from which typical hæmoglobin and oxyhæmoglobin are obtained. The equilibrium of the reaction between globin and hæmatin with which it reacts over the range p_H 5—10 has been investigated. Globin yields compounds with certain porphyrins and their metallic derivatives. Oxyhæmoglobins have been prepared from the iron compounds of hæmatoporphyrin and mesoporphyrin.

Protoporphyrin was prepared by inoculating fresh defibrinated sheep's blood with *Bacillus coli*, precipitating the reduced blood with concentrated hydrochloric acid, and extracting the hydrochloride of the porphyrin with 97% alcohol. S. S. ZILVA.

Use of light filters in colorimetry. Determination of hæmoglobin. R. P. KENNEDY (Amer. J. Physiol., 1926, **78**, 56—63).—In the eye-piece of the colorimeter is fitted a colour filter transmitting light of a wave-length which is prominent in the absorption spectrum of the substance to be determined. A standard neutral grey Wratten filter replaces the usual colour standard, and the depth of the solution is then adjusted so that the transmission matches that through the standard filter. The method is illustrated by determinations of hæmoglobin as carboxyhæmoglobin, the results being controlled by the oxygen capacity of the hæmoglobin and by a spectrophotometric method. Certain theoretical principles of colorimetry are discussed. R. K. CANNAN.

Ammonia in blood. P. B. REHBERG (Physiol. Papers dedicated to August Krogh, 1926, 248—267).—For the determination of ammonia in blood, vacuum aeration is followed by micro-titration; the content, which increases 2—3 hrs. after a meal, varies from 0·03 to 0·22 mg. per 100 c.c. CHEMICAL ABSTRACTS.

Photo-oxidation by means of fluorescent pigments. H. GAFFRON (Biochem. Z., 1926, **179**, 157—185).—Blood-serum, in presence of small amounts of various porphyrins, of chlorophyll, and of certain dyes, absorbs large amounts of oxygen, with simultaneous evolution of carbon dioxide and formation of ammonia; the $CO_2 : O_2$ ratio is 1 : 4 and the $NH_3 : O_2$ ratio 1 : 7; the greater part of the carbon dioxide is liberated from the hydrogen carbonate of the serum by acids set free during the oxidation. Results of a similar type were obtained with solutions of caseinogen.

Hæmin and the heavy metal derivatives of hæmatoporphyrin have no activating effect, but the zinc derivative is as active as hæmatoporphyrin itself. That the photo-oxidation is concerned exclusively with the colloidal constituents of serum is shown by the absence of the phenomenon from the ultrafiltrate of the latter. The rate of photo-oxidation is accelerated considerably by the presence of bile salts and by increase in the partial pressure of oxygen, and to a slight extent by rise in temperature. Photo-oxidation of tyrosine and of phenol takes place readily in presence of 1 equivalent of sodium hydroxide; in the former case, the uptake of oxygen is more than 4·5 mols., and the $CO_2 : O_2$ ratio is 1 : 3. In the photo-oxidation of uric acid, 1 mol. of oxygen is absorbed, an equivalent amount of carbon dioxide being evolved. C. R. HARINGTON.

Plasma calcium-ion concentration. E. J. WARBURG (Biochem. Z., 1926, **178**, 208—223).—The formulæ for the calculation of the calcium-ion concentration of the plasma are brought into accord with Bjerrum's ionic activity theory (cf. Marrack and Thacker, A., 1926, 855). In the expression $Ca^{\cdot\cdot} = A[H^{\cdot}]/[HCO_3']$ for plasma, K^{18} is 515 and K^{38} 275. It is uncertain whether or not plasma is normally saturated with calcium ions, but it is improbable that it is supersaturated. J. PRYDE.

Calcium–phosphate compounds of the serum. H. DOLHAINE (Biochem. Z., 1926, **178**, 233—242).—From experiments on the isolated frog heart it is concluded that the removal from solution of ionic calcium by phosphate in the presence of fresh serum

is not immediate, but commences some 2—24 hrs. later. This behaviour is in strong contrast to that shown in circulating blood. J. PRYDE.

Determination of phosphorus in blood. J. H. GADDUM (Biochem. J., 1926, **20**, 1204—1207).—The "inorganic phosphate" in 0·5 c.c. of blood is determined by dissolving the precipitate of phosphomolybdate in 0·1*N*-sodium hydroxide and titrating the excess of the alkali with 0·1*N*-hydrochloric acid by means of a micrometer syringe (cf. Trevan, A., 1926, 211). The maximum deviation in four determinations in normal horse-serum was 0·0004 mg. S. S. ZILVA.

Degradation of dextrose by the blood corpuscle of the rabbit. II. J. T. IRVING (Biochem. J., 1926, **20**, 1320—1325).—The addition of dextrose to a suspension of blood-corpuscles does not lead to the formation of an organic phosphorus compound, nor does the initial concentration of free phosphorus have any appreciable influence on the rate of glycolysis. Potassium hexosediphosphate is only very slowly attacked by the action of the corpuscles. The optimum p_H for glycolysis by blood-corpuscles lies between 8 and 9. Very small quantities of acid inhibit the reaction very markedly. Fluorides and oxalates have also an inhibiting effect. Dextrose, lævulose, and mannose are degraded equally fast by the corpuscles of the adult rabbit, but galactose is much more slowly attacked. In the infant rabbit, on the other hand, galactose is degraded as fast as dextrose. S. S. ZILVA.

Distribution of reducing sugar and mode of glycolysis in human blood. J. H. DOWDS (Biochem. J., 1926, **20**, 1173—1176).—In human blood, the red corpuscles contain a considerable amount of reducing sugar. In capillary blood, there is generally more sugar in the plasma than in the corpuscles; the reverse is the case in venous blood. In separated plasma, glycolysis is very slight compared with that in the whole blood. In the latter case, the decrease in the sugar is mainly in the plasma. Glycolysis is therefore almost entirely due to the activity of the leucocytes. S. S. ZILVA.

Blood-coagulation. XV. Relation of glycolysis to coagulation of blood. B. STUBER and K. LANG (Biochem. Z., 1926, **179**, 70—85).—The disappearance of sugar from shed blood and the simultaneous increase of lactic acid are inhibited by those substances which prevent the coagulation of blood; no change in the glycogen content was observed to be associated with coagulation, but the presence of anti-coagulants inhibited the uptake of oxygen by plasma. The respiratory quotients observed with normal plasma indicated formic acid as the probable oxidation product of the lactic acid derived from the dextrose, and this was confirmed by observation of an increase of the formic acid of the blood during coagulation. It is concluded that the anti-coagulants act by interfering with the oxidative phase of the degradation of dextrose; coagulation is regarded as being brought about by a change in physical conditions due to the formation of acids from the dextrose, rather than by a specific coagulation enzyme. C. R. HARINGTON.

Preparation and properties of prothrombin. E. B. CEKADA (Amer. J. Physiol., 1926, **78**, 512—532).—Howell's acetone method is preferred. Prothrombin may be activated by ethyl alcohol, chloroform, and carbon tetrachloride, by calcium ions, spontaneously, on keeping for 36 hrs. at the ordinary temperature. A precipitate is formed, and both this and the residual solution are active. These soluble and insoluble forms of thrombin differ in that the insoluble form leads only to a temporary clotting of fibrin, followed by solution of the clot. Insoluble thrombin contains phosphorus, soluble thrombin does not. Precipitation of prothrombin by ammonium sulphate begins at a salt concentration of 35% and is complete at 50%. It is suggested that prothrombin is an aggregate of two thrombin groups. Activation consists in the precipitation of one in a modified form and the liberation of the other in the solution. R. K. CANNAN.

Regulation of the blood-sugar. H. C. HAGEDORN (Physiol. Papers dedicated to August Krogh, 1926, 80—100).—A comparison, before and after ingestion of carbohydrate, of blood from the ear and from the median cubital vein shows that the ingestion of carbohydrate causes a much higher hyperglycæmia in the arterial blood than in that of the median cubital vein. Dextrose is stored in the peripheral tissues during alimentary hyperglycæmia. During the hyperglycæmia following the administration of adrenaline, no difference between arterial blood and that from the median cubital vein was observed. Experiments were also performed in which the administration of adrenaline was followed by that of dextrose, and *vice versa*. CHEMICAL ABSTRACTS.

Hepatic amylase and its probable role in the regulation of blood-sugar. H. A. DAVENPORT (J. Biol. Chem., 1926, **70**, 625—638).—Neither the course of hydrolysis of starch by hepatic amylase nor the optimum p_H for the reaction was affected by addition of adrenaline or of insulin. The amylase was activated to about the same extent by addition of 0·1*N*-sodium chloride as by addition of the mixture of chlorides employed by Cammidge and Howard (J. Metabol. Res., 1924, **5**, 95). This type of experiment did not therefore throw any light on the possible part played by hepatic amylase in controlling the concentration of sugar in the blood. C. R. HARINGTON.

Inverse change between the concentration of dextrose and chloride in the blood. T. G. NI (Amer. J. Physiol., 1926, **78**, 158—167).—Histamine, sham feeding, and partial obstruction of the intestine cause a fall in blood chlorides often accompanied by a rise in blood-sugar. The inverse effects are probably related only through a reflex stimulation of the adrenals. Hyperglycæmia following depancreatisation is accompanied by a fall in blood chlorides. Insulin reduces the blood-sugar and raises the chlorides. There is evidence that there is here a direct attempt at osmotic or other compensation. R. K. CANNAN.

Micro-determination of blood-sugar. K. SALOMON (Biochem. Z., 1926, **178**, 228—232).—Contrary

to Dresel and Rothmann (A., 1925, i, 714), blood samples dried on the paper and kept for some days show a decrease in reducing power. Blood-sugar determinations carried out on such samples are therefore not trustworthy. Blood samples may be kept in zinc hydroxide solution for periods of 3 days or more without diminution in their reducing power.
J. PRYDE.

Colorimetric determination of sugar. L. FABIAN (Biochem. Z., 1926, **179**, 59—61).—A reagent prepared by mixing a solution of potassium carbonate, hydrogen carbonate, and thiocyanate with one of copper sulphate is heated with the sugar-containing solution; the reduction in intensity of colour as compared with that of the original reagent gives the amount of sugar. Within physiological limits of blood-sugar concentration, the error of the method is $\pm 5\%$. C. R. HARINGTON.

Determination of sugar. M. SOMOGYI (J. Biol. Chem., 1926, **70**, 599—612).—The apparent concentration of dextrose as determined by the method of Shaffer and Hartmann (A., 1921, ii, 417) varies with the p_H of the solution during the process of reduction; a modification of the original alkaline copper solution, described by these authors, is therefore recommended, by the use of which a more constant degree of alkalinity is obtained; with the improvement in the reagent, the method becomes applicable to the determination of sugar in 0·2 c.c. of blood. C. R. HARINGTON.

Determination of p_H of blood with the aid of the Duboscq colorimeter. J. F. MCCLENDON, S. RUSSELL, and E. TRACY (J. Biol. Chem., 1926, **70**, 705—711).—By the use of an indicator such as "orthochrome-T" or *p*-nitrophenol, which shows only change in intensity of colour, and not a mixture of colours, with change in the reaction, it is possible to determine the p_H of blood plasma directly in a colorimeter of the Duboscq type.
C. R. HARINGTON.

Detection of enzymic processes conditioned by immunisation. V. E. KUPELWIESER. **VI.** E. KUPELWIESER and E. NAVRATIL. **VII. Modification of Van Slyke's apparatus for the determination of primary aliphatic amino-nitrogen.** E. KUPELWIESER and K. SINGER. **VIII.** K. SINGER (Biochem. Z., 1926, **178**, 298—318, 319—323, 324—331, 332—341).—V and VI. Further attempts (cf. A., 1926, 86) with sera, obtained during the anti-anaphylactic condition, from guinea-pigs which had received preliminary treatment with horse-serum, to detect proteolytic action on the antigen were again negative.

VII. A modification of Van Slyke's apparatus for the determination of primary aliphatic nitrogen is described which allows of both micro- and macro-determination in the same apparatus with the same accuracy.

VIII. The modified Van Slyke apparatus (VII) is used to detect proteolytic action in the above sera (V and VI). Of 12 experiments, 11 were nil, 1 was positive in the case of anti-anaphylactic serum, and of 8 experiments with anaphylactic serum, 6 were nil, 1 was positive, and 1 negative. The evidence is therefore still against the presence of such proteolytic action. P. W. CLUTTERBUCK.

Application of Löwe-Zeiss interferometer to investigation of blood. J. W. AMSCHLER (Biochem. Z., 1926, **179**, 199—209).—A detailed description of technique. C. R. HARINGTON.

Collagen. II. R. O. HERZOG and W. JANCKE (Ber., 1926, **59**, [*B*], 2487—2489; cf. A., 1925, i, 1488).—Röntgen spectrographic investigation of stretched fibres confirms the identity of the collagen from various sources (*loc. cit.*). H. WREN.

Chemistry of corpus luteum. VI. Lipins of ether extract. VII. Kephalin fraction. M. C. HART and F. W. HEYL (J. Biol. Chem., 1926, **70**, 663—674, 675—682; cf. A., 1926, 424).—VI. An ethereal extract of corpus luteum was precipitated with acetone; the kephalin fraction so obtained varied in composition with different samples and was contaminated with small amounts of a substance of the nature of protagon. From the mother-liquor were prepared samples of lecithin free from kephalin which, on hydrolysis, yielded palmitic, arachidonic, and oleic acids; a small amount of a hexabromo-arachidic acid was also obtained, but stearic, linoleic, and linolenic acids could not be detected.

VII. The kephalin fraction (see above) was of similar composition to the corresponding fractions obtained by previous workers from the lipins of heart, liver, and brain. C. R. HARINGTON.

Basic proteins. I. Nitrogen distribution and percentages of amino-acids in the protamine of the sardine, *Sardinia cœrulea*. M. S. DUNN (J. Biol. Chem., 1926, **70**, 697—703).—By extraction of the ripe testes of the sardine with 1% sulphuric acid and subsequent precipitation of the extract with alcohol, there was obtained 0·5% of a protamine sulphate, having 18·35% of total nitrogen; figures are given for the distribution of nitrogen determined by the method of Van Slyke. The substance contained arginine, 15·8%; cystine, 0·95%; histidine, 15·7%; lysine, 5·22%; tyrosine, 1·09%; tryptophan, 0·87%. The fact that the free amino-nitrogen of the protamine is greater than half the lysine-nitrogen suggests the presence of free amino-groups other than those accounted for by this amino-acid. C. R. HARINGTON.

Muscle hæmoglobin as a source of bile pigment. G. H. WHIPPLE and F. S. ROBSCHEIT-ROBBINS (Amer. J. Physiol., 1926, **78**, 675—682).—Injection of muscle hæmoglobin into the blood, peritoneum, or muscles of dogs was followed by excretion of bile pigment in the urine.
R. K. CANNAN.

Colorimetric determination of phosphoric acid in muscle extracts. K. LOHMANN and L. JENDRASSIK (Biochem. Z., 1926, **178**, 419—426).—The colorimetric method of Fiske and Subbarow (A., 1926, 443) for the determination of phosphorus, with slight modification, is quite satisfactory for the determination of phosphoric esters of muscle extracts, taking quantities of 0·05—0·5 mg. of phosphoric oxide per determination. P. W. CLUTTERBUCK.

Distribution of chlorides and proteins between blood plasma and synovial fluid. F. FREMONT-

SMITH and M. E. DAILEY (J. Biol. Chem., 1926, 70, 779—784).—The ionic equilibrium between blood plasma and synovial fluid is similar to that observed previously (cf. Loeb and others, J. Gen. Physiol., 1921—1922, 4, 591) to exist between blood plasma and ascitic and pleural fluids. C. R. HARINGTON.

Caseinogen. H. MEYER (Biochem. Z., 1926, 178, 82—104).—Human milk from different individuals varies greatly in the ease with which it may be flocculated. The variations are ascribed to differences in the heat coagulation points, *i.e.*, the temperature below which flocculation does not occur even at the isoelectric point, which may differ by as much as 10°. The flocculation point of the milk of any one individual is characteristic and does not vary, at least during one lactation period. The purified caseinogen obtained from different human milks exhibits the same behaviour, and the variations encountered in whole milk are therefore ascribed to the caseinogen. Cow's milk and caseinogen prepared from it give similar results. On this basis, it is suggested that not only does the individuality of caseinogen vary from species to species, but also with each individual within the species.

J. PRYDE.

Hydrogen-ion concentration of calcium chloride serum from normal and pathological cow's milk. W. FREI and H. LIENHARD (Biochem. Z., 1926, 178, 1—27).—A detailed study of the variations in degree of acidity, p_H, and refractive index of the serum from calcified cow's milk. Various normal and pathological milks were examined, and in general the hydrogen-ion concentration, but not always the acidity, are diminished in pathological cases. J. PRYDE.

Colorimetric determination of p_H of milk, whey, and cream. P. F. SHARP and T. J. MCINERNEY (J. Biol. Chem., 1926, 70, 729—758).—Dilution of whole milk to twenty times its original volume with distilled water gives a fluid which is sufficiently translucent for the colorimetric determination of its p_H; the change in p_H of milk and of whey induced by such dilution has been determined, so that the application of a specified correction to the observed p_H of the diluted fluid gives the p_H of the original milk. The p_H of cream is determined indirectly, on the assumption that it is the same as that of the corresponding skimmed milk. The error of the method is $\pm 0{\cdot}1$ p_H unit. C. R. HARINGTON.

Employment of liquid paraffin in colloidal and physiological chemistry. H. BOHN (Biochem. Z., 1926, 179, 220—226).—The carbon dioxide content, ammonia content, and p_H of urine remained constant over long periods when the fluid was kept in sterile vessels under liquid paraffin. A layer of the latter, therefore, constitutes a useful protective cover for such unstable solutions. C. R. HARINGTON.

Colloid chemistry of urine. I. Dependence of surface tension of urine on its specific gravity. II. Relationship of surface tension to the amount, colour, rotation, and urea content of urine. III. Surface tension of urine and the rate of sinking of blood-corpuscles. IV. Relationship of the colloid content of normal urine to its surface tension and viscosity. V. Are surface-active substances excreted in the urine in regular daily amounts? VI. Relationship of the viscosity of normal urine to its specific gravity, volume, and rotation. F. V. VON HAHN (Biochem. Z., 1926, 178, 245—253, 254—261, 262—264, 265—269, 277—281, 282—285).—I. The view of Donnan that the surface activity of urine depends on its density is confirmed, the equation $Gh=690(d-1{\cdot}004)$, in which Gh=surface activity (%), being found to apply for 1182 out of 1224 urines examined.

II. The surface activity does not vary absolutely sharply with the volume, but the activity of the urine of females increases with decreasing volume, whilst that of males has a mean value when the volume is maximal. Surface activity and intensity of colour of urine do not vary directly together, but mean values indicate that the more highly pigmented the greater is the activity. A definite relationship between optical rotation and surface activity was not obtained, but mean values indicate that the more highly active the more lævorotatory is the urine. The dependence of surface activity on carbamide content, assumed by Donnan, could not be confirmed.

III. In normal urine, the dependence of the rate of sinking of blood-corpuscles on the surface activity could not be confirmed.

IV. The view that substances which decrease surface activity increase the viscosity does not hold in respect to the constituents of urine.

V. A large number of curves show that the excretion of surface-active substances in the urine varies from person to person and in the same person from day to day.

VI. Increase of viscosity with specific gravity is related by the formula $V_c=2200(d-1{\cdot}001)$, where V_c=increase in viscosity. Of 162 urines, 80% gave values within the limits $\pm 2{\cdot}5\%$. Generally, the smaller the urinary volume the greater the viscosity and the more strongly is the urine lævorotatory.

P. W. CLUTTERBUCK.

Volumetric determination of urea in urine. Constitution of mercury urea nitrates and the reactions between urea, mercuric nitrate, and water. B. GLASSMANN and S. SKUNDINA (Z. physiol. Chem., 1926, 160, 77—90).—A new method for the titration of urinary urea by means of mercuric nitrate is described and the theory of the reactions discussed. P. W. CLUTTERBUCK.

Terwen's method for the determination of urobilin in urine and fæces. E. GREPPI (Fol. Clin. Chim. Micro., 1926, 1, 61—67).—A full description and discussion of this method (A., 1925, i, 1351).

T. H. POPE.

Reversible interchange between secondary alcohols and ketones of their degree of oxidation. H. W. KNIPPING and W. PONNDORF (Z. physiol. Chem., 1926, 160, 25—60; cf. A., 1926, 520).—New methods for the determination of acetone and *iso*propyl alcohol in the breath and urine of animals are devised and used to investigate quantitatively the interchange of these substances in the body.

P. W. CLUTTERBUCK.

Alcaptonuria in a rabbit. J. H. Lewis (J. Biol. Chem., 1926, **70**, 659—661).—A case of typical alcaptonuria, occurring in a rabbit, is recorded.
C. R. Harington.

Blood-gases in adrenal insufficiency. O. P. Estrada and V. Deulofeu (Rev. Soc. Argent. Biol., 1926, **2**, 359—366).—In adrenalectomised dogs, a diminution in the oxygen saturation of the venous blood is observed; this is due partly to the decreased and disturbed circulation. In some cases, there is an increase in the total oxygen capacity of the blood, consequent on an increased concentration of the blood, an effect which depends on the previous state of hydration of the tissues. Diminution in the content of carbon dioxide is more marked in the arterial blood, probably as a consequence of hyperpnœa. The oxygen saturation of arterial blood is unaffected. G. W. Robinson.

Adrenal insufficiency in dogs. II. J. M. Rogoff and G. N. Stewart (Amer. J. Physiol., 1926, **78**, 711—730).—A study is reported of the composition of the blood of adrenalectomised dogs. There is an increase in non-protein nitrogen due, chiefly, to a rise in urea. Changes in blood-sugar, uric acid, creatinine, calcium, and chlorides are also reported. R. K. Cannan.

Avian diabetes and glycosuria. T. Koppanyi, S. C. Ivy, A. L. Tatum, and F. T. Jung (Amer. J. Physiol., 1926, **78**, 666—674).—The normal blood-sugar of the chicken varies from 0·15 to 0·45%. Injection of dextrose or adrenaline produces hyperglycæmia and glycosuria. Total removal of the pancreas leads to a temporary diabetic condition. After 8 days, hyperglycæmia and glycosuria disappear and the liver stores glycogen. R. K. Cannan.

Bülow acetone reaction. R. Loetze (Pharm. Ztg., 1926, **71**, 1490; cf. A., 1925, ii, 1210).—A stronger solution of 2 : 4-dinitrophenylhydrazine (5 g. in 250 c.c. of boiling 90% alcohol with 25 c.c. of hydrochloric acid) is used. The acetone solution or diabetic urine is treated with a little concentrated hydrochloric acid, and then one tenth of the volume of the warmed hydrazine reagent. The milky, yellow precipitate separates quickly. An approximate value for the acetone content of urine can quickly be obtained by comparing the speed and extent of precipitation from 10 c.c. of urine, 1 c.c. of hydrochloric acid, and the reagent with those from 0·5%, 0·1%, and 0·05% solutions of acetone and later with intermediate strengths. A. Wormall.

Urea concentration test. H. W. Jones and A. Cantarow (Arch. Int. Med., 1926, **38**, 581—589).—The urea concentration test of MacLean and de Wesselow (Brit. J. Exp. Path., 1920, **1**, 53) is modified by comparing urea concentration of the urine after ingestion of 15 g. of urea in 150 c.c. of water ("urea response level") with that after 150 c.c. of water alone ("resting level"). The percentage variation between the two levels is much lower in the case of nephritic patients, and it is claimed that this value is more significant than the urine-urea concentration alone. The results of 93 normal and 30 nephritic cases are given and divided into 5 groups, according to the "resting level" urea concentration. A. Wormall.

Glutathione content of normal animals. J. W. Thompson and C. Voegtlin. **Glutathione content of tumour animals.** C. Voegtlin and J. W. Thompson (J. Biol. Chem., 1926, **70**, 793—800, 801—806).—The utility of the method of Tunnicliffe (A., 1925, i, 752) for the determination of glutathione is confirmed. The tissues of the normal rat contain glutathione almost entirely in the reduced form; the total concentration of glutathione declines progressively from the early fœtal stage to adult life; glutathione is present in the blood-corpuscles, but not in the serum.

Actively-growing cancerous tissue contains a concentration of glutathione of the same order as that found in normal liver, which is the richest of the organs in this substance. As the tumour increases in size, the glutathione content of the rest of the body becomes progressively less; it is suggested that this may help to account for the general malnutrition associated with extensive cancer.
C. R. Harington.

Possible source of energy in anaerobic metabolism with notes on the properties of sorbitol. J. G. Davis, W. K. Slater, and V. Smith (Biochem. J., 1926, **20**, 1155—1166).—The heats of combustion in dilute solution of dextrose, gluconic acid, and *d*-sorbitol are 676·08, 618·59, and 732·44 kg.-cal. per g.-mol., respectively. The small amount of heat produced by the autoxidation and reduction of dextrose to gluconic acid and sorbitol is therefore negligible as a source of anaerobic energy. The chemical and physical properties of sorbitol and conditions for the reduction of dextrose to sorbitol by metallic reducing agents have been investigated.
S. S. Zilva.

Regulation of the hydrogen-ion concentration and its relation to metabolism and respiration in the starfish. L. Irving (J. Gen. Physiol., 1926, **10**, 345—358).—In two starfish, *Patiria miniata* and *Asterias ochraceus*, the cæcium and the cœlomic fluid are maintained at p_H 6·7 and 7·6, respectively, apparently by the carbon dioxide produced during metabolism. W. O. Kermack.

Physico-chemical properties of dissociated sponge cells. P. S. Galtsoff and V. Pertzoff (J. Gen. Physiol., 1926, **10**, 239—255).—The effect of variations of hydrogen-ion concentration on cells of two species of sponges, *Microciona prolifera* and *Cliona celata*, in a medium of known composition has been studied with particular reference to the acid-combining power and to their vitality.
W. O. Kermack.

Human metabolism with enemata of alcohol, dextrose, and lævulose. T. M. Carpenter (Carnegie Inst. Wash. Pub., 1925, **369**, 1—197).—After rectal administration of 5, 7·5, and 10% alcohol solutions, less than 2% was unabsorbed; the urine contained 0—0·40, 0—0·56, and 0·10—0·33 mg. per c.c., respectively, representing 0—0·9, 0—1·2, and 0·4—0·7% of the dose. After oral administration, the urine values were 0·19—0·32 mg. per c.c., representing 0·5—1·1% of the alcohol administered. When 60 g. of dextrose were administered in 1 litre of 0·6% sodium chloride solution, 34·6 g. were

absorbed in 5 hrs. 25 min. The amount of lævulose absorbed was 16·2—21·8 g. for a 25 g. dose, 24·8—48·0 g. for a 50 g. dose. Rectal administration of alcohol, dextrose, or lævulose decreased the urinary elimination of nitrogen and sodium chloride.

CHEMICAL ABSTRACTS.

Role of phosphates in carbohydrate metabolism in skeletal muscle. II. Comparison of the muscles of normal, fatigued, and depancreatised animals. F. BEATTIE and T. H. MILROY (J. Physiol., 1926, 62, 174—191).—In the normal muscle of the cat, the lactacidogen phosphoric acid is not less than 0·18%, the glycogen not less than 0·5%, and the lactic acid concentration between 0·08 and 0·2%. After hydrolysis, the total phosphate averages 0·48% and the lactic acid 0·5—0·8%. In the presence of fluoride, a synthesis of lactacidogen occurs to the extent of 75% of the total phosphate, and when phosphate and glycogen are added in the correct proportions for the formation of hexosediphosphate, 90% of the added phosphate is converted into lactacidogen with the loss of all the glycogen. In severe pancreatic diabetes, the original lactic acid content of the muscles may be 0·03—0·06%, the lactacidogen less than 0·17%, and the lactic acid maximum after hydrolysis less than 0·4%. There is diminished capacity for synthesis of lactacidogen and for decomposition of glycogen in the presence of fluoride. R. K. CANNAN.

Brain metabolism. III. Carbohydrate metabolism; relationship of glycogen and lactic acid. E. G. HOLMES and B. E. HOLMES (Biochem. J., 1926, 20, 1196—1203).—The lactic acid content of rabbits' brains shows no appreciable rise, nor does the glycogen content show any significant fall when the chopped tissue is kept at the ordinary temperature, or incubated under anaerobic conditions at alkaline p_H. Under aerobic conditions, lactic acid rapidly disappears from chopped brain, but glycogen suffers no significant change. The glycogen content of rabbits' brains is small and very variable.

S. S. ZILVA.

Chemical changes in the blood during fasting in the human subject. W. G. LENNOX, M. O'CONNOR, and M. BELLINGER (Arch. Int. Med., 1926, 38, 553—565).—A study of thirty fasting periods varying from 3 to 21 days, the water intake being unlimited. Non-protein nitrogen and urea-nitrogen gave varying values with only transient increases, the amino-nitrogen remained constant, but the uric acid nitrogen increased considerably. After the fast, the amino-nitrogen still remained constant, but the other nitrogen values became subnormal. During the first week of the fast, the sugar and plasma hydrogen carbonate values fell considerably, but a gradual rise in each case nearly to the pre-fasting level followed. Inorganic phosphorus and total calcium remained constant, whilst cholesterol and fibrin gave conflicting results. In a fast of 3 days without water, the results suggested unusually rapid destruction of body proteins. A. WORMALL.

Metabolism of hydantoins and carbamido-acids. O. H. GAEBLER and A. K. KELTCH (J. Biol. Chem., 1926, 70, 763—777).—After administration of hydantoin to dogs the compound is largely excreted unchanged and no increase occurs in the excretion of oxalic acid; methylhydantoin and methylcarbamidoacetic acid, however, under similar conditions, are excreted unchanged to a small extent only, and their administration is followed by a marked increase in the output of oxalic acid; this increase was greater after methylhydantoin than after methylhydantoic acid, and is thought to be due to the direct oxidation of the former substance to methylparabanic acid.

C. R. HARINGTON.

Synthesis of amino-acids in the animal body. IV. Synthesis of histidine. B. HARROW and C. P. SHERWIN (J. Biol. Chem., 1926, 70, 683—695).—Histidine may be replaced, in the diet of young rats, with good results, by glyoxaline-4(or 5)-lactic acid; glyoxaline-4(or 5)-pyruvic acid was a less efficient substitute, and glyoxaline-4(or 5)-acrylic acid was still less useful; glyoxaline itself was of no use in this respect (cf. Cox and Rose, A., 1926, 973).

C. R. HARINGTON.

Growth and reproduction on synthetic diets. I. G. A. HARTWELL (Biochem. J., 1926, 20, 1273—1278).—A description of various synthetic diets which produce good but not maximal growth. Some diets were found suitable for growth but not for reproduction; one functioned in the reverse way.

S. S. ZILVA.

Yeast extract as a supplement to gelatin. G. A. HARTWELL (Biochem. J., 1926, 20, 1279—1281). Yeast extract supplements gelatin in a synthetic diet. S. S. ZILVA.

Sodium deficiency in a maize ration. H. G. MILLER (J. Biol. Chem., 1926, 70, 759—762).—A diet containing 80% of maize and no other source of sodium was not sufficient for normal growth in rats; this amount of maize contained sufficient chlorine for normal growth and reproductive cycle.

C. R. HARINGTON.

Influence of inorganic and organic alkali salts on the urinary C : N ratio. T. TASLAKOWA (Biochem. Z., 1926, 178, 270—276).—Addition to a diet of carrots, with rabbits, of tap-water did not materially affect the urinary C : N ratio, of distilled water increased it, and of solutions of sodium citrate and tartrate either increased it or had no effect.

P. W. CLUTTERBUCK.

Influence of feeding sodium chloride, bromide, and iodide on the urinary C : N ratio in rabbits. M. WATANABE and T. TASLAKOWA (Biochem. Z., 1926, 178, 286—297).—Peroral doses of 0·3—0·75 g. of sodium chloride per kg. do not affect the urinary C : N ratio in rabbits. With sodium bromide (5 experiments), in one the ratio was unchanged, in two it was increased, and in two diminished. With sodium iodide the ratio always decreases, the absolute amount of carbon decreasing, the nitrogen being either increased, unchanged, or very little decreased.

P. W. CLUTTERBUCK.

Penetration of basic dye into *Nitella* and *Valonia* in the presence of certain acids, buffer mixtures, and salts. M. IRWIN (J. Gen. Physiol., 1926, 10, 271—287).—When cells of *Nitella* are exposed to sodium acetate–acetic acid or phosphate

buffer mixtures and then transferred to a solution of brilliant-cresyl-blue, the rate of entrance of the dye into the cell is less than when the cells are transferred directly into the dye from tap water. Phosphate buffer mixtures are less active than acetate mixtures in producing this decrease in the rate of entry of the dye, and the action would seem to be due to ions other than hydrogen ions. In the case of cells of *Valonia*, increase of the p_H by ammonia or decrease by acetic acid results in a decrease in the rate of entrance of the dye. W. O. KERMACK.

Derivatives of phenylarsinic acid in the treatment of trypanosomiasis. II. Relation between the therapeutic action of aromatic arsinic acids and their constitution. E. FOURNEAU, [M.] TREFOUEL, [MME.] TREFOUEL, and [MME.] DE LESTRANGE-TRÉVISE (Ann. Inst. Pasteur, 1926, **40**, 933—951; cf. A., 1923, i, 983).—The authors have prepared three new hydroxyphenylarsinic acids (no details), so that the ten possible isomerides are now known and have been compared as to their action on trypanosomiasis in mice. The best results are obtained with substituents in the *ortho* and *para* positions. The effect of the introduction of a methyl group into phenylarsinic acid derivatives is in general to decrease the chemotherapeutic index (tolerated dose/curative dose). Similarly, the effect of the introduction of a chlorine atom is in general to decrease the index except in the cases of 6-chloro-3-aminophenylarsinic acid and 4-acetamidoamino-2-chlorophenylarsinic acid. Many derivatives have been prepared with the view of determining the effect of the acylation of an amino-group, but the results are not uniform. W. O. KERMACK.

Hyperglycæmia and glycosuria in the dog under ether anæsthesia. I. FUJII and K. TAKAI (J. Biophysics, 1924, **1**, xxxviii).—Dogs under ether anæsthesia present hyperglycæmia and glycosuria, which may be considerably reduced by keeping the temperature at the ambient level. The adrenaline content of the adrenals is reduced.

CHEMICAL ABSTRACTS.

Experimental liver intoxication with a by-product of chloranil. I. Attempted isolation of the toxic substance. H. STAUB (Biochem. Z., 1926, **178**, 167—180).—A commercial preparation of chloranil, tetrachloroquinone, $C_6O_2Cl_4$ (Höchst, 1922), was found to contain a highly toxic impurity with a marked action on the liver of rabbits. The toxic substance was soluble in benzene, ether, alcohol, acetone, sulphuric acid, and dilute alkali, and was volatile in steam. The most active fraction was obtained by distillation in superheated steam, the lethal dose being 0·25 g. per kg. body-weight. About 1% of the toxic substance was present in the chloranil, but it has not yet been isolated. J. PRYDE.

Influence of hydrazine and its derivatives on metabolism. I. Effect of substitution in the hydrazine molecule on the hypoglycæmic action of hydrazine. S. IZUME and H. B. LEWIS (J. Pharm. Exp. Ther., 1926, **30**, 87—93).—When administered to a rabbit, equimolecular amounts of hydrazine hydrate, hydrazine sulphate, and hydrazine acetate have equal effects in lowering the blood-sugar and also equal toxicities. Hypoglycæmia is also caused by benzoylhydrazine, hippurylhydrazine, *s*-acetylbenzoylhydrazine, *s*-di*iso*propylidenehydrazine, *iso*propylideneacetylhydrazine, and *iso*propylidenebenzoylhydrazine. Although the introduction of the benzoyl radical increased the hypoglycæmic activity, *o*-, *m*-, and *p*-hydroxybenzoyl decreased this activity and also the toxicity, except in the case of *o*-hydroxybenzoyl, in which the toxicity was increased. Thiocarbaminylhydrazine and dithioformylhydrazine possess great toxicity but no hypoglycæmic, but rather a hyperglycæmic, action.

W. O. KERMACK.

Cyanamide poisoning. II. Action of cyanamide on cysteine and cystine *in vitro*. S. GLAUBACH (Arch. exp. Path. Pharm., 1926, **117**, 257—265; cf. A., 1926, 1274).—Solutions of cysteine containing cyanamide rapidly lose the power of combining with iodine, particularly at p_H approximately 7·0. Evidence is adduced to indicate that the effect is due to a change in the internal constitution of the cysteine molecule, and not to an alteration of cystine–cysteine equilibrium. It is considered that these observations on solutions of cysteine are analogous to the effects observed in cyanamide poisoning, where the power of the tissues to combine with iodine is lessened. W. O. KERMACK.

Pharmacology of the cholesterol and sitosterol series. H. SEEL (Arch. exp. Path. Pharm., 1926, **117**, 282—305).—Cholesterol, cholesterol oxide, cholestantriol, cholestandionol, cholestendione, cholestandione, sitosterol, and sitostantriol tend to increase the tonus of the heart and of smooth muscle, but the various compounds differ in the intensity of their effects. They all show remarkable power in antagonising many toxic substances. On the other hand, certain acid derivatives of cholesterol are highly toxic. W. O. KERMACK.

Influence of arsenious acid on respiration and fermentation. K. DRESEL (Biochem. Z., 1926, **178**, 70—74).—Arsenious acid markedly inhibits the respiration of Jensen's rat sarcoma, but does not affect the fermentative action of the tumour on dextrose to the same extent. On the contrary, both the respiratory and fermentative processes of yeast are inhibited by arsenious acid, but the action of the latter varies with the concentration of the sugar in the substrate.

J. PRYDE.

Mercury poisoning. II. Parenteral mercury poisoning. E. HESSE (Arch. exp. Path. Pharm., 1926, **117**, 266—278).—Certain compounds containing sulphur, particularly strontium thioacetate, act as antidotes in poisoning by mercury and bismuth compounds. W. O. KERMACK.

Effect of snake venom on the diffusion of potassium, phosphorus, and hæmoglobin, and on the formation of lactic acid in different organs. B. A. HOUSSAY and P. MAZZOCCO (Rev. Soc. Argent. Biol., 1926, **2**, 383—391).—As a consequence of the action of cobra venom, the red blood-corpuscles of dogs lose hæmoglobin and potassium at an approximately parallel rate. The elimination of phosphates is less regular. Elimination of potassium, and to a less degree of phosphorus, occurs in different

isolated organs. There is also a certain liberation of lactic acid. The diffusion of potassium is the best index of cytolysis. G. W. ROBINSON.

Action of snake venom *in vivo* on the gases and salts of the blood. B. A. HOUSSAY, A. D. MARENZI, and P. MAZZOCCO (Rev. Soc. Argent. Biol., 1926, 2, 392—405).—Intravenous injection of the venom of *Lachesis alternatus*, *L. neuwiedii*, and *Naja tripudians* produces diminution in red corpuscles, hæmoglobin, and oxygen in the blood of dogs. There is also, as a result of hæmolysis, a marked increase in the inorganic potassium and phosphorus of the plasma. A small, fugitive increase in the alkaline reserve occurs during the primary shock after injection of *Lachesis* venom. G. W. ROBINSON.

Inorganic salt balance. VI. Influence of radium emanation on salt balance of the rabbit. E. STRANSKY (Biochem. Z., 1926, **179**, 19—45).—The negative salt balance observed in rabbits on a diet of oats and ordinary tap water is changed to a positive balance by the presence of radium emanation in the water; substitution of Carlsbad mineral water for tap water also brings about a positive salt balance, which is further increased by radium emanation. The effect of the emanation is to increase the storage of calcium and still more that of phosphate, so that the increased storage is chiefly observed in the anions. C. R. HARINGTON.

Photoactivity. VII. Effect of unsaturated fatty acids on blood sugar. S. LEE (Biochem. Z., 1926, **179**, 210—214).—Subcutaneous injection of 1—2 c.c. of oleic, linoleic, or ricinoleic acids into rabbits causes a definite hyperglycæmia; the result was not constantly affected by preliminary irradiation of the acids. This observation confirms the hypothesis that part at least of the hyperglycæmic action of vegetable oils is due to their content of unsaturated acids. C. R. HARINGTON.

Existence of "disaggregating" enzymes. C. OPPENHEIMER (Biochem. Z., 1926, **179**, 261—262).—In view of the results of Waldschmidt-Leitz (Naturwiss., 1926, H. 8), it is no longer necessary to assume the existence of enzymes with the specific function of introducing water of hydration (cf. the author's "Die Fermente und ihre Wirkungen"). C. R. HARINGTON.

Enzyme purification by adsorption: pancreatic amylase. H. C. SHERMAN, M. L. CALDWELL, and M. ADAMS (J. Amer. Chem. Soc., 1926, **48**, 2947—2956).—The procedure of Willstatter, Waldschmidt-Leitz, and Hesse (A., 1923, i, 507; 1925, i, 736) for the purification of pancreatic amylase was critically studied, special attention being directed to establishing the most favourable conditions for each step in the process. It was found possible in this way to increase the amylase activity per mg. of nitrogen of the original extract three- to four-fold, but this activity is only about half that previously obtained by Sherman and Schlesinger (A., 1911, i, 827; 1912, i, 815; 1923, i, 621). These results indicate that pancreatic amylase either is protein or contains protein as an essential constituent. It appears to be amphoteric and to have an isoelectric zone in the region of p_H 7, which coincides with its zone of optimum activity (cf. Sherman, Thomas, and Caldwell, A., 1924, i, 1142). F. G. WILLSON.

Formation of lactic acid from methylglyoxal by the action of enzymes. Keto-aldehyde mutases. I. R. KUHN and R. HECKSCHER (Z. physiol. Chem., 1926, **160**, 116—153).—The average yield of methylglyoxal, using the method of Fischer and Taube (A., 1924, i, 1167), is 40% (not 100%). A 0·4% solution may be stabilised by adding a few drops of dilute sulphuric acid and covering with a layer of toluene, the loss then amounting to 3—4% in a month and to 9—10% in 2—3 months. In mixtures of methylglyoxal and lactic acid, the amount of the former is obtained by an iodometric method, and of the latter is calculated from the result of oxidation with permanganate in acid solution, knowing that, under similar conditions, lactic acid gives 95% and methylglyoxal 8% of acetaldehyde. A 95% yield of lactic acid is obtained when methylglyoxal is treated with 2*N*-sodium hydroxide. In phosphate-buffered solution, whereas at p_H 4·5—7 the transformation is negligible, at p_H 8, 2% is converted in 5 hrs. at 30° and 11% in 25 hrs., and at p_H 9 the change becomes very considerable. At p_H 7·5, however, which is optimal for enzymic transformations, the conversion due to buffer may be neglected, providing the time of the experiment is not too long. In the enzymic conversion, activity is optimal at p_H 7·5, decreasing slowly on the alkaline side and quickly on the acid, at p_H 5·5 being only half that of the optimal. Enzyme solutions prepared from the livers of freshly-killed animals differ greatly in activity and in stability, the stability in dialysed solution being considerably increased by addition of a little acetic acid. The corresponding conversion of phenylglyoxal into mandelic acid is followed polarimetrically. The optimal p_H is 8·2 (7·5—9), but at p_H 5·5, whereas methylglyoxalase retained half of its activity, phenylglyoxalase is inactive. The stability of phenylglyoxalase is very small, the activity of solutions decreasing to one half on keeping at the ordinary temperature for 15 hrs. P. W. CLUTTERBUCK.

Insulin and co-zymase in their relation to glyoxalase; separation of antiglyoxalase and trypsin. Keto-aldehyde mutases. II. R. KUHN and R. HECKSCHER (Z. physiol. Chem., 1926, **160**, 154—168).—The dismutation of ketoaldehydes by liver glyoxalase is followed, with and without addition of insulin, by three methods, first, by iodometric titration with methylglyoxal as substrate, secondly, by polarimetric determination of the active mandelic acid formed from phenylglyoxal, and thirdly, by analysis of the total mandelic acid (active+racemic) formed. All methods showed that insulin, if sufficiently purified, is without effect on the reaction velocity. Many commercial preparations of insulin contain an impurity which inhibits both lactic acid and mandelic acid formation (possibly the antiglyoxalase of Dakin and Dudley). By heating such preparations in aqueous solution for ¼ hr. on the water-bath, the inhibiting action is completely lost. English insulin is practically free from, but German insulin contains considerable amounts of, this inhibiting substance. Differing from Meyerhof, the authors

find that glyoxalase is not activated, using methylglyoxal or phenylglyoxal as substrate, by co-zymase solutions prepared from dried and fresh yeasts and from muscle of calf, pig, or pigeon. Antiglyoxalase can be obtained free from insulin and is present in tryptic preparations which are without insulin action. Antiglyoxalase may be separated from trypsin by Willstatter's adsorption method.

P. W. CLUTTERBUCK.

Enzymic formation of lactic acid in muscle extracts. I. and II. Hydrolysis of polysaccharides and hexosediphosphoric acid. O. MEYERHOF (Biochem. Z., 1926, **178**, 395—418, 462—490).—I. The methods for separation of the lactic acid-forming enzyme from muscle and for the measurement of glycolysis in aqueous solution are described. The enzyme solution (almost carbohydrate-free) forms lactic acid from added starch or glycogen for several hours with a velocity which, referred to the weight of muscle, corresponds with the rate of spontaneous formation of lactic acid in muscle pulp. The stability of the enzyme is small. Further data are given for the separation of the co-enzyme, for the determination of the effect of dilution and of the addition of phosphate on the rate of enzyme action. By the precipitation of the enzyme solution with acetone and drying, a powder is obtained which possesses 40% of the activity of the extract.

II. Glycogen, starch, amylopectin, amylose, and di- and tri-hexosan are converted into lactic acid by the above muscle-enzyme solutions at the same concentrations with almost the same velocity, thus differing from the fermentable hexoses, which, under ordinary conditions, are either not at all or only faintly glycolysed by muscle extracts. Hexosediphosphoric acid is converted into lactic acid, on the average, more slowly than polysaccharides by fresh muscle extracts, the reverse being true of old extracts. The ester-hydrolysing enzyme is much more stable than the glycolytic enzyme. Complete separation of the enzymes responsible for hydrolysis of the ester and of the polysaccharides can be attained (*a*) by keeping the extracts 24 hrs. on ice, (*b*) by heating the extracts at 37° for 15 min., (*c*) by separation of the co-enzyme either by dialysis or by washing the tissue before preparation of the enzyme solution. During hydrolysis of the polysaccharides, phosphoric ester accumulates at first quickly, then more slowly, and can be completely decomposed into lactic acid and phosphate by warming at 37°. By hydrolysis of fermentation hexosediphosphoric acid, equimolecular amounts of lactic and phosphoric acids are formed. If hydrolysis of hexosediphosphoric acid by an active extract has come to a standstill, addition of polysaccharide causes the formation of further amounts of lactic acid, in which considerable amounts remain as phosphoric ester. The increase of hexosediphosphoric acid in muscle preparations on addition of sodium fluoride and oxalate (Embden) depends on the inhibition of the decomposition of phosphoric ester and not on increased synthesis. Calcium does not appear to be necessary to the glycolytic enzyme complex.

P. W. CLUTTERBUCK.

Dissociation constants of hexosediphosphoric acid and glycerophosphoric acid. O. MEYERHOF and J. SURANYI (Biochem. Z., 1926, **178**, 427—443).—The electrotitration curves of orthophosphoric acid and of two samples of hexosediphosphoric acid are given, pK'_1, pK'_2 for the former being 1·99, 6·81, and for the latter 1·48, 6·29, respectively. Dilution of the phosphoric acid from $M/25$ to $M/270$ causes a shift of the second dissociation constant from 6·82 to 7·15 and of hexosediphosphoric acid from 6·37 to 6·73. The effect of addition of anions on the second dissociation constant is greater for hexosediphosphoric acid than for phosphoric acid, pK'_2 for phosphoric acid in presence of 0·1M-solutions of water, potassium chloride, potassium iodide, sodium fluoride, potassium sulphate, sodium oxalate, and sodium tartrate being 6·89, 6·77, 6·75, 6·74, 6·75, 6·78, 6·76, and for hexosediphosphoric acid 6·25, 6·01, 5·99, 6·02, 5·92, 6·01, 5·99, respectively. The electrotitration curve for glycerophosphoric acid is also given, pK'_1, pK'_2 being 1·40, 6·326, respectively. The effect of addition of salts on the value of pK'_2 is similar to but rather less than that of hexosediphosphoric acid. Finally, the shift of p_H of muscle extracts during esterification of inorganic phosphate and during breakdown of phosphoric esters is examined and discussed in the light of the dissociation constants found.

P. W. CLUTTERBUCK.

Hydrolysis of glycogen by the diastatic enzyme of muscle. K. LOHMANN (Biochem. Z. 1926, **178**, 444—461).—By the use of a not too permeable membrane, the greater part of the dialysable, non-fermentable carbohydrate formed by the diastatic decomposition of glycogen consists of a saccharide which is shown by the following determinations both in the free condition and as the acetyl derivative to be closely similar to the amylotriose obtained by Pringsheim from glycogen and amylopectin by decomposition with hydrochloric acid: for the free saccharide, mol. wt., 480, $[\alpha]_D^{17}$ +137·5°, reducing power, 18·1%, comparable with, for amylotriose, mol. wt. 504, $[\alpha]_D^{20}$ +124°, reducing power 22%; for the acetyl derivative, mol. wt. 1010, $[\alpha]_D^{17}$ +127°, acetyl groups 46·2%, reducing power 45·2%, comparable with, for acetylamylotriose, mol. wt. 1020, $[\alpha]_D^{17}$ +125°, acetyl groups, 48·97%, and for reducing power 45·2%. Elementary analyses agreed fairly closely, but the amount of the material was too small for complete identity to be shown.

P. W. CLUTTERBUCK.

Hydrolysis of corn [maize] starch by commercial pancreatin. J. H. WALTON and H. R. DITTMAR (J. Biol. Chem., 1926, **70**, 713—728).—The rate of hydrolysis of maize starch by commercial pancreatin is slower than that of potato starch, owing to the presence in the former of a resistant hemicellulose; the hydrolysis ceased when the maltose had reached 85% of the original starch. The rate of hydrolysis of the starch was not accelerated by treatment by the method of Lintner (A., 1886, 386), by autoclaving in presence or absence of water, by freezing, or by extraction with ether. As activating salts, potassium or ammonium chloride could be substituted for the sodium chloride, and sodium citrate, sodium succinate, or sodium ammonium hydrogen phosphate for the sodium dihydrogen phosphate usually employed for this purpose.

C. R. HARINGTON.

Elutriation of various peptidase systems and the activation of elutriates. A. FODOR and R. SCHOENFELD (Z. physiol. Chem., 1926, **160**, 169—188).—Further experiments on the elutriation of kaolin adsorbates with amino-acid solutions yielding active filtrates (cf. A., 1925, i, 1214, 1215). Glycine and still more so *dl*-leucine activate fresh, strongly active yeast macerates, but do not activate if the macerate is old and less active. The action of leucine is optimal at p_H 8. *dl*-Leucine and, much more so, *l*-tyrosine inhibit the activity of glycine elutriate.

P. W. CLUTTERBUCK.

Effect of enzyme purity on the kinetics of tryptic hydrolysis. H. B. MERRILL (J. Gen. Physiol., 1926, **10**, 217—225).—When keratose, obtained from keratin by partial hydrolysis by alkali, is treated with trypsin at p_H 8·0 the rate of hydrolysis is more nearly unimolecular the weaker the enzyme preparation used. It is suggested that in the weak enzyme solutions trypsin is absorbed by inactive material and is gradually liberated as the free trypsin is destroyed, so that the effective trypsin concentration remains constant throughout the reaction. In the case of the stronger trypsin preparations, destruction of the enzyme occurs, so that the rate of reaction decreases more rapidly than would that of a purely unimolecular reaction.

W. O. KERMACK.

Nephelometric determination of trypsin. P. RONA and H. KLEINMANN (Biochem. Z., 1926, **177**, 107—108).—In the method already described (A., 1926, 543), it is recommended that in place of 5 c.c. of a slightly alkaline or neutral solution of quinidine hydrochloride, 7·5 c.c. of a slightly acid solution should be used.

J. PRYDE.

Optimal for the determination of trypsin by Gross' method. J. A. SMORODINZEV and A. N. ADOWA (Z. physiol. Chem., 1926, **160**, 189—195).—The p_H optima for the digestion of caseinogen by trypsin, using distilled water for dilution, are 6·83—7·95, using 0·85% saline 6·68—7·4, and using sodium hydroxide 7·71—8·7.

P. W. CLUTTERBUCK.

Distribution of xanthine oxydase. I. E. J. MORGAN (Biochem. J., 1926, **20**, 1282—1291).—The organs of the sheep, goat, rabbit, cat, hedgehog, domestic pigeon, and fowl and the tissues of the lobster, oyster, and the caterpillar and pupæ of *Pieris brassicæ* have been investigated for the presence of xanthine oxydase. The evidence obtained favours the assumption that xanthine oxydase and Schardinger's enzyme are identical.

S. S. ZILVA.

Action of oxydo-reductase on glyceraldehyde, dihydroxyacetone, and methylglyoxal. A. LEBEDEV (Z. physiol. Chem., 1926, **160**, 97—115).—The intensity of the reduction of methylene-blue by glyceraldehyde in presence of the Schardinger enzyme of milk depends on the concentrations of both aldehyde and enzyme, the optimal concentration of the former being about 2%. An acid, probably glyceric acid, is produced, but the formation of glycerol was not detected. The reduction of methylene-blue by acetaldehyde in presence of oxydo-reductase is not influenced by the presence of sodium sulphite, ferrous chloride or sulphate, nor are these substances oxidised during the reduction. Glyceraldehyde in buffered solution in presence of methylene-blue is dehydrogenated almost twice as quickly as dihydroxyacetone, the process being accelerated by the presence of oxydo-reductase. It is considered that dihydroxyacetone in aqueous and in buffered solution passes to an equilibrium mixture of dihydroxyacetone and glyceraldehyde. Methylglyoxal, which is present in solution probably as the hydrate, is dehydrogenated under similar conditions at only 1/30 the rate of glyceraldehyde, a circumstance favouring the author's view that glyceraldehyde and not methylglyoxal is the intermediate in fermentation processes. The action of the enzyme on crotonaldehyde under similar conditions also depends on the concentrations of both enzyme and aldehyde.

P. W. CLUTTERBUCK.

Role of hydrogen peroxide in biological oxidations. A. VON SZENT-GYORGYI (Biochem. Z., 1926, **178**, 75—76).—Hydrogen peroxide oxidises reduced glutathione, the reaction being unaffected by the presence of cyanides. It proceeds more rapidly at higher than at lower p_H, is not accelerated by peroxydases, and has a temperature coefficient of 2—3 for 10°. It is therefore necessary to consider glutathione in relation to the decomposition of hydrogen peroxide in biological oxidations.

J. PRYDE.

Significance of cyanic acid in the carbamide-urease system. W. R. FEARON (J. Biol. Chem., 1926, **70**, 785—792).—An answer to the criticisms of Sumner (A., 1926, 758) regarding the author's previous conclusions (*ibid.*, 1924, i, 351) as to the role of cyanic acid in the enzymic hydrolysis of carbamide.

C. R. HARINGTON.

Phytochemical reduction of quinones. H. LUERS and J. MENGELE (Biochem. Z., 1926, **179**, 238—247).—By addition of an aqueous solution or suspension of the substance to actively fermenting yeast, the following quinones were reduced to the corresponding dihydroxy-compounds in yields of 9—65%; benzoquinone, thymoquinone, bromoanil, tetrabromo-*o*-benzoquinone, α-naphthaquinone, α-juglone, αβ-naphthaquinone, and phenanthraquinone. Anthraquinone could not be reduced; *p*-nitrosophenol and benzoquinonedioxime gave *p*-aminophenol and *p*-phenylenediamine, respectively.

C. R. HARINGTON.

Relationship between the total exchange of carbohydrate and its enzymic combination with phosphoric acid. H. VON EULER and E. BRUNIUS (Z. physiol. Chem., 1926, **160**, 242—255).—The combination with phosphoric acid and the rate of fermentation of various sugars with dry bottom yeast are studied at p_H 6·3 and at 30° in presence and absence of phenol. The two processes are inhibited by the same concentration of phenol (0·07*N*). With smaller concentrations, the reaction has a latent period, the delay being greater the greater is the concentration of phenol. No difference could be detected in the velocities of combination with phosphoric acid of α- and of β-dextrose. Combination with phosphoric acid occurs at the same rate with sucrose and lævulose, but more slowly with dextrose.

It is concluded that of the invert-sugar, lævulose is first attacked, and that this sugar more readily passes into the labile-(γ) form than does dextrose. Both the rate of fermentation and that of combination with phosphoric acid are slightly greater for maltose than for dextrose. In presence of phenol, however, maltose ferments more slowly than dextrose and in neither is combination with phosphate detectable. It is concluded that an enzyme takes part in the fermentation of maltose which is unnecessary for dextrose fermentation and is partly inactivated by phenol. P. W. CLUTTERBUCK.

Co-zymase and co-reductase. H. VON EULER and R. NILSSON (Z. physiol. Chem., 1926, **160**, 234—241).—No support could be obtained for the view that co-zymase acts as a co-isomerase of dextrose. The stability of apo-zymase, co-zymase, and total zymase and the mechanism of the action of co-reductase are discussed. P. W. CLUTTERBUCK.

Enzymic metabolism of bacteria. III. H. W. NICOLAI (Biochem. Z., 1926, **179**, 86—103; cf. A., 1926, 868).—The method of Rona and Lasnitzki (A., 1925, i, 471) has been applied to the determination of lipase in bacteria. The rate of respiration of *Bacillus coli* is proportional to the logarithm of the tension of oxygen in the gas to which the culture is exposed; it is independent of the between the limits 4·63 and 7·37; the isoelectric point of the organisms is about p_H 4·5. In presence of varying amounts of dextrose and of inorganic salts, the respiration reaches a maximum when the total osmotic concentration is 1·5 times that of blood-serum. Comparison of the respiratory quotients observed with different substrates indicates that the latter can be divided into two groups, in one of which the quotient is independent of the number of organisms and in the other of which it shows variations. C. R. HARINGTON.

Preparation of bacterial proteolytic enzymes from liquid cultures by precipitation with mastic. M. SCHIERGE (Biochem. Z., 1926, **179**, 248—251).—The culture medium is treated with an aqueous emulsion of mastic and acidified with acetic acid; the precipitate after keeping for 24 hrs. is filtered off and the mastic removed by extraction with alcohol and ether. The residual precipitate shows strong proteolytic activity. The method is not applicable to the separation of proteolytic enzymes from blood-serum. C. R. HARINGTON.

Bacterial nutrition. III. Phosphates and the growth of *Streptococci*. H. R. WHITEHEAD (Biochem. J., 1926, **20**, 1147—1154).—A tryptic digest of caseinogen was rendered first 66% and then 86% alcoholic. Three fractions were thus obtained, the two precipitates, A and B (both water-soluble) and the residual liquid, C. All the inorganic phosphate of the medium was found in fraction A, whilst fractions B and C contained some phosphorus in organic combination. None of the fractions singly showed any growth. A combination of the three fractions behaved like the original broth, that of A and C was almost as good, whilst the combination BC showed a lag period before growth occurred. In the presence of disodium hydrogen phosphate, fractions AC showed no significant growth after 48 hrs.; fractions BC, on the other hand, showed growth as good as the control. No inhibition was observed in this case even if the concentration of phosphate was made double that present in AC. A combination of A and B gave slight growth in presence or absence of added phosphate.

The deterioration and darkening of caseinogen medium which occur on steaming are probably due to the presence of phosphate, a growth factor present among the simpler protein derivatives being inactivated. S. S. ZILVA.

Soluble specific substance of *Pneumococcus*. IV. Nature of specific polysaccharide of type III *Pneumococcus*. M. HEIDELBERGER and W. F. GOEBEL (J. Biol. Chem., 1926, **70**, 613—624; cf. A., 1926, 545).—The yield of the specific polysaccharide from type III *Pneumococcus* has been increased to a little above 0·01% of the broth by addition of 0·3% of dextrose to the medium. Hydrolysis of the polysaccharide with sulphuric acid in the cold yielded, exclusively, acidic products with equivalent weight about 340, which showed no specific properties towards anti-pneumococcus serum. More intensive hydrolysis gave dextrose, together with an *acid*, $C_{12}H_{20}O_{12}$, $[\alpha]_D$ +10·0° in water (*morphine* salt, m. p. 153—156°, $[\alpha]_D$ −47·9°, mutarotating to −54·0° in water). The acid had one half the reducing power of dextrose and gave a positive reaction with naphthoresorcinol; oxidation with hypoiodite indicated an aldehyde group; on oxidation with nitric acid, saccharic acid was obtained, and, after prolonged acid hydrolysis, a small amount of dextrose was detected. It is thought, therefore, that this acid is a disaccharide of dextrose with an acid of the type of glycuronic acid, and that the specific substance itself is a polymeride of this compound. C. R. HARINGTON.

Determination of the digestibility of foodstuffs containing cellulose with the help of stomach bacteria. C. BRAHM (Biochem. Z., 1926, **178**, 28—35).—Measurements have been made of the amounts of carbon dioxide evolved during the digestion of cellulose-containing and other animal foodstuffs by stomach and other gastro-intestinal bacteria from horses, rabbits, oxen, and goats. It is found that when the straws etc. are soaked, or imbibition is induced by alkali treatment, the extent of digestion is markedly increased. The amount of carbon dioxide obtained from straws previously treated with alkali is increased when salts of simple aliphatic, lactic, or hippuric acids are present. Of individual straw components, xylan and xylose are readily digested, lignin only with great difficulty. J. PRYDE.

Experiments with insulin *in vitro*. E. GLASER and G. HALPERN (Biochem. Z., 1926, **179**, 144—156).—In presence of certain catalysts, especially ferric chloride and nickel chloride, the action of insulin on dextrose *in vitro* causes a decrease in the fermentable sugar with no simultaneous change in the reducing power of the solution. It is suggested that this observation may have some bearing on the fact that the non-fermentable anhydro-sugars are metabolised in the diabetic organism. The presence of acetone does not affect the course of the reaction, and in no

case were the results sufficiently constant for the quantitative determination of insulin. It is shown that the reaction proposed by Wyss (A., 1925, i, 1220) for the determination of insulin is given, with even greater intensity, after the insulin has been inactivated by heat; further, preparations of insulin accelerate the oxidation of dextrose by permanganate, but the effect is due, not to the active insulin, but to the proteins and the higher degradation products of protein which accompany it. C. R. HARINGTON.

Changes in the physiological action of insulin induced by exposure to ultra-violet light. M. M. ELLIS and E. B. NEWTON (Amer. J. Physiol., 1925, **73**, 530—538).—When insulin solutions are exposed, in an atmosphere of nitrogen, in silica vessels, to ultra-violet light, the hypoglycæmic activity is lost, and a hyperglycæmic activity is substituted. These results were not observed when "pyrex" glass vessels were used. With ozone and free oxygen in daylight, the former, but not the latter, effect is observed. A. A. ELDRIDGE.

Effect of insulin on the respiratory exchange of decerebrate and decapitate cats. A. C. TAYLOR and J. M. D. OLMSTED (Amer. J. Physiol., 1926, **78**, 17—27).—The oxygen consumption remained fairly constant, but the respiratory quotient rose. The total metabolism in calories did not change notably, but the proportion due to carbohydrate rose from a low value until it accounted for nearly the whole of the metabolism. Similar results were obtained on injection of insulin into curarised animals. Secondary changes are recorded in oxygen consumption, respiratory exchange, and total metabolism accompanying hypersensitivity and convulsions.
R. K. CANNAN.

Respiratory exchange in frogs during muscular exercise and after injection of insulin. J. M. D. OLMSTED and J. M. HARVEY (Amer. J. Physiol., 1926, **78**, 28—33).—Insulin did not raise the metabolic rate of winter frogs kept at the ordinary temperature, but changed the incidence of metabolism from fat to carbohydrate. The frogs did not retrieve an oxygen debt by increased oxygen consumption, but by a reduction in the normal metabolism.
R. K. CANNAN.

Influence of the pancreatic hormone on the fate of infused dextrose. T. KUROKAWA (J. Biophysics, 1925, **1**, lxviii).—Infusion of large quantities of dextrose was not followed by increased glycogen storage in the liver of the normal rabbit if a strongly hypoglycæmic pancreatic extract was given at the same time. When sugar was injected for therapeutic purposes the extract caused a more rapid reduction of blood sugar, whilst glycosuria was not affected. CHEMICAL ABSTRACTS.

Effect of injections of dextrose and of insulin and dextrose on blood-sugar. W. THALHIMER, F. RAINE, M. C. PERRY, AND J. BUTTLES (J. Amer. Med. Assoc., 1926, **87**, 391—392).—The intravenous injection of 10% dextrose at a slow rate into normal persons induces a more rapid removal of sugar from the blood, so that during the latter part of the injection the blood-sugar level, instead of continuing to rise, actually falls. Insulin mixed with the dextrose solution and given intravenously causes a more rapid and greater removal of sugar from the blood than when the insulin is given subcutaneously.
CHEMICAL ABSTRACTS.

Insulin and co-zymase. II. A. I. VIRTANEN (Z. physiol. Chem., 1926, **160**, 308—312).—Polemical.
P. W. CLUTTERBUCK.

Sexual hormone (feminin) of human placenta. E. GLIMM and F. WADEHN (Biochem. Z., 1926, **179**, 1—18).—The occurrence of hypertrophy of the uterus of the virgin rabbit after treatment with ovarian or placental extract is a useful qualitative indication of activity in the latter, positive results being obtained with doses of 5—10 mouse units; no evidence was obtained of any difference between the substance causing this hypertrophy and that which brings about the œstrus cycle in ovariectomised rats and mice (cf. Doisy and others, A., 1924, i, 1387). A method is described for the preparation, from human placenta, of extracts with a maximum activity of 1 mouse unit per 0·1 mg., the total yield being 500—1000 mouse units per kg. of fresh placenta. The extract may be administered subcutaneously, or, in larger doses, orally; administration of large doses to young male animals causes atrophy of the generative organs. Extracts of corpus luteum, but of no other tissues investigated, showed similar physiological properties. C. R. HARINGTON.

Nature of Fearon's colour reaction and its non-specificity for vitamin-*A*. O. ROSENHEIM and T. A. WEBSTER (Biochem. J., 1926, **20**, 1342—1345).—Fearon's reaction (A., 1926, 207) has no relation to vitamin-*A*, since the unsaponifiable fraction of cod-liver oil does not give it, and the substance responsible for the reaction can be recovered from the soaps. From biological experiments, it is also found that this colour reaction is not specific for vitamin-*A* activity. S. S. ZILVA.

Effects of various agents on colour tests for vitamin-*A*. S. G. WILLIMOTT, T. MOORE, and F. WOKES (Biochem. J., 1926, **20**, 1292—1298).—From experiments on cod-liver oil in which vitamin-*A* was destroyed by concentrated sulphuric acid, phosphorus pentoxide, or ultra-violet light, it is concluded that Fearon's "pyrogallol" test (A., 1926, 207) for the vitamin is non-specific (cf. Rosenheim and Webster, *ibid.*, 1181). In following the destruction by ultra-violet light of vitamin-*A* with the aid of the arsenic trichloride (*ibid.*, 1925, i, 1515) and antimony trichloride tests (*ibid.*, 1926, 870), parallel results were obtained. S. S. ZILVA.

Physiological role of vitamin-*B*. Relation of vitamin-*B* to tissue oxidations. J. C. DRUMMOND and G. F. MARRIAN (Biochem. J., 1926, **20**, 1229—1255).—The oxidative activity of the muscle and liver-tissue of rats and pigeons is not reduced as a result of the animals being deprived of vitamin-*B*. Muscle from pigeons poisoned by potassium cyanide to simulate polyneuritis behaves similarly. The resting oxygen consumption of rats deprived of vitamin-*B* falls from the normal only during the final phase of the condition of malnutrition induced by the vitamin deficiency when the body-weight, rectal temperature, and food consumption also fall. Starving rats

receiving a supply of vitamin-*B* behave in an analogous way. Animals exhibiting a fall of body temperature and oxygen consumption in the premortal stage will return to the normal consumption of oxygen after their temperature has been artificially raised to normal. In rats suffering from inanition and vitamin-*B* deficiency, a state of hyperglycæmia associated with a hypertrophy of the adrenal glands develops, and this is followed by a hypoglycæmic stage, which coincides with the period characterised by the fall of body temperature and oxygen consumption. Deprivation of vitamin-*B* does not therefore interfere with the oxidative mechanisms of the tissues.

S. S. Zilva.

Relation between vitamin-*B* and protein in the diet of growing rats. Physiological role of vitamin-*B*. II. V. Reader and J. C. Drummond (Biochem. J., 1926, **20**, 1256—1263).—The inadequate growth of rats on a diet consisting largely of protein (caseinogen) may be made good by raising the vitamin-*B* content of the diet. This confirms Hartwell's (A., 1924, i, 1372) and Tscherkes' (Biochem. Z., 1926, **167**, 203) observations. The hypertrophy of the kidneys of rats on a high protein diet previously observed by the authors (J. Physiol., 1925, **59**, 472) is present only when the animal does not grow at a normal rate. S. S. Zilva.

Effect of p_H on rate of destruction of vitamin-*B* by heat. H. C. Sherman and G. W. Burton (J. Biol. Chem., 1926, **70**, 639—645).—The vitamin-*B* of tomato juice is destroyed to the extent of 20% in 4 hrs. on heating at 100° at the natural acidity of the juice (p_H 4·28). As the reaction is made more alkaline, the rate of destruction by heat becomes progressively greater, the loss of activity being complete after 1 hr. at p_H 10·9. C. R. Harington.

Vitamins and other constituents of grape-fruit rind. S. G. Willimott and F. Wokes (Biochem. J., 1926, **20**, 1299—1305).—Grape-fruit rind contains considerable amounts of vitamin-*B*, but practically no vitamin-*A*. The content of oxidising enzymes as compared with the vitamin-*A* content in the orange, lemon, and grape-fruit is tabulated. Naringin, the specific glucoside of the grape-fruit, is present in the rind and can be extracted from it with alcohol. S. S. Zilva.

Effect of administration of cod-liver oil to thyreoparathyroidectomised dogs. J. H. Jones (J. Biol. Chem., 1926, **70**, 647—657).—Administration of cod-liver oil to dogs for some time previous to removal of the parathyroid glands prevented the occurrence of tetany; no such effect was obtained by treatment with cod-liver oil after the operation. Similar, but less definite, results were obtained by pre-operative irradiation of the dogs with ultra-violet light. In those animals in which tetany was prevented, the usual fall in the concentration of calcium in the blood took place nevertheless; the tetany cannot therefore be entirely ascribed to the reduction of the blood calcium. C. R. Harington.

Antirachitic vitamin of cod-liver oil. S. G. Willimott and F. Wokes (Pharm. J., 1926, **117**, 473—476, 495—497, 521—524).—The differentiation of vitamins-*A* and -*D* is reviewed. A modification of Fearon's test for vitamin-*A* is advocated in which resorcinol replaces pyrogallol (see, however, A., 1926, 1181). The methods of assay of vitamin-*D* by means of bone changes are discussed. An alcohol–acetone extract of spinach may be used as a standard source of vitamin-*A* free from -*D*. The evidence for an intestinal factor in rickets is considered and preliminary experiments on the relation of the p_H of the fæces to rickets and the calcium balance are described. R. K. Cannan.

Antirachitic action of irradiated sawdust. O. Rosenheim and T. A. Webster (Biochem. J., 1926, **20**, 1340—1341).—The chloroform extract of sawdust when irradiated acquires antirachitic activity. The growth effect observed by Hume and Smith (A., 1923, i, 728; 1925, i, 211) is therefore most probably due to the ingestion by the rats of sawdust, the sterols of which had become antirachitic by irradiation. There is no association between antirachitic activity and the chemical action on a photographic plate.

S. S. Zilva.

Influence of the cow's diet on the fat-soluble vitamins of winter milk. J. Golding, K. M. Soames, and S. S. Zilva (Biochem. J., 1926, **20**, 1306—1319).—The inclusion of kale in the winter ration of the cow raises the vitamin-*A*, but not the vitamin-*D* content of the milk. The inclusion of cod-liver oil in the winter ration of the cow raises the vitamin-*A* and the vitamin-*D* content of milk. The administration of high doses of cod-liver oil to cows reduces the percentage of fat in their milk (cf. B., 1923, 623A; 1925, 23). S. S. Zilva.

Test for vitamin-*D*. H. Jephcott and A. L. Bacharach (Biochem. J., 1926, **20**, 1351—1355).—The alkalinity of the fæces which albino rats develop on high calcium–low phosphorus diets can be brought to the acid side of neutrality by administering cod-liver oil or irradiated cholesterol and by direct irradiation of the animal. The latter treatment prevents the production of alkalinity in the fæces of rats on the rachitic diet. S. S. Zilva.

Ionic activation of plant enzymes in relation to nutrition. II. Invertase of sugar beets poor in potassium. G. Doby and R. P. Hibbard (Biochem. Z., 1926, **178**, 139—151).—Nitrate up to concentration of 0·1*N* activates the invertase of beet, whilst higher concentrations and chlorides inhibit its action. The inversion constant is diminished in the presence of salts. Plants poor in potassium contain more invertase than normal plants, but in the latter the amount of the enzyme increases more rapidly with development than in the former plants. In beets deprived of potassium and in the presence of nitrate, invertase is liberated by autolytic processes, but subsequently undergoes a rapid destruction, presumably by a substance which is itself activated by nitrates and is absent from normally grown beets. Importance is attached to electrolytes in regulating the action of plant enzymes. J. Pryde.

Assimilation of iron by plants. M. I. Sidorin (Nauch. Agron. Zhur., 1925, **2**, 47—63).—When furnished with iron to which sulphur was added, only young rootlets of maize exhibited partial penetration; older plantlets showed normal development of colour.

Sulphur appeared to act in much the same partial manner as iron when given separately.

CHEMICAL ABSTRACTS.

Sucrose formation in potatoes during drying. II. C. J. DE WOLFF (Biochem. Z., 1926, **178**, 36—59).—The formation of sucrose from starch when intact potatoes or potato slices are dried (cf. A., 1926, 1183) is regarded as a different process from the reverse formation of starch from sucrose. Within limits, an equilibrium of the type: starch+water —sucrose, holds, and after slight drying leading to increased sucrose formation; restoration of water leads to an increase of starch at the expense of the previously formed sucrose. The starch-forming enzyme (or process) is more liable to destruction than is the other when water is removed, whereas the latter condition promotes the activity of the sucrose-forming enzyme, but if drying is carried too far the original state cannot be regained. Addition of water to a potato which has not been previously dried lowers the sucrose content, but the decrease in sucrose per percentage increase in water content is less than the corresponding increase per percentage diminution of water during drying, since in the latter instance the starch-forming enzyme is partly destroyed. During the formation of sucrose from starch by drying, the reducing sugars of the potato do not increase. The difficulties of reconciling such a reversible sucrose formation with the accepted constitution of starch are discussed. J. PRYDE.

Lecture experiment on the chemistry of chlorophyll. A. VON LINGELSHEIM (Ber. deut. bot. Ges., 1926, **44**, 502—504).—Fresh leaves of *Phaseolus coccineus*, viewed by transmitted light, show the colour changes produced by the action of 25% hydrochloric acid on the chlorophyll of the leaf.

W. ROBSON.

Incrustive substances of plants. VII. Determination of hexoses by fermentation. E. SCHMIDT, F. TREFZ, and H. SCHNEGG (Ber., 1926, **59**, [*B*], 2635—2646; cf. A., 1925, i, 1370). The total hexoses (dextrose, lævulose, mannose, and galactose) in the products of the hydrolysis of hemicelluloses are determined by fermentation with Löwenbräu yeast at p_H 5·5 (phosphate buffer) within 24 hrs.; autofermentation of the yeast is avoided by previous exposure to the air for 24 hrs. Zymohexoses are determined by fermentation with *Schizosaccharomyces Pombe* at p_H 3·7 (acetate buffer). The difference between the data thus obtained is a measure of the galactose present. The latter sugar is not involved in the structure of the hemicelluloses of *Linum usitatissimum* or *Picea excelsa*. H. WREN.

Mucilaginous extracts of seaweeds. P. HAAS and B. RUSSELL-WELLS (Yearbook Brit. Pharm. Conference, 1923, 644—645).—The mucilaginous extract obtained from Irish moss, which has been designated as an ethereal sulphate in which an organic complex is combined with calcium sulphate, is a colloidal electrolyte. Similar extracts have been obtained from *Ceramium rubrum*, *Delesseria sanguinea*, *D. alata*, *Polysiphonia fastigiata*, *Plumaria elegans*, and *Ascophyllum modosum*.

CHEMICAL ABSTRACTS.

Free iodine in *Faulkenbergia Doublettii*, Sauv. E. CHEMIN and R. LEGENDRE (Compt. rend., 1926, **183**, 904—906).—Contrary to the statement of Sauvageau (*ibid.*, 1925, **181**, 293), free iodine is not present in *Faulkenbergia Doubletii*, Sauv., but it is liberated when any part of the plant, excepting the young growing cells, is treated with an acid, even carbonic acid. The iodine cannot be present as iodide, but must be in loose organic combination.

H. E. F. NOTTON.

Non-protein cysteine in plants. Attempted isolation of glutathione from the pea (*Pisum sativum*). A. KOZLOWSKI (Biochem. J., 1926, **20**, 1346—1350).—The pea contains non-protein cysteine in the ovules, young and ripe seeds, and in the green shells of the unripe fruit. Cystine is present in the leaves. Histochemical tests suggest that cysteine is probably widespread in the higher plants, not only in the meristem, but also in the "reserve" tissues and in latex. S. S. ZILVA.

Acetyl groups in pectin. E. K. NELSON (J. Amer. Chem. Soc., 1926, **48**, 2945—2946).—The acetyl group is not an essential constituent of lemon, apple, or tomato pectin (cf. Ehrlich and von Sommerfeld, A., 1926, 441). F. G. WILLSON.

Presence of amines in distillate from Kjeldahl nitrogen determinations. R. A. GORTNER and W. F. HOFFMAN (J. Biol. Chem., 1926, **70**, 457—459).—At the end of a normal Kjeldahl digestion, about 7% of the nitrogen is present in the form of volatile amines; these may amount to as much as 20% of the nitrogen if the digestion has been carried out in the presence of a salt of a dibasic metal, *e.g.*, magnesium sulphate. C. R. HARINGTON.

Duplicate determinations as a measure of accuracy in quantitative analysis. A. FLEISCH Biochem. Z., 1926, **177**, 375—388).—A method for the calculation of mean errors of biochemical determinations is described. P. W. CLUTTERBUCK.

Dialysis of readily oxidisable colloid-disperse systems. A. GUTBIER and B. OTTENSTEIN (Biochem. Z., 1926, **177**, 249—252).—An apparatus is described for dialysis out of contact with air, provision being made for taking samples of both inner and outer solutions. P. W. CLUTTERBUCK.

Determination of carbon in dilute organic solutions: application to urine and other biological fluids. O. KAUFFMANN-COSLA (Bull. Soc. chim., 1926, [iv], **39**, 1485—1492).—The standard combustion method for determining carbon is modified to deal with the difficulties arising from the evaporation of the solution and condensation of the water. R. BRIGHTMAN.

BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

FEBRUARY, 1927.

General, Physical, and Inorganic Chemistry.

Measurement of absorption over a wide spectral range, including its application to glasses. K. SCHACHTSCHABEL (Ann. Physik, 1926, [iv], **81**, 929—951).—Hansen's step-aperture arrangement (Z. Physik, 1924, **29**, 356) has been used in conjunction with the measurement of photographic negatives by a photo-electric registering photometer. Transparency factors for seventeen types of glass and two platinum films have been determined.

R. A. MORTON.

Vacuum spectroscopy. I. S. BOWEN (J. Opt. Soc. Amer., 1926, **13**, 89—93).—A discussion of technique.

L. F. GILBERT.

Measurement of the intensity of spectrum lines. T. R. MERTON (Proc. Roy. Soc., 1927, **A, 113**, 697—703).—The disadvantages of the neutral wedge method for the determination of the relative intensities of spectral lines (cf. Merton and Nicholson, A., 1916, ii, 461; 1917, ii, 433; 1920, ii, 69), and of the method involving the measurement of the densities of the photographic images of the lines, are discussed. A new method is described, by which the relative intensity of a line is determined directly in terms of a standard continuous source of radiation, *e.g.*, the positive crater of a carbon arc. The spectrum under investigation is photographed without the interposition of a wedge, whilst the standard continuous spectrum is photographed on the same plate through a wedge system, which consists of a glass plate coated with "Cellire (Black)" varnish, ruled, and cemented on to a Goldberg gelatin neutral wedge with the ruled surface in contact with the gelatin. When the wedge is mounted, the rulings are perpendicular to the slit. Two methods may be used to determine the intensities of the lines, one involving the use of a magnifying glass only, whilst for more complex spectra a comparator is used, by means of which identification and intensity measurement can be made simultaneously. The method is specially adapted to the measurement of the relative intensities of lines in the spectra of gases in vacuum tubes, where the physical width of the lines is very small.

L. L. BIRCUMSHAW.

Singlet and triplet systems with their inter-combinations forming one unit. L. S. ORNSTEIN and H. C. BURGER (Z. Physik, 1926, **40**, 403—413).—The whole of the singlet and triplet lines together with their inter-combination lines having the same n and k values are regarded as an "extended multiplet." For singlets and triplets without inter-combination lines, the summation rule for intensities holds for lines not far apart. When inter-combination lines have to be taken into account, the problem is more complex. The decrease of intensity along a series is discussed.

E. B. LUDLAM.

Specific oscillations characteristic of continuous spectra. A. WINTNER (Ann. Physik, 1926, [iv], **81**, 846—854).—Mathematical.

Fine structure and wave-lengths of the Balmer lines. W. V. HOUSTON (Astrophys. J., 1926, **64**, 81—92).—Each of the first three lines of the Balmer series in hydrogen (studied at the temperature of liquid air) is a doublet with wave-number differences H_α 0·315, H_β 0·331, H_γ 0·353, and absolute wave-lengths H_α 6562·852, 6562·716; H_β 4861·362, 4861·284; H_γ 4340·497, 4340·429, giving $109677{\cdot}70 \pm 0{\cdot}04$ as the value of Rydberg's constant. The apparent doublet separation decreases with an increase in current density, whilst the component of short wave-length increases in relative intensity. At a sufficiently high current density, the light polarised with its electric vector perpendicular to the tube shows a wider doublet separation than the light with the electric vector parallel to the tube. It is assumed that those forbidden components for which $\Delta k=0$ are present are polarised with the electric vector parallel to the tube and increase in intensity with increase of current.

A. A. ELDRIDGE.

Continuous spectrum of hydrogen. I. M. FREEMAN (Astrophys. J., 1926, **64**, 122—127).—The excitation of the continuous spectrum of hydrogen in tubes employing hot, activated filaments is trustworthy and reproducible. The spectral energy is maximal between 4800 and 5100 Å.

A. A. ELDRIDGE.

Hydrogen spectrum in the new quantum theory. C. ECKART (Physical Rev., 1926, [ii], **28**, 927—935).—Mathematical. The Born and Jordan matrices are calculated. Computed intensity ratios for the two brighter components of H_α and H_β are not in agreement with observed values, the discrepancy being too great to be ascribed to the incompleteness of the model.

A. A. ELDRIDGE.

Continuous spectrum of hydrogen. W. H. CREW and E. O. HULBURT (Physical Rev., 1926, [ii], **28**, 936—946).—The character of the continuous spectrum of hydrogen is similar, but the intensity differs, when arising from various sources. The intensity is appreciable near H_α, rises slowly to a maximum in the near ultra-violet, and falls slowly from 300 to 220 A formula for the distribution of energy across the continuous spectrum, involving an unknown probability that the atom exists through

the nth orbit, the region beyond being unquantised, is in qualitative agreement with observation.
A. A. ELDRIDGE.

Certain regions in the helium spectrum. W. LEO (Ann. Physik, 1926, [iv], **81**, 757—799).—The intensities and frequencies of the fine lines composing the line groups 4686 and 3203 of the helium spectrum when excited by direct current and by damped wave-train oscillations have been examined by means of a Rowland grating having a photographic dispersion of 0·97 Å. per mm. The results are held to be in agreement with the theory of Sommerfeld rather than with that of Bohr and Kramers. The value deduced for $\Delta\nu_H$ is 0·3459 cm.$^{-1}$ R. W. LUNT.

Effects of changes in potential and frequency on the line spectrum of certain gases. J. A. SWINDLER (Physical Rev., 1926, [ii], **28**, 1136—1146).—The spectra of hydrogen, helium, neon, krypton, xenon, nitrogen, mercury, and chlorine exhibit no differences for changes in frequency between 2 and $0{\cdot}4 \times 10^6$ alternations per sec. when the potential is constant; the high-frequency and 60-cycle spectra are identical for pressures between 1 and 6 mm., but not for low pressures. The lines of mercury in a helium tube were strong when stimulated with Tesla frequencies, and the bands of nitrogen in chlorine tubes with 60-cycle currents. The differences are due to a trigger action on the part of the high-frequency waves, making possible the release in the atom of a greater variety of quanta. A. A. ELDRIDGE.

Regularities in the arc spectra of fluorine and chlorine. T. L. DE BRUIN (Z. Physik, 1926, **39**, 869—876).—The experimental data for fluorine and chlorine have been examined. Fluorine has fewer lines in the visible region than other halogens; they are grouped into quadruplet and doublet systems; the results so far obtained for the Zeeman effect are in good agreement with the interval rule. Difference curves for chlorine are drawn, but their interpretation is difficult in the absence of data for the Zeeman effect. E. B. LUDLAM.

Double normal state of the arc spectrum of fluorine. T. L. DE BRUIN (Nature, 1926, **118**, 804).—The line 606·9 is identified as a ^4P-P' combination, and the lines 657·69, 658·31 as a ^2P combination. One of the ^2P term differences 145·5 (0·02 volt) or 325·6 (0·04 volt) is assigned to the double normal state (" Grundterm ") of the fluorine atom.
A. A. ELDRIDGE.

Double normal state of the arc spectrum of fluorine. H. DINGLE (Nature, 1927, **119**, 86).—De Bruin's assignation of Millikan's complex hot spark lines of fluorine at 607, 657, to F I is criticised (cf. preceding abstract). It is probable that the extreme ultra-violet lines are emitted by a fluorine atom which has been ionised one or more times.
A. A. ELDRIDGE.

***M*-Doublet of argon.** W. GROTRIAN (Z. Physik, 1926, **40**, 10—11).—Calculating from the results of Meissner (A., 1926, 766), the value for the screening constant for the M ring of argon is 7·3, in agreement with the figure 7·5 obtained by Turner (*ibid.*, 550) for chlorine. This value is about one unit less than for elements of high atomic number.
E. B. LUDLAM.

Electrical discharge in mixed gases. F. R. TERROUX (Physical Rev., 1926, [ii], **28**, 1242—1249).—The principal lines and relative intensities of spectra of argon, hydrogen, and oxygen in the negative glow and positive column of a discharge tube containing argon–hydrogen (10 : 90, 50 : 50) and argon–oxygen (10 : 90; 50 : 50) mixtures are tabulated. Whereas in hydrogen and helium the Balmer lines are more strongly developed in the striation than in the negative glow, the reverse is the case in hydrogen and argon. Striæ were always produced. A. A. ELDRIDGE.

Intensities of multiplets. R. FRERICHS (Ann. Physik, 1926, [iv], **81**, 807—845).—The relative intensities of the multiplets of a large number of lines in the arc spectra of iron, chromium, manganese, titanium, and vanadium have been examined by an improved photometric method. The results are held to sustain the relation advanced by Burger and Dorgelo (Physikal. Z., 1925, **26**, 756) between the sum of the intensities of a group of lines and their corresponding quantum number. R. W. LUNT.

New terms in the spectra of zinc and mercury. R. A. SAWYER and N. C. BEESE (Science, 1926, **64**, 44—46).—The four-line pp' group in the arc spectrum of zinc, re-examined by Zumstein, shows fine sharp reversals, whereas the diffuse pair, 2086·72 and 2070·11 Å., shows broad diffuse reversals, and hence arises from deep-lying terms, being classified as $2p_2$—$2D''$ and $2p_1$—$2D''$. The mercury spectrum has been photographed from 2100 to 1500 Å., and a group 2002·7, 1900·1, 1832·6, 1774·9 is classified as the pp' group of Hg I. The lines 1987·2 and 1662·6 Å. are classified as the first pair of the sharp series of Hg II. The terms $1s$, $2p_1$, and $2p_2$ in the Hg II spectrum are computed as 156,300, 106,000, and 96,200, respectively. A. A. ELDRIDGE.

Stripped yttrium (Y III) and zirconium (Zr IV) I. S. BOWEN and R. A. MILLIKAN (Physical Rev., 1926, [ii], **28**, 923—926).—The hot spark spectra of Y III and Zr IV have been identified and series relationships and term values are tabulated. In yttrium and zirconium, the normal position of the electron is in a $4d$ orbit rather than in a $5s$ orbit.
A. A. ELDRIDGE.

Interpretation of spectra, especially of the second long period. O. LAPORTE (J. Opt. Soc. Amer., 1926, **13**, 1—24).—The three prevailing systems of atomic quantum nomenclature are mentioned, and the interpretation of spectra of atoms with several valency electrons is discussed.
S. BARRATT.

New lines in the arc spectrum of europium at normal pressure between 3500 and 3100 Å. S. PINA DE RUBIES (Anal. Fis. Quim., 1926, **24**, 524—527).—A number of new lines in the arc spectrum of europium at normal pressure between the above limits are described. G. W. ROBINSON.

Continuous spectrum of mercury. (LORD) RAYLEIGH (Nature, 1926, **118**, 767).—The effect of heat on a stream of mercury vapour, showing the continuous spectrum as it distilled away from the

electric discharge in which it originated, is to cause the disappearance of the visual glow, but the resonance line 2537 Å. survives, together with a continuous spectrum in the region 3300 Å. A. A. ELDRIDGE.

Spark spectra of mercury in the ultra-violet region. G. DEJARDIN (Compt. rend., 1926, **183**, 1340—1342).—Lists of lines, many of which are new, with their intensities, are given for the three successive groups of spark spectra Hg II, Hg III, and Hg IV resulting from the emission of the ions Hg^+, Hg_2^+, Hg_3^+, respectively. The corresponding extreme wave-lengths are 1860·10—2296·12, 1894·06—2301·22, and 1881·31—2277·46 Å. They extend into the ultra-violet as far as the Schumann region, and thus link up the ordinary and extreme ultra-violet. J. GRANT.

Effect of helium on the intensity of the mercury spectrum. W. G. NASH (Science, 1926, **64**, 190).—A study of the influence of inert and radiating helium on the spectrum of mercury. The intensities of the mercury lines increase on the admission of helium; with radiating helium, helium lines appear. Up to a helium pressure of 0·03 mm., the intensity increase is greater for inert helium, but above 0·06 mm. the effect is the same for inert and radiating helium. A. A. ELDRIDGE.

Time intervals between the appearance of certain spectrum lines of helium and of mercury. J. W. BEAMS and P. N. RHODES (Physical Rev., 1926, [ii], **28**, 1147—1150).—Values are tabulated of the times ($0·07—5·06 \pm 0·3 \times 10^{-8}$ sec.) between the appearance of various lines in the visible region of the spectra of helium and mercury. The time intervals are practically independent of the conditions of excitation, and are believed to be of the same order of magnitude as the differences in the total times between excitation and emission. A. A. ELDRIDGE.

Spectrographic junction between the *X*-ray region and the extreme ultra-violet. R. THORÆUS (Nature, 1926, **118**, 771).—A criticism of the interpretation of Dauvillier's results (A., 1926, 1072). A. A. ELDRIDGE.

Effects of temperature on *X*-ray absorption. H. S. READ (Physical Rev., 1926, [ii], **28**, 898—906).—It is confirmed that with silver and nickel, rise of temperature (to 700—1000°) decreases the average transmission (1·3—1·7%). The effect varies with the wave-length, particularly near the *K* absorption limit of silver. A. A. ELDRIDGE.

Direct measurement of *X*-ray mass scattering coefficient. P. MERTZ (Physical Rev., 1926, [ii], **28**, 891—897).—Values of σ/ρ in cm.^{2}/g. were obtained as follows for wave-lengths of 0·32, 0·43, 0·54, 0·66, and 0·79 Å., respectively: lithium, 0·133, 0·165, 0·157, 0·169, 0·200; boron, 0·154, 0·162, 0·169, 0·165, 0·179; carbon, 0·166, 0·182, 0·194, 0·214, 0·234; water, 0·198, 0·206, 0·210, 0·216, 0·228; sodium, 0·173, 0·191, 0·248, —, —. A. A. ELDRIDGE.

Absorption of *X*-rays from 0·08 to 4·0 A. S. J. M. ALLEN (Physical Rev., 1926, [ii], **28**, 907—922).—The fluorescence absorption coefficients cannot always be represented by a formula of the type $\tau/\rho = C\lambda^n$, but each element must be considered by itself. Aluminium is suitable as a standard of reference. In several cases, the absorption of a low series of an element of high atomic weight is the same as that of the next higher series of some element of lower atomic weight. A. A. ELDRIDGE.

Precision measurements in the *L*-series of the elements tungsten to uranium. E. FRIMAN (Z. Physik, 1926, **39**, 813—827).—A new tubular spectrometer is described and the method of making exact measurements is given in some detail. The wave-lengths of the α_1, α_2, β_1, β_2, and γ lines of the nine elements are given and a table of frequency differences for $L\beta_1 - L\alpha_2$ and $L_2 - L_1$. E. B. LUDLAM.

Theory of dispersion of *X*-rays. R. DE L. KRONIG (J. Opt. Soc. Amer., 1926, **12**, 547—557).—The quantum theory of dispersion is applied to the refraction of *X*-rays. A general formula is given for the index of refraction in terms of the atomic absorption coefficient and the critical frequencies, and other results are obtained. S. BARRATT.

Quantum theory and intensity distribution in continuous spectra. J. R. OPPENHEIMER (Nature, 1926, **118**, 771).—Estimates of the intensity distribution in continuous *X*-ray absorption spectra based on the quantum theory of aperiodic phenomena support the theory (cf. Proc. Camb. Phil. Soc., 1926, **23**, 422). A. A. ELDRIDGE.

Zeeman effect and the structure of the arc spectrum of copper. L. A. SOMMER (Z. Physik, 1926, **39**, 711—750).—In addition to the well-known alkali-like doublet system in the arc spectrum of copper, a second system has been established by measurements of the Zeeman effect, consisting of doublet and quadruplet terms. The alkali-like series is emitted by an electron revolving round a core containing ten 3_3 electrons; the new system is emitted by an electron revolving round a core of nine 3_3 electrons and one 4_1 electron. A combination relationship is deduced and represented graphically in the form of a cycle of electron jumps to which the appropriate energy changes are assigned. E. B. LUDLAM.

Intensities of the Zeeman components in the partial Paschen-Back effect. W. C. VAN GEEL (Z. Physik, 1926, **39**, 877—878).—The intensities of the components in the magnesium triplet, 3838·29, 3832·30, 3829·36, were found to be in good agreement with the values predicted by quantum mechanics. E. B. LUDLAM.

New quantum theory and the Zeeman effect. P. S. EPSTEIN (Proc. Nat. Acad. Sci., 1926, **12**, 634—638).—Mathematical. The difficulties encountered in the treatment of the Zeeman effect by means of Schrodinger's theory are avoided by a new derivation of the fundamental equation for the behaviour of a hydrogen atom in a uniform magnetic field. It is claimed that this treatment is more rigorous, since the terms of the second order are not neglected, as in the older theory. R. W. LUNT.

Graphical constructions for movements in the Stark effect. E. BUCHWALD (Ann. Physik, 1926, [iv], **81**, 958—973).

Compton effect according to Schrödinger's theory. W. GORDON (Z. Physik, 1926, **40**, 117—133).—The quantum frequency and intensity of the Compton effect are found to be equal to the geometric mean of the corresponding classical magnitudes for the initial and final states in the process.

E. B. LUDLAM.

Directional distribution of electrons set free by polarised *X*-rays. F. KIRCHNER (Ann. Physik, 1926, [iv], **81**, 1113—1128).—An extended account of work published earlier (A., 1926, 768).

R. A. MORTON.

β-Rays associated with scattered *X*-rays. J. M. NUTTALL and E. J. WILLIAMS (Mem. Manchester Phil. Soc., 1925—1926, **70**, 1—15).—The Wilson cloud method has been used to investigate short β-ray tracks produced in a gas traversed by homogeneous *X*-rays which have been identified with recoil electrons associated with the scattering of the *X*-rays. Data have been obtained in oxygen and in nitrogen for 0·614 Å., and in air for 0·57, 0·35 Å. According to the theory of quantum scattering, the ratio of the number of short tracks to the number of long tracks should be equal to the ratio of the scattering coefficient to the absorption coefficient multiplied by the fraction of scattered quanta which give sufficient energy to the scattering electrons to enable them to leave their parent atoms. This fraction has been calculated on theoretical grounds, and the data now cited give values agreeing within 15% with those calculated.

R. W. LUNT.

Source for resonance radiation. M. A. TUVE (Nature, 1927, **119**, 85).

Polarisation by electron impact. J. A. ELDRIDGE and H. F. OLSON (Physical Rev., 1926, [ii], **28**, 1151—1156).—The spectrum of mercury vapour, excited by low-velocity electrons, shows polarisation of the lines of the first subordinate series in directions in accord with theory. Results for the second subordinate series are not in agreement with theory.

A. A. ELDRIDGE.

Lattice energy and the work of escape of electrons from calcium. J. J. WEIGLE (Z. Physik, 1926, **40**, 539—544).—The lattice energy of calcium is calculated on the assumption that the electrons in the metal are arranged in a lattice similar to that of the fluorine in fluorite. The work of escape is calculated as 2·17 volts, in satisfactory agreement with values found by others. The inner configuration of the metallic crystal is discussed.

E. B. LUDLAM.

Coupling of the quantum vectors for neon, argon, and some hydrocarbon groups. S. GOUDSMIT and E. BACK (Z. Physik, 1926, **40**, 530—538).—The possibilities of coupling are applied to the case of the interaction of two electrons. The spectroscopic evidence, particularly that furnished by the Zeeman effect, shows that the scheme due to Russell and Saunders is applicable for silicon and the ground terms of neon and argon, but in all other cases another scheme must be adopted which is in better agreement with observation as one passes from neon and silicon to tin and lead.

E. B. LUDLAM.

Voltage-intensity relations of mercury lines below ionisation. D. R. WHITE (Physical Rev., 1926, [ii], **28**, 1125—1135).—Accelerating voltage-intensity curves were obtained for 28 mercury lines between 5500 and 2500 Å., and the photographic densities of the lines at 10·2 volts are tabulated. The extrapolated minimum accelerating potentials for excitation of the lines agree with the theoretical values, except for the line 4078 Å. Where two or more lines had the same outer orbit, the curves were identical when the intensity scales were so chosen that the curves coincided at one point.

A. A. ELDRIDGE.

Electron affinity of hydrogen. G. JOOS and G. F. HÜTTIG (Z. Physik, 1926, **40**, 331—332; cf. A., 1926, 1189).—A new determination of the lattice constant of sodium hydride leads to the value 0·927 for the density, and this gives, by different methods of calculation, values for the electron affinity of hydrogen between +15 and +35 kg.-cal.

E. B. LUDLAM.

Critical potentials and *X*-ray term values. (MISS) A. C. DAVIES and F. HORTON (Phil. Mag., 1926, [vii], **2**, 1253—1263).—A general discussion on the measurement of critical potentials, the interpretation of the results, and their relationships with *X*-ray spectral determinations.

A. E. MITCHELL.

Ferromagnetism of nickel and the quantum state of the atom. D. ROZANSKY (Physikal. Z., 1926, **27**, 779—787).—An attempt has been made to determine the quantum states of the nickel atom from the ferromagnetic behaviour of nickel in the neighbourhood of the Curie point. Two states, corresponding with s and d_2 terms, suggest themselves. A new hypothesis concerning the number of ferromagnetic atoms has been introduced. At the lowest temperatures, this number corresponds with 25% of the nickel atoms, whilst at the Curie point it has increased to 40%. A decrease in the concentration of ferromagnetic atoms occurs at higher temperatures. The temperature variations follow linear relations outside the region 610—680° Abs. (Curie point 631·8° Abs.). These ideas provide a satisfactory account of the magnetic behaviour of nickel.

R. A. MORTON.

Thermionic properties of the rare-earth elements. E. E. SCHUMACHER and J. E. HARRIS (J. Amer. Chem. Soc., 1926, **48**, 3108—3114).—The thermionic emission of the rare-earth metals (those of the cerium group in powder form and those of the yttrium group alloyed with aluminium) was investigated by two simple methods. The electron emission of these metals is about 10^6 times that of tungsten; it is hindered when the metal is alloyed with aluminium.

S. K. TWEEDY.

Photo-electric properties of thin films of alkali metal. II. Phenomena at high temperatures. H. E. IVES (Astrophys. J., 1926, **64**, 128—135; cf. A., 1925, ii, 344).—Thermionic currents and, on illumination, photo-electric currents, obtained when a platinum ribbon is electrically heated in cæsium vapour at low pressure, increase with the temperature to a sharp maximum, and then decrease to negligible values. Thermionically emitted electrons

cannot be due to an internal photo-electric excitation. A. A. ELDRIDGE.

Active nitrogen. R. C. JOHNSON (Nature, 1927, **119**, 9—10).—The view of Willey and Rideal (A., 1926, 893, 1213) that active nitrogen consists of metastable molecules having an energy of about 42,500 g.-cal. per g.-mol. is not readily reconciled with spectroscopic data. The formation and decomposition of a quasi-stable molecule, *e.g.*, N_2I_2, can scarcely account for the excitation of the iodine line 2061 Å., and activated nitric oxide molecules cannot account for all the spectra which active nitrogen is capable of exciting. The theory that active nitrogen is atomic nitrogen is preferred. A. A. ELDRIDGE.

Directional distribution of electrons liberated by X-rays. F. KIRCHNER (Physikal. Z., 1926, **27**, 799—801; cf. A., 1926, 768).—The electrons can be liberated by either a photo-effect or a Compton effect. Experiments on the former, using carbon dioxide and argon, show that over the range investigated the distribution curve is independent of wave-length and the work necessary for electron liberation; the distribution curve follows approximately a third-power sine function. For the Compton effect, there is an accumulation in a direction perpendicular to the electric vector. R. A. MORTON.

Significance of certain critical potentials of mercury in terms of metastable atoms and radiation. H. A. MESSENGER (Physical Rev., 1926, [ii], **28**, 962—975).—When the critical potentials of mercury are examined by a method distinguishing between effects due to metastable atoms and those due to true radiation, all the breaks found by Franck and Einsporn (Z. Physik, 1920, **2**, 18) except those at 5·76, 6·73, and 8·35 volts are shown to be associated with increased production of metastable atoms, and breaks at 6·04, 6·30, 7·12, 7·46, and 8·09 volts are shown to be due mainly to the formation of metastable atoms. Breaks at 6·7 and 8·35 volts are due to radiation of wave-length 1849 Å.
A. A. ELDRIDGE.

Kinematics of an electron with an axis. L. H. THOMAS (Phil. Mag., 1927, [vii], **3**, 1—22).—Mathematical.

Configuration of a Lorentz electron moving arbitrarily along a straight line. S. C. WANG (Physical Rev., 1926, [ii], **28**, 1309—1314).—A differential equation is obtained which is invariant under a Lorentz transformation. The exact solution of the equation is obtained. A. A. ELDRIDGE.

Value of the potential in the interior of a moving group of electrons. P. BRICOUT (Compt. rend., 1926, **183**, 1269—1271).—Poisson's equation for the determination of the distribution of the potential between two electrodes is applied to plane electrodes, and to coaxial cylindrical electrodes. It is concluded that in the determination of the resonance potential of a gas by the method of electronic shock the electrodes should be placed so that the electronic current is sufficiently feeble to maintain a constant potential at different points in the gas.
J. GRANT.

Velocity filter for electrons and ions. W. R. SMYTHE (Physical Rev., 1926, [ii], **28**, 1275—1286).—As a substitute for magnetic analysis, particularly in positive-ray work, a method employing two identical alternating electric fields is proposed, and theoretically worked out. A. A. ELDRIDGE.

Effect of light on the electron emission from hot filaments. W. H. CREW (Physical Rev., 1926, [ii], **28**, 1265—1274).—Hot, oxide-coated platinum filaments show increased electron emission when exposed to the light from a quartz mercury arc. The results suggest that the action of the light is to free electrons from a thin film of metal of which the work-function varies with the temperature of the filament. A. A. ELDRIDGE.

Determination of electronic charge from measurements of shot-effect in aperiodic circuits. N. H. WILLIAMS and H. B. VINCENT (Physical Rev., 1926, [ii], **28**, 1250—1264).—The mean value $4{\cdot}774\times10^{-10}$ e.s.u. is obtained. A. A. ELDRIDGE.

Experiments with high-voltage cathode rays outside of the generating tube. W. D. COOLIDGE and C. N. MOORE (J. Franklin Inst., 1926, **202**, 722—735).—The effect of cathode-ray bombardment on a variety of substances, including quartz, diamond, halite, rosin, shellac, milk, bacteria, fruit, flies, plant and animal tissues, is described in a general manner. The cathode-ray tube was operated with potentials in the range 100—200 kilovolts. R. W. LUNT.

Ionisation by electrons in a homogeneous electric field. F. M. PENNING (Z. Physik, 1926, **40**, 4—9).—The number of collisions, the loss of energy on elastic collision, and the number of ionisations per unit length are calculated. For neon more than 10% of the electrons leaving the cathode produce excitation and rather less than 90% produce ionisation. E. B. LUDLAM.

Ionisation of atoms by electron impact. E. O. LAWRENCE (Physical Rev., 1926, [ii], **28**, 947—961).—By the use of electron beams having sharp upper limits of velocity distribution, critical potentials in mercury vapour were determined as follows: 10·40, 10·60, 11·29 (all $\pm0{\cdot}2\%$), 11·70 ($\pm0{\cdot}3\%$), 12·06 volts. The relative maximum probabilities of the several types of inelastic impacts are calculated. It is suggested that light quanta and electrons obey the same general laws in processes involving ionisation of atoms and molecules. In particular, the probability of atomic ionisation of a certain type by a light quantum is the same function of its energy, except as regards constants, as that of the corresponding electron inelastic impact.
A. A. ELDRIDGE.

Collisions of the second kind between ions and atoms or molecules. H. D. SMYTH, G. P. HARNWELL, T. R. HOGNESS, and E. G. LUNN (Nature, 1927, **119**, 85—86).—Mixtures of two gases, in equal amounts, were ionised by electron impact, the impact electrons having velocities well above the ionisation potentials. The relative amount of that ion corresponding with the higher ionisation potential decreased regularly with increase of pressure, indicating collision between ions and atoms or molecules. The cases

studied were: $He^+ + Ne = Ne^+ + He$; $Ne^+ + A = A^+ + Ne$; $A^+ + NO = NO^+ + A$; $He^+ + NO = NO^+ + He$. The ionisation potentials of helium, neon, argon, and nitric oxide are 24·5, 21·5, 15·4, and 9 volts, respectively. Computed relative probabilities of ionisation accord with the results of Compton and Van Voorhis (A., 1926, 769). A. A. ELDRIDGE.

Electrification of dust clouds. V. E. WHITMAN (Physical Rev., 1926, [ii], **28**, 1287—1301).—All dust clouds contain positive, negative, and neutral particles. The sign does not depend on the size; the large particles carry most of the charge. A. A. ELDRIDGE.

Gas ion mobilities in ether–hydrogen mixtures. L. B. LOEB (Proc. Nat. Acad. Sci., 1926, **12**, 617—621).—Measurements, by the Franck modification of the Rutherford alternating-current method, have been made of the mobilities of the ions in mixtures of pure ethyl ether and dry hydrogen in fields of the order of 25—50 volts cm.$^{-1}$, and in the pressure range 600—760 mm., at 21—23°. The results are in agreement with the law of mixtures proposed by Blanc (J. Physique, 1908, [iv], 7, 825) for concentrations of ether greater than 30%. At lower ether concentration, abnormally low values are obtained for the positive ions, which are held to sustain the view that these are to be associated with selective changes in concentration of one of the gases about an ion in a cluster. R. W. LUNT.

Spectroscopic interpretation of magneton numbers in the iron group. O. LAPORTE and A. SOMMERFELD (Z. Physik, 1926, **40**, 333—343).—A theoretical paper in which, by developing the work of Hund (A., 1925, ii, 912) on the spectroscopic determination of the magneton numbers of the rare earths, the author proceeds to a discussion of the magneton numbers of the metals of the iron group, with particular reference to the anomalies shown by copper and nickel, and of the temperature variation of their susceptibilities. R. W. LUNT.

Magnetic displacement of spectral lines. W. WIEN (Ann. Physik, 1926, [iv], **81**, 994—998; cf. A., 1923, ii, 349).—The nature of the carriers in the emission of spectral lines can be ascertained by experiments on electrical deflexion. Magnetic deflexion is now shown to extend and confirm the earlier work. R. A. MORTON.

Susceptibility of gases, Curie's law, and diamagnetism of flame gases. W. GERLACH and E. LEHRER (Ann. Physik, 1926, [iv], **81**, 1129—1134).—Two simple experiments in demonstration of Curie's law for paramagnetic gases are described. The well-known experiment in demonstration of the diamagnetism of flame gases is not unequivocal. R. A. MORTON.

Revision of the atomic weight of titanium. Analysis of titanium tetrachloride. II. G. P. BAXTER and A. Q. BUTLER (J. Amer. Chem. Soc., 1926, **48**, 3117—3121; cf. A., 1923, ii, 498).—The atomic weight previously found for titanium, viz., 47·90 (Cl=35·458), is confirmed by the use of more refined analytical methods. S. K. TWEEDY.

Existence and half[-value] period of radium-*C′*. A. W. BARTON (Phil. Mag., 1926, [vii], 2, 1273—1282).—The previous work of Fajans (A., 1911, ii, 569; 1912, ii, 824) and of Jacobsen (*ibid.*, 1924, ii, 142) on the existence and half-value period of radium-*C′* is discussed and the experiments of Jacobsen have been repeated. These experiments confirm the results of Jacobsen in showing that radium-*C′* does exist and that its half-value period is of the order of 10^{-6} sec. A. E. MITCHELL.

Separation of radium and of mesothorium-1 from barium by the ionic migration method. J. KENDALL, E. R. JETTE, and W. WEST (J. Amer. Chem. Soc., 1926, **48**, 3114—3117).—Migration experiments by the moving boundary method indicate that the isotopic radium and mesothorium-1 ions have greater mobilities than the barium ion and a separation of the latter from the former by this method is practicable. The ionic mobility increases with atomic weight throughout the alkaline-earth group. S. K. TWEEDY.

Influence of the nature of the source on the liberation of radon. G. VAUGEOIS (Compt. rend., 1926, **183**, 1277—1279).—Sources of radon for therapeutic purposes have been prepared from radioactive salts, the liberation of the emanation being assisted by moistening them with aqueous glycerol, which absorbs very little of the emanation. Pure carbon, quartz, or silica was used as an inert base for the source. When the source had assumed a state of radioactive equilibrium, the emanation was allowed to accumulate, and was determined daily by aspirating the air charged with emanation into a gas condenser. After a year, the activities of the sources were constant. In 24 hrs., 44·5, 55, and 58% of the accumulated emanation was obtained from radioactive iron hydroxide, iron chromate, and a radioactive solution absorbed on pure charcoal, respectively. J. GRANT.

Radioactivity of rubidium extracted from lepidolite and zinnwaldite of Japan. S. IIMORI and J. YOSHIMURA (Bull. Chem. Soc. Japan, 1926, **1**, 215—219).—Rubidium was separated from some Japanese lithia micas by a method involving its precipitation as rubidium chlorostannate. The β-ray activity of preparations of rubidium sulphate from Tanokami zinnwaldite and Nagatori lepidolite and of a Kahlbaum's specimen was found to be nearly constant, and hence it is concluded that the activity of rubidium bears no relation to its mineral source (cf. Campbell, A., 1909, ii, 288). A. S. CORBET.

Radioactivity of potassium and its geological significance. A. HOLMES and R. W. LAWSON (Phil. Mag., 1926, [vii], 2, 1218—1233).—It has been shown that in the earth's crust the rate of production of heat from the radioactive disintegration of rubidium must be insignificant in comparison with that produced by potassium, which latter is of the same order as that developed by uranium and thorium, and must have exerted an important, if not a controlling, influence on the igneous history of the earth. The yearly production of heat from the disintegration of uranium, thorium, and potassium has been estimated to be, in an average igneous rock, $11{\cdot}4 \times 10^{-6}$; in an

average granite, $15{\cdot}9\times10^{-6}$; and in an average plateau basalt, $3{\cdot}9\times10^{-6}$ g.-cal./g. It is concluded that not more than 1% of the radioactive rays can be expended in any other way than by conversion into heat. When a geothermal gradient of 35°/km. and an average thermal conductivity of 0·006 c.g.s.u. are assumed for the earth's crust, the above figures lead to the result that the thickness of the continental crust must be less than 30, and probably does not exceed 20 km., on the average, a result which is in fair agreement with recent seismic observations. For reconciliation with isostatic data, this thickness of crust requires that the substratum must have a density of 3·4—3·5, and it is concluded that it is most probably composed of eclogite.

A. E. Mitchell.

Radioactivity of certain Czechoslovakian rocks. J. Sebor (Chem. Listy, 1926, 20, 511—516).

Absorption of β-rays by matter. H. Brennen (Compt. rend., 1926, **183**, 1342—1344).—A generalised form of Fournier's formula (A., 1926, 880) for the coefficient of mass absorption of β-rays (μ/ρ) by compound bodies is deduced. The formulæ, however, give different values of μ/ρ for molecules which contain different isotopes of the same element. This is improbable, since μ/ρ depends on the atomic number, and not on the atomic weight. If Fournier's atomic masses are replaced by atomic numbers, an expression is obtained which may be simplified in cases where the atomic numbers of the components are approximately equal. The two last expressions then give values of μ/ρ in better agreement with the experimental values than do Fournier's equations.

J. Grant.

Temperature coefficient of γ-ray absorption. L. Bastings (Nature, 1927, **119**, 51).—The coefficient of γ-ray absorption of lead over a range of 250° is shown to increase by about 0·2% per 100° rise of temperature (cf. Read, A., 1926, 551).

A. A. Eldridge.

Properties of high-frequency radiations. J. A. Gray (Nature, 1926, **118**, 801—802).

Natural ionisation in spherical containers. Theoretical. J. W. Broxon (Physical Rev., 1926, [ii], 28, 1071—1085).

Artificial disintegration of the lead atom. A. Smits and A. Karssen (Z. Elektrochem., 1926, **32**, 577—586).—Details are given of experiments previously reported (A., 1926, 106) on the production of traces of mercury (1) during the operation of a silica–lead lamp with high currents at low voltages and (2) during the dispersion of lead electrodes by a high-voltage discharge under carbon disulphide. Although by the former method strong mercury spectra were obtained (photographs given) and in one case 5 mg. of mercury were isolated from 850 g. of lead which had been used in the lamp for 188 hrs., conditions favourable to transmutation were difficult to reproduce; the latter method is better in this respect. With a frequently interrupted current of 10 milliamp. at 160,000 volts for 1 hr., 30 g. of dispersed lead yielded 0·1—0·2 mg. of mercuric iodide. The former method is now being modified to permit the use of high voltages and currents as high as possible in an atmosphere of nitrogen.

H. J. T. Ellingham.

Synthesis of elements. F. H. Loring (Chem. News, 1926, **133**, 356—358).—A continuation of previous attempts (A., 1926, 656) to synthesise elements in the *X*-ray tube. Although the results are not always reproducible, some spectroscopic evidence has been obtained which suggests that under appropriate conditions atoms condense to form elements not present in the original mixture. It is suggested that the masses of the atoms which condense are additive, and also their atomic numbers, but from the latter sum 4 must be subtracted.

J. S. Carter.

Synthesis and disintegration of atoms as revealed by the photography of Wilson cloud tracks. W. D. Harkins and H. A. Shadduck (Nature, 1926, **118**, 875—876).—An examination of 34,000 photographs, showing about 270,000 α-particle tracks of 8·6 cm. range, revealed two cases in which an α-particle attached itself to a nitrogen nucleus (cf. Blackett, A., 1925, ii, 256). Values for one case are given; 11% of the kinetic energy is stored in the atom, presumably oxygen of mass 17, which is synthesised. The smallest velocity of the α-particle which has so far been sufficient to disintegrate a nitrogen atom corresponds with a remaining range at 15° of 6·2 cm.; thus positive results would not have been obtained with α-particles from polonium, which have been stated to liberate hydrogen particles from aluminium.

A. A. Eldridge.

Existence of the sub-electron. J. Mattauch (Z. Physik, 1926, **40**, 551—556).—Polemical. Ehrenhaft's criticisms of the author's work are controverted (cf. A., 1926, 880).

E. B. Ludlam.

Structure of sodium. H. Collins (Chem. News, 1926, **133**, 501—405).—Speculative.

Atomic structure and the quantum theory. I. H. Mark (Z. angew. Chem., 1927, 40, 16—20).—A review of modern atomic theories showing how they have developed from the older theories and discussing the principles on which they are based.

A. R. Powell.

Quantum theory of the specific heat of hydrogen. I. Relation to the new mechanics, band spectra, and chemical constants. J. H. van Vleck (Physical Rev., 1926, [ii], **28**, 980—1021).—Satisfactory specific heat curves are obtained when whole quanta are used, or when the state $m=\frac{1}{2}$ is excluded. Recent theories of the secondary spectrum of hydrogen give moments of inertia more easily reconciled than older values with the specific heats. According to the correspondence principle, the angular momentum, even in a non-polar molecule, can change by zero or $h/2\pi$, provided there are simultaneous electron jumps, thus causing difficulty in Ehrenfest and Tolman's theory. Croze and Dufour's peculiar Zeeman doublets may be due to loose coupling of the spin axis of the valency electron in either the initial or final state, but not in both. The Stern–Tetrode formula for chemical constants requires modification. The moment of inertia, 10^{-41}

g. cm.^{2}, often deduced for the hydrogen molecule from chemical constants, is erroneous. A. A. ELDRIDGE.

Quantum theory of the specific heat of hydrogen. II. Comparison of various theories with experiment. E. HUTCHISSON (Physical Rev., 1926, [ii], 28, 1022—1029).—A review. Average values for temperatures up to 1000° are tabulated. A satisfactory temperature-specific heat curve for both high and low temperatures, based on an elastic model, is obtained with (*a*) the *a priori* probability $p=2m$ for whole quanta, and (*b*) $p=2m$, $m=\frac{1}{2}$ excluded, for half quanta. Half integral vibrational quantum numbers do not appreciably affect the specific heat except to change an arbitrary constant (cf. preceding abstract). A. A. ELDRIDGE.

Principle of correspondence. E. O. LAWRENCE (Science, 1926, 64, 142).—When mercury vapour is bombarded by electrons of homogeneous velocities, critical potentials are observed at 10·6, 11·2, 11·6, and 11·9 volts, the minimum ionising potential being 10·4 volts. The probability of ionisation is finite when the electron has just enough energy to ionise the mercury atom, decreasing with increasing electron energy to the next critical potential, thereafter rising and falling alternately. It is suggested that electrons and radiation quanta obey the same general laws, expressed as functions of their energy, concerned with ionisation of atoms. In particular, the probability that an electron will produce a given type of ionisation expressed as a function of its energy is of the same form as the corresponding probability function for radiation quanta. A. A. ELDRIDGE.

Grouping of electrons in the atom. H. LESSHEIM and R. SAMUEL (Z. Physik, 1926, 40, 220—236; cf. Samuel and Markowicz, A., 1926, 881).—The electrons in the elements in the short periods are divided into sub-groups from a consideration of the spectroscopic evidence for the normal state. The term with the smallest inner quantum number is taken as that of the normal state, both for regular and irregular terms. The elements nitrogen and phosphorus differ from the rest, the three outer electrons being symmetrical. The same principle of grouping is extended to the elements from scandium to copper and discussed in connexion with the chemical evidence, variable valency, and stability of compounds. E. B. LUDLAM.

Electronic structure of the atom and the quantum theory. A. SOMMERFELD (Mem. Manchester Phil. Soc., 1925—1926, 70, 141—151).

Undulatory theory of the mechanics of atoms and molecules. E. SCHRODINGER (Physical Rev., 1926, [ii], 28, 1049—1070).—Theoretical. In the new theory, the existing discrepancy between the frequency of motion and the frequency of emission disappears in so far as the latter frequencies coincide with the differences of the former. A definite localisation of the electric charge in space and time can be associated with the wave-system, and this with the aid of ordinary electrodynamics accounts for the frequencies, intensities, and polarisations of the emitted light and makes superfluous all kinds of correspondence and selection principles. In several cases, where the new theory is at variance with the old, the former is the better supported by experiment. A. A. ELDRIDGE.

Quantum mechanics and the magnetic moment of atoms. E. FERMI (Nature, 1926, 118, 876).—Mathematical. Schrodinger's hypothesis (Ann. Physik, 1926, [iv], 81, 109) connecting the field scalar of his undulatory mechanics with the electric density of current leads to the right expression for the magnetic moment of a hydrogen-like atom. A. A. ELDRIDGE.

Screening constants of relativistic or magnetic *X*-ray doublets. L. PAULING (Z. Physik, 1926, 40, 344—350).—Mathematical. It is shown that the theory of circular electron orbits may be used to calculate values of the screening constants in good agreement with those observed experimentally. R. W. LUNT.

Possible significance of the tetrahedral numbers in the natural system for the arrangement of protons and electrons in the atom. H. STINTZING (Z. Physik, 1926, 40, 92—106; cf. A., 1926, 7; Reinicke, *ibid.*, 773).—The author extends his hypothesis that the configuration of the protons in the nucleus of all elements follows a scheme of tetrahedra. His new postulate is that the configuration of the electrons in the atoms of all elements follows a tetrahedral scheme and assumes the symmetry of the tetrahedral type in alternating relation to that of the protons. E. B. LUDLAM.

Conservation of photons. G. N. LEWIS (Nature, 1926, 118, 874—875).—The objections to the hypothesis of the existence of a new kind of atom, the "photon," which acts as the carrier of radiant energy and persists after absorption as an essential constituent of the absorbing atom until again sent out bearing a new amount of energy, are not insuperable. Photons are postulated to be intrinsically identical, to carry all radiant energy, and to be present in constant number in any isolated system; the energy of an isolated photon, divided by the Planck constant, gives its frequency; all photons are alike in one property which has the dimensions of action or of angular momentum, and is invariant to a relativity transformation; the condition that the frequency of a photon emitted by a certain system be equal to some physical frequency existing within that system is not in general fulfilled, but comes the nearer to fulfilment the lower is the frequency. The thermodynamics of Wien and Planck is criticised, and a new thermodynamics, a fuller account of which is promised, adds the number of photons to the variables previously deemed sufficient to define the state of a system. The new theory does not conflict with spectroscopic observations if the existence of a number of atomic states with nearly the same energy but different numbers of photons is assumed. The rigorous rule that only one photon is lost in each elementary radiation process forbids the majority of processes which are now supposed to occur; hence it must be assumed that atoms frequently change their photon number by the exchange of photons of very small energy. The

theory predicts that many atomic processes will be inhibited at very low temperatures.

A. A. ELDRIDGE.

Maxwell's equations and atomic dynamics. A. BRAMLEY (J. Franklin Inst., 1926, **202**, 775—808).—Mathematical.

Apparatus for producing spark spectra of solutions. B. A. LOMAKIN (Z. Physik, 1926, **40**, 548—550).—A simple method of producing a spark between drops of the solution is described.

E. B. LUDLAM.

Spectroscopic examination of light emitted during reaction. K. LJALIKOV and A. TERENIN (Z. Physik, 1926, **40**, 107—116).—The action of iodine vapour on the vapours of sodium, potassium, rubidium, and lithium has been studied. The lines observed were those of the principal series of the alkali metals; in addition, faint bands were observed which appeared to be continuous and are ascribed to the alkali molecule. No emission peculiar to the reaction was observable, but the *D*-lines were broader and more diffuse than would be expected for the temperature and pressure of the vapour.

E. B. LUDLAM.

Absorption spectrum of hydrogen and the analysis of its ultra-violet band spectrum. G. H. DIEKE and J. J. HOPFIELD (Z. Physik, 1926, **40**, 299—308; cf. A., 1926, 1078).—The absorption spectrum was obtained by photographing the light from a condensed discharge through a capillary tube in a vacuum spectrograph containing hydrogen at reduced pressure. The bands between 1000 and 1650 Å. could be grouped in two systems having a common final state. The resonance potential of the molecule is 11·1 volts. The absorption bands get closer together towards the extreme ultra-violet, and, when the limit value for the oscillatory energy is exceeded, pass into continuous absorption with the dissociation of the molecule. This limit is clearly marked at 849·4 Å. (=14·53 volts). A normal atom results, together with an excited atom, in the second quantum state, with 10·15 volts energy. The difference, 4·38 volts, represents the energy of dissociation. The continuous emission spectrum from the visible far into the ultra-violet is regarded as a dissociation spectrum.

E. B. LUDLAM.

"H and K" bands of carbon. A. S. GANESAN (Nature, 1926, **118**, 842).—During experiments, using an uncondensed discharge, on the spectrum of neon at low pressure, carbon and oxygen being present as impurity, the "H and K" bands of carbon were observed to consist each of a central sharp line bounded on each side by a diffuse line, the less refrangible diffuse towards the red, and the more refrangible diffuse towards the violet, the wave-lengths being 2897·23, 2896·25, 2895·35, and 2883·74, 2882·84, 2881·97 I.Å., respectively.

A. A. ELDRIDGE.

Impact-broadening of spectral lines and the sharpness of quantum states. G. HETTNER (Physikal. Z., 1926, **27**, 787—789).—Theoretical. The sharpness of a quantum state depends strictly on its duration period. Whether a quantum theoretically equivalent to the collisional damping of Lorentz can be found is discussed. It has been shown that addition of foreign gases can in fact bring about a broadening of lines by collisions. The breadth and broadening of lines in the ultra-red rotation and rotation–vibration spectra of gases with pressure increases are regarded as essentially due to impact-damping.

R. A. MORTON.

Line-spectrum for wave-lengths of a few decimetres. G. MIE (Physikal. Z., 1926, **27**, 792—795).—Weichmann (A., 1922, ii, 5, 331) has measured the refractive index of water for wave-lengths from 27 to 65 cm., and has found several sharply-defined regions of anomalous dispersion. The water he employed had a conductivity varying from 20×10^{-6} to 40×10^{-6}. When specially purified water of conductivity 2×10^{-6} is used, no trace of anomalous dispersion is now found, and the refractive index of water is 8·975 approx. over the range 52—58 cm.

Weichmann's results can be reproduced by adding a trace of a solution made up from chemically pure sodium hydrogen silicate ($NaHSiO_3$). The curve, refractive index–wave-length, shows three maxima between 54 and 57 cm. The curve for clean solutions of sodium hydrogen silicate can now be expressed by the ordinary dispersion formula, the resonance wave-lengths being 54·49, 55·55, and 56·29 cm. The physical interpretation of the curve is discussed.

R. A. MORTON.

Influence of foreign gases on the infra-red absorption band at 4·2 μ of carbon dioxide. Application to analysis. M. WIMMER (Ann. Physik, 1926, [iv], **81**, 1091—1112).—The infra-red absorption band at 4·27 of carbon dioxide increases in intensity and is shifted in the direction of longer wave-length as the pressure of gas is increased. The addition of an indifferent gas causes the absorption to increase as the partial pressure of the foreign gas is increased. With a constant partial pressure of carbon dioxide in the presence of foreign gases at equal partial pressures the absorption of the mixed gases decreases in the order: hydrogen, nitrogen, air, argon (partial pressure of carbon dioxide, 1·62 mm., of indifferent gas, 198·38 mm.). The increased absorption is due to line broadening within the unresolved band.

These results have been utilised for a method of determining the partial pressure of carbon dioxide in mixed gases. The area of the absorption curve is a measure of the carbon dioxide present in a mixture in which the nature of the indifferent gas and the total pressure are known. A series of curves is given, in each of which the area of the absorption curve is plotted against partial pressure of carbon dioxide at a constant total pressure. The method is accurate to 2% in the region of 0·02—1·0 mm. partial pressure, but to only 10% at higher pressures.

R. A. MORTON.

Theory of intensity distribution in band systems. E. CONDON (Physical Rev., 1926, [ii], **28**, 1182—1201).—A theory of the relative intensities of the bands in an electronic system predicts the existence of two especially favoured values of the change in the vibrational quantum numbers. A means of calculating the intensity distribution from

the known constants of the molecule is roughly in agreement with experiment for SiN, AlO, CO (fourth positive group of carbon), O_2 (Schumann-Runge system), CN (violet system), CO (first negative group of carbon), N_2 (second positive group of nitrogen), and N_2 (first negative group of nitrogen).

A. A. ELDRIDGE.

Production of selective emission by flames. D. A. KREIDER (J. Opt. Soc. Amer., 1926, **13**, 83—86).—An apparatus is described by means of which illuminating gas discharging through a type of Bunsen burner may be loaded with salts producing notable selective emission. The flames produced are about 1 cm. in diameter and 20 cm. high, and have an exceptionally rich and constant colour.

L. F. GILBERT.

Absorption spectra of nitrates in the region 300 μμ. R. A. MORTON and R. W. RIDING (Proc. Roy. Soc., 1927, **A**, **113**, 717—731).—The effects of varying the positive ion, the concentration, and the solvent have been investigated. Metallic nitrates and nitric acid in dilute solution (0·025—0·0025*N*) show a band at 300 μμ, $\epsilon_{max.}$ 7·2, which is due to the nitrate ion. A region of continuous end absorption extends from about 270 μμ towards the ultra-violet. This is regarded as due to inter-ionic attractions, which result in the formation of activated quasi-molecules. Beer's law is valid over the range 0·025—0·0025*N*, but breaks down at higher concentrations owing to the shifting of the band in the direction of higher extinction coefficients. By subtracting the 0·025*N*-curve from the *N*-curve, a superimposed band of selective absorption is disclosed, which is approximately reproduced when very concentrated solutions are examined. Concentrated nitric acid and the alkyl nitrates show no selective absorption. A detailed study of the absorption of calcium nitrate shows that a shift in the head of the band and an increase in $\epsilon_{max.}$ can be brought about by addition of, or solution in, a non-ionising solvent, by a greatly increased concentration in water, or by addition of a salt likely to throw back dissociation. The superimposed selective absorption is therefore thought to be due to undissociated molecules. Since all the absorbing entities considered contain the nitrate group, possible correlation of the characteristic frequencies has been considered by the methods underlying Baly's absorption theory. It is shown that the frequencies of the three bands deduced in the ultra-violet are integral multiples of a band in the short-wave infra-red due to the nitrate grouping. An explanation, based on the views of Born and Franck, is offered for the fact that von Halban, in his work with photo-electric cells, did not observe a region of general absorption with the metallic nitrates (cf. A., 1925, ii, 1083).

L. L. BIRCUMSHAW.

Penetrability of various rays through glasses. I. Ultra-violet ray penetration through alkali-lime glasses, and the method of manufacture of glass transparent to ultra-violet rays. II. Ultra-violet ray penetration through alkali-barium glass and alkali-zinc glass. III. Glasses non-transparent to visible, but transparent to ultra-violet rays. S. SUGIE (Rep. Osaka Ind. Res. Lab., 1924, **5**, No. 11, 1—26; No. 15, 1—19; **6**, No. 4, 1—26).—I. An examination of glasses of the composition 0·7—1·6Na_2O (part or all substituted by potassium oxide), 0·9—1·5CaO,6SiO_2. No systematic relation was found between the absorption of ultra-violet rays and the composition of the glass. Glass of the composition 1·0Na_2O,1·4CaO,6SiO_2 transmits down to 2370 A., for thickness 1·5 mm., whereas one of composition 1·0Na_2O,1·5CaO,6SiO_2 transmits only to 2790 Å. Antimony, titanium, ferric, magnesium, and aluminium oxides decrease the penetration, whilst phosphoric oxide has no effect.

II. Barium oxide tends to decrease, and zinc oxide to increase, penetrability to ultra-violet rays. Substitution of sodium in soda–zinc glass by potassium has the unusual effect of decreasing the penetrability.

III. In potash glass containing nickel, the shortest transmitted visible ray has a greater wave-length than in similar soda glass; the transparency to ultra-violet rays is not affected by the kind of alkali used. Cobalt behaves like nickel in increasing transparency to ultra-violet rays, but when employed together they absorb both red and ultra-violet rays.

CHEMICAL ABSTRACTS.

Absorption spectrum of solid benzene at −180°. A. KRONENBERGER and P. PRINGSHEIM (Z. Physik, 1926, **40**, 75—91).—A thin wedge of benzene between quartz plates was frozen in a silica Dewar flask constructed so that a beam of light could be passed through four plane parallel plates of silica and focussed on the slit of a spectrograph. The bands beyond 270 μμ, which at the ordinary temperature are diffuse, form a series of narrow bands at −180°, closely resembling the absorption spectrum of the vapour. The bands are grouped in series and energy levels suggested, but no entirely satisfactory scheme is obtained; it is evident that the characteristic vibrations of the atoms in the benzene vapour remain with little change when the molecule is in the crystalline state at a temperature sufficiently low to avoid disturbance by neighbouring molecules. Experiments using liquid hydrogen have been begun.

E. B. LUDLAM.

Absorption spectra of pyrone derivatives in the near infra-red. A. ROSS (Proc. Roy. Soc., 1926, **A**, **113**, 208—220).—The infra-red absorption spectra of pyrone derivatives and their solutions have been investigated. Liquid films of pyrone show absorption maxima at 2·95, 3·2, 5·9, 6·22, 7, 7·6, 8·3, and 9·8 Of these, the 2·95 and 5·9 are due to hydroxyl, the 3·2 and 9·8 to the benzene nucleus, and the 6·22 possibly to carbonyl oxygen. The weaker bands, with one exception, agree well with the equation of Henri ("Structure des Molecules") for infra-red bands of benzene, $1/\lambda = 921{\cdot}7n - 162p$, where n and p are integers signifying quantisation. Solutions of pyrone and dimethylpyrone in chloroform with and without hydrochloric acid were examined, and also similar solutions of pyridine, and a solution of pyridine methiodide in pyridine. The solution spectra of dimethylpyrone show bands at 3 μ due to hydroxyl, 3·43 μ due to methyl, and 6·15 μ due possibly to the carbonyl group. The results indicate the presence of a benzene nucleus and a hydroxyl group in the pyrone

molecule, both in the free state and in solution. The solution spectra agree with the structure proposed by Hantzsch (A., 1920, i, 72), but for the films of liquid pyrone a multimolecular complex is suggested.
W. HUME-ROTHERY.

Absorption of ultra-violet light by alkaloids and glucosides. V. BRUSTIER (Bull. Soc. chim., 1926, [iv], 39, 1527—1543).—The curves of absorption of ultra-violet light of numerous alkaloids and glucosides were determined spectrographically. All the substances exhibiting band spectra have similar absorption curves exhibiting one or more points of inflexion at positions depending on the wave-length of the light, and on the nature of the substance. Some alkaloids containing common nuclei or groups exhibit identical points of inflexion (*e.g.*, cocaine and aconitine). Alkaloids of the cocaine group are more absorbent than those of the atropine group, and their spectra are shifted more towards the red region. Spectrographic methods of identifying and determining approximately certain alkaloids or glucosides in a mixture are described. S. K. TWEEDY.

Resonance absorption and yield of fluorescence in the *X*-ray region. V. POSEJPAL (Compt. rend., 1926, 183, 1097—1099).—A general expression for the yield of fluorescence R at the K- and L-levels has been deduced from the probability that resonance absorption will occur in the X-ray region. Thus an atom ionised at its K-level will emit radiation as fluorescence, and consequently become ionised at its L-level; this ionisation will then immediately be absorbed by resonance at the K-level. The probability is governed by the coefficient of absorption of the fluorescence, and by the probability that the quantum producing ionisation, and consequently radiation of the frequency concerned, will penetrate below the level under consideration. The calculated values agree completely with those obtained experimentally by Auger (A., 1926, 551, 659). J. GRANT.

Fluorescence of superheated mercury vapour. H. NIEWODNICZANSKI (Nature, 1926, 118, 877).—The fluorescence of mercury, just sufficient to fill a quartz tube with saturated vapour at 240°, is practically unchanged when the vessel is heated at 300—355°. The fluorescence changes, however, on variation of the temperature of the saturated vapour. Hence for a given exciting light the fluorescence of the mercury vapour depends mainly on the density of the vapour, its age being unimportant.
A. A. ELDRIDGE.

Relation between intensity of fluorescence and concentration in solid solutions. E. MERRITT (J. Opt. Soc. Amer., 1926, 12, 613—622).—Perrin's second suggestion as to the cause of the decrease in luminescence of solid solutions when the active material is increased beyond a few per cent. (A., 1919, ii, 177) is applied to fluorescence in solid solutions and is developed quantitatively. The results of Nichols and Slattery (*ibid.*, 1926, 659) for uranium phosphors are in approximate agreement with the theory. L. F. GILBERT.

Links connecting fluorescence and the luminescence of incandescent solids. E. L. NICHOLS (J. Opt. Soc. Amer., 1926, 13, 661—677).—Evidence connecting the luminescence of incandescent bodies with the fluorescence of solids at the ordinary temperature is collected and reviewed. It is concluded that the luminescence superposed on the incandescence of the various solids is to be regarded as essentially identical with ordinary fluorescence.
C. J. SMITHELLS.

Luminescence from solid nitrogen, and the auroral spectrum. L. VEGARD (Nature, 1926, 118, 801).—Polemical against McLennan and others (A., 1926, 985, 1081). Present knowledge of the auroral line 5230 Å., and of the experimental conditions for obtaining the N_2-band, do not permit a comparison of their structures. The identification of the auroral line with an oxygen line seems to be in contradiction to observed facts; solid nitrogen gives the whole typical auroral spectrum from red to ultra-violet. The position of the N_1-band for small concentrations of nitrogen c is given by the expression $\lambda = 5577{\cdot}56 - 0{\cdot}8754c$. A. A. ELDRIDGE.

Alkali halide phosphors. R. POHL and E. RUPP (Ann. Physik, 1926, [iv], 81, 1161—1166).—Pure sodium chloride crystals are practically transparent down to 186 and do not show phosphorescence. The yellow or brown crystals formed in various ways and showing a broad absorption band in the visible are only weakly phosphorescent. These crystals are described as coloured in the first way: by amicrons with a very simple absorption spectrum; crystals may be coloured in a second way: by the presence of ultramicrons of a foreign metal. Blue sodium chloride appears to be of this type, which is characterised by narrow absorption bands in the ultra-violet and strong phosphorescence. A spark provides sufficient light to excite phosphorescence visible in an undarkened room. Whilst sodium chloride coloured in the first way has a very poor optical efficiency, a very high value is found for the salt coloured in the second way. A close resemblance thus exists between these phosphors and the sulphide phosphors, and the relationship between photoelectric conduction and absorption is common to both.
R. A. MORTON.

Measurements of the thermo-phosphorescence of glass produced by radium radiation. R. E. NYSWANDER and S. C. LIND (J. Opt. Soc. Amer., 1926, 13, 651—660).—The intensity of the light emitted by glass, previously exposed to radium, when heated at temperatures at which thermo-phosphorescence takes place was measured. The total quantity of light emitted by equal areas of similarly irradiated glass of the same thickness was found to be constant, independent of temperature or rate of light emission. The rate of decay at constant temperature approximately fits the equation $dx/dt = k(a-x)^2$ for a second order chemical reaction. The values of k increase with temperature, in accordance with van 't Hoff's equation $\log k = C - a/T$. Measurements with a silver–bismuth thermopile failed to reveal any increased heat radiation accompanying the luminescence. C. J. SMITHELLS.

Critical potentials of the vapours of mercuric halides. V. I. PAVLOV and A. I. LEIPUNSKY (Nature, 1926, 118, 843).—The following values were

obtained: mercuric chloride, 1·6, 2·7, 3·9, 6·6 volts; mercuric bromide, 1·5, 2·9, 6·6, 8·9 volts; mercuric iodide, 1·4, 2·7, 6·2, 7·8 volts; iodine, 1·2, 2·3, 3·8, 5·1, 7·5 volts. A. A. ELDRIDGE.

Optical excitation of the vapours of mercuric halides. A. TERENIN (Nature, 1926, **118**, 843).—When the vapours, of low density, are illuminated by the spark, bright, visible fluorescence is observed as follows: mercuric chloride, green; mercuric bromide, blue; mercuric iodide, violet, with abrupt intensity maxima at 5600, 5000, and 4400 Å., respectively. The lines stimulating the bands are confined to the limits 1900—1850, 2100—1900, and 2200—2100, respectively. A. A. ELDRIDGE.

Photo-electric polarimetry. H. VON HALBAN (Nature, 1927, **119**, 86).

Method of molecular rays. O. STERN (Z. Physik, 1926, **39**, 751—763; cf. following abstracts).—The method of producing and utilising streams of molecules is discussed in general and its unique value for a number of problems is considered, *e.g.*, (*a*) measurement of magnetic moments of molecules: electron moments of the magnitude of one Bohr magneton, moments of a nucleus of the order 1/2000 of a Bohr magneton, induced moments; (*b*) measurement of the electric moment of molecules; natural dipole moments, quadrupol moments; (*c*) investigation of the field of force of a molecule; (*d*) testing fundamental ideas: whether an atom on emitting a light-quantum is subject to a corresponding recoil (and a similar effect for absorption), the real existence of De Broglie waves. E. B. LUDLAM.

Method of molecular rays. F. KNAUER and O STERN (Z. Physik, 1926, **39**, 764—779; cf. preceding and following abstracts).—The experimental difficulties are fully discussed and apparatus is described. It is possible to obtain a stream of molecules 20 cm. long and 0 01 mm. thick which will produce a visible deposit in about 10 sec. E. B. LUDLAM.

Determination of small magnetic moments of molecules. F. KNAUER and O. STERN (Z. Physik, 1926, **39**, 780—786; cf. preceding abstracts).—The apparatus is described by means of which the magnetic moment of the water molecule was determined and a value of the order of one nuclear magneton was obtained. For mercury a negative result was obtained, and this is discussed. E. B. LUDLAM.

Variation of the dielectric constant of liquids with pressure up to 3000 kg./cm.² S. KYROPOULOS (Z. Physik, 1926, **40**, 507—520).—The dielectric constants were determined for undamped waves of 350 metres at 20° for ether, methyl alcohol, carbon disulphide, chloroform, light petroleum, ethyl alcohol, acetone, water, and pyridine up to 3300 kg./cm.²; for carbon tetrachloride up to 1000, and for benzene up to 390 kg./cm.², as these begin to solidify at these pressures. The experimental values are compared with the Lorenz–Lorentz equation $(\varepsilon-1)/d(\varepsilon+2)=f_{(p)}$. E. B. LUDLAM.

Dielectric constant of "rod-like-particle" sols. J. J. BIKERMAN (Physikal. Z., 1926, **27**, 769—771).—A statistical computation of the orientation of ellipsoids in a homogeneous electric field has been made, and the conclusions have been applied to the behaviour of vanadium pentoxide sols with rod-like particles (cf. A., 1924, ii, 835). R. A. MORTON.

Lack of effect of a magnetic field on the dielectric constant of hydrogen chloride and nitric oxide. L. M. MOTT-SMITH and C. R. DAILY (Physical Rev., 1926, [ii], **28**, 976—979).—A field of 4800 gauss produced no detectable change. A. A. ELDRIDGE.

Electrical anisotropy of crystalline liquids. M. JEZEVSKI (Z. Physik, 1926, **40**, 153—160).—The dielectric constants of *p*-azoxyphenetole and *p*-azoxyanisole were determined by a resonance method, using an oil thermostat to obtain the requisite temperature. Measurements were made from the m. p. up to and beyond the clearing point, (1) with no magnetic field, (2) with a magnetic field of 5000 gauss parallel to the lines of electric force in the condenser, (3) varying the angle between the electric and magnetic fields. Tables and curves of the results are given. A magnetic field perpendicular to the electric field produces no effect on the dielectric constant. The magnetic moment for *p*-azoxyphenetole at 143° is $1\cdot23\times10^{-15}$, and at 154° $0\cdot82\times10^{-15}$, for *p*-azoxyanisole the value at 122° is $1\cdot1\times10^{-15}$. E. B. LUDLAM.

Molecular and atomic volumes. XI. Volumes of chloro- and aquo-cobaltammines. E. BIRK (Z. anorg. Chem., 1926, **158**, 111—116; cf. Ephraim and Schütz, A., 1926, 785).—The molecular volume of trichlorotriamminecobalt is additively constituted of the molecular volumes at 0° Abs. of its constituents. If the chlorine atoms pass outside the nucleus and their places are taken by fresh ammonia molecules, their volume gradually diminishes, until in hexamminecobaltic chloride it is only two thirds of the volume at 0° Abs. (cf. A., 1923, ii, 768). Replacement of a molecule of ammonia by a molecule of water lowers the molecular volume by about 2·5, whereas the difference in the volumes of ammonia and water at 0° Abs. is 5·0. It therefore seems that the volume of the cation is primarily determined by its volume in the hexammine. R. CUTHILL.

Physico-chemical properties of cæsium eosinate. R. DELAPLACE and N. MARINESCO (Compt. rend., 1926, **183**, 1106—1107).—Eosin and cæsium eosinate prepared by the method of Delaplace (A., 1926, 949) contain 4 atoms of bromine. Measurements of the volumes in various solvents of the calcium and cæsium eosinate molecules by the method of Marinesco (*ibid.*, 673) confirm the validity of the formula proposed by the latter. Values of the ratio c/S of $7\cdot5\times10^{14}$ and $4\cdot8\times10^{14}$ were obtained for the cæsium and sodium salts, respectively, where c is the number of dipoles of solvent attached to the molecule and S the surface of the large molecule. Solutions in pure water of the cæsium salt have p_H values corresponding with neutrality, and for a molecular concentration of $2\cdot\times10^{-4}$, Λ is 700 times less than for a potassium chloride solution of the same concentration. Mol. wt. determinations by the method of Marinesco (this vol., 17) gave a value of 892 in place of 911. J. GRANT.

Magnetic double-refraction in liquids. I. Benzene and its derivatives. C. V. RAMAN and

K. S. KRISHNAN (Proc. Roy. Soc., 1927, **A**, **113**, 511—519).—The magnetic double-refraction of liquids is discussed from the point of view of Langevin's theory, which explains this phenomenon as being due to the orientation of the molecules in the magnetic field, and connects the absolute value of the Cotton–Mouton constant with the optical refractivity and the magnetic susceptibility of the molecules along three mutually perpendicular axes. The light scattered by the ideal, spherically symmetrical molecule in a direction transverse to the incident beam would be completely polarised, and the optical anisotropy of the molecule may be calculated from the degree of polarisation of the scattered light. The optical anisotropy of the paraffins is less than that of the aromatic hydrocarbons. The Cotton–Mouton constant is calculated from the polarisation data, the magnetic susceptibility, and the refractive indices. With benzene, assuming an axis of optical symmetry, it is shown that the observed value of the constant can be explained only on the assumption that the molecule exhibits a very pronounced magnetic anisotropy, the susceptibility in the direction of the axis being about twice as large as in the perpendicular direction. On the basis of these results, it is suggested that at least twelve of the electron orbits binding the atoms in the molecules must be oriented in a plane parallel to the ring. In the case of some simple benzene derivatives, where it can be assumed that the optical ellipsoid is still a spheroid of revolution (as in benzene), and that the group which replaces the hydrogen atom is magnetically isotropic, the Cotton–Mouton constant has been calculated and the values have been found to be in fair agreement with the observed values. L. L. BIRCUMSHAW.

Dispersion of atomic hydrogen. I. and II. R. M. LANGER (Proc. Nat. Acad. Sci., 1926, **12**, 639—644, 644—648).—I. The dispersion of hydrogen when subjected to ionisation by collision excited by damped wave-trains of high voltage and unspecified current or frequency has been determined for 6000 $\mu\mu$, and in the pressure range 1·0—20·0 mm., by an interferometer method. The correction for the partial pressure of monatomic hydrogen has been evaluated on the basis of Bonhoeffer's work on the rate of recombination of monatomic hydrogen (A., 1925, ii, 52). On the assumption of an extreme estimate for this correction, the results lead to the value $(\mu_H^2-1)=(1{\cdot}36\pm0{\cdot}34)\times10^{-4}$ (μ_H=refractive index of monatomic hydrogen).

II. Mathematical. It is shown that the values calculated for μ_H^2-1 (cf. above) on the basis of the dispersion theory of Kramers and Heisenberg (Physikal. Z., 1925, **31**, 693) and of the empirical data of Ladenburg (Ann. Phys., 1912, [iv], **38**, 249) are two to three times greater than the values obtained experimentally above This discrepancy is held to question the validity of the correspondence principle. R. W. LUNT.

Anomalous dispersion in electrically excited hydrogen, helium, neon, and mercury. R. LADENBURG (Physikal. Z., 1926, **27**, 789—790).—See A., 1926, 994.

Optical rotation and atomic dimension. VI. D. H. BRAUNS (J. Amer. Chem. Soc., 1926, **48**, 2776—2788; cf. A., 1925, ii, 633).—The specific rotations, $[\alpha]^{20}$, of the following sugars are recorded: halogenated cellobiose hepta-acetates: fluoro-compound, +30·62°; chloro-compound, +71·70°; bromo-compound, +95·76°; iodo-compound, +125·70°; cellobiose β-octa-acetate, −14·11°; *fluoro-4-glucosidomannose hexa-acetate*, m. p. about 145°, +20·75°; 4-glucosidomannose octa-acetate, +36·20°; 4-glucosidomannose, +5·8° (after 24 hrs.); halogen 4-glucosidomannose hepta-acetates: *fluoro*-compound, m. p. 155—156°, +13·60°; *chloro*-compound, m. p. 172°, +51·20°; *bromo*-compound, m. p. 168—169°, +77·90°; *iodo*-compound, m. p. (decomp.?) 140°, +111·50°. The methods of preparation are given in detail. The rotations for the two sets of biose derivatives deviate from the regular relationship observed for the corresponding derivatives of the monose sugars, although an agreement is obtained if the fluoro-compounds are ignored.

S. K. TWEEDY.

Scattering of light by gaseous mixtures at high pressures. L. A. RAMDAS (Physical Rev., 1926, [ii], **28**, 1030—1033).—Experiments with oxygen and carbon dioxide are described.

A. A. ELDRIDGE.

Scattering and polarisation of light in disperse carbon. G. I. POKROVSKI (Z. Physik, 1926, **40**, 278—282; cf. A., 1926, 779).—The scattering and polarisation of light by carbon from flames, from dilute Indian ink, and reflexion from soot are calculated and compared with experiment, with fairly good agreement. E. B. LUDLAM.

Crystallised nitrogen. D. VORLANDER and W. H. KEESOM (Proc. K. Akad. Wetensch. Amsterdam, 1926, **29**, 1069—1074).—See A., 1926, 1082.

Vibrational energy of the molecules CO and CO_2. F. MATOSSI (Z. Physik, 1926, **40**, 1—3).—For CO, the coefficient of deformation, calculated from the electric moment of the molecule, is $1{\cdot}10\times10^{-21}$; for CO_2, the value is $4{\cdot}58\times10^{-25}$; the corresponding figures obtained from the molecular refraction are 1·73 and $1{\cdot}43\times10^{-21}$, respectively. E. B. LUDLAM.

Molecular constitution of water. G. TAMMANN (Z. anorg. Chem., 1926, **158**, 1—16).—Examination of the specific volume–temperature and compressibility–temperature curves of water indicates that the difference between these curves and those for normal liquids is due to the presence in the water of relatively large molecules of "water-I," having the space-lattice of ice-I. These molecules diminish in concentration with rise of temperature or pressure, and are incapable of existence above 50°, or under more than 2500 kg./cm.^{2} pressure. The other types of molecules present probably differ so little in volume that variation in their concentrations does not appreciably influence the specific volume or compressibility. From existing compressibility data, it seems likely that water-I has the formula $(H_2O)_6$, and that the other molecular species are isomerides, with the formula $(H_2O)_3$. The effect of water-I on the surface tension and refractivity is proportional to its concentration. R. CUTHILL.

***cis–trans*-Isomerism in the case of metallic salts of the type R_2MX_2.** A. HANTZSCH (Ber.,

1926, 59, [*B*], 2761—2765).—The two forms of the salt $[Cl_2Pt(C_5H_5N)_2]$ are unimolecular in molten phenol, thus establishing the possibility of *cis–trans*-isomerism with this type of substance (cf. Reihlen, A., 1926, 888). The explanation of the plane configuration of molecules R_2EX_2 (in which R and X are positive and negative groups, respectively), whereas molecules of the type ER_4 (in which the substituents are four similar positive or negative groups) are tetrahedral is found in the mutual attraction of the groups R and X, which causes them to be brought into closer proximity with one another than is possible with a tetrahedral configuration. The plane configuration is always possible when the substituents are unsaturated, and is independent of the nature of the central atom. H. WREN.

Electrical polarisation of some carbon compounds. Geometrical and position isomerism. J. ERRERA (Physikal. Z., 1926, 27, 764—769).—Electrical polarity has been investigated by direct experiment. The total polarisation suffered by a substance in an electric field is approximately equal to the sum of the effects due to electronic, atomic, and molecular polarisations. The latter is a measure of the polarity of a molecule with a permanent dipole. Measurement of dielectric constants under various conditions permit of an analysis of the gross polarisation into the three effects enumerated. Near the m. p., the dielectric constant increases with decreasing frequency for solids which possess permanent dipoles in the liquid state, whereas at a temperature a few tenths of a degree below the m. p. the true dielectric constant characteristic of the solid state is obtained, and is independent of frequency and much less in magnitude than the value for the liquid state. On the other hand, those liquids which have no permanent dipole possess no dispersion on solidification, and at once attain a steady value for the dielectric constant in which the value for the solid is somewhat greater than that for the liquid. These considerations have been applied to dihalogen isomerides of the *cis–trans* and *o*-, *m*-, *p*-types. *Trans*- and *p*-isomerides have no detectable electric moment, whilst *cis*- and *o*-isomerides show a relatively large polarisation; *m*-isomerides show an intermediate effect. Asymmetric ethylene derivatives (two chlorine atoms attached to the same carbon atom) have a weaker moment than the corresponding *cis*-form. In both isomeric series the electric moment increases in the order chlorine, bromine, iodine; the moment for an *o*-substitution product of benzene is greater than that for the corresponding *cis*-derivative of ethylene. Association does not appear to occur in *trans*- and *p*-derivatives. Evidence is given that the deformation of the benzene ring which results from substitution is greater for substituents of greater atomic weight.

The electronic polarisation, molecular refraction, and absorption spectra in the ultra-violet all exhibit higher values for *trans*- than for *cis*-derivatives and for *p*- than for *o*-derivatives. Certain aspects of "polarity" theories do not receive experimental support from the work. It is concluded that the dielectric constant of an organic substance depends less on the nature of the constituent atoms than on their relative positions (cf. A., 1924, ii, 810; 1925, ii, 362, 738). R. A. MORTON.

Valency theory and the electrical resistance of metals. H. BURGARTH (Z. Elektrochem., 1926, **32**, 552—553).—According to the author's valency theory (A., 1926, 560), a point in the outer shell of an atom where an A- and a B-valency neutralise one another (neutralisation point) is a place where a free electron may easily be loosely attached. The electrical conductivity of a metal should thus be determined by the number of these neutralisation points, viz., $\kappa = k(d/A)N.f(M)$, where density, A=atomic weight, N=number of neutralisation points on each atom, k=a constant, and $f(M)$ is an undetermined factor to allow for any effect of the relative positions or movement of neutralisation points. Neglecting $f(M)$, the relation for two different metals is $\kappa_1/\kappa_2 = d_1N_1A_2/d_2N_2A_1$. It is shown that there is a parallelism between relative values calculated from this relation and the observed values for metals of groups 1, 2, and 3 of the periodic classification. The greatest discrepancy is with mercury, but $f(M)$ may be an important factor here. H. J. T. ELLINGHAM.

Law of homopolar combination of atoms. Co-ordination compounds of platinum metals. H. REMY (J. pr. Chem., 1926, [ii], **114**, 337—347).—The law of homopolar combination of atoms, which was formulated in connexion with the oxy-acids (A., 1921, ii, 501), may also be applied to metallic co-ordination compounds in general, and particularly to the new compounds of ferric iron of co-ordination number 5 and 7 (see Remy and Rothe, J. pr. Chem., 1926, [ii], **114**, 137). The co-ordination number of a metallic ion represents the number of electrons which must be added to the outer sphere to bring the total up to a value which represents a stable electronic configuration. a is independent of valency, but may have more than one value for the same element. Values of a for a number of elements are tabulated. H. E. F. NOTTON.

Colour and magnetism of ions. G. JOOS (Ann. Physik, 1926, [iv], **81**, 1076—1085).—Spectroscopic, chemical, and magnetic evidence shows that the colour and magnetism of the transition elements are due to complexes rather than to simple ions; the complexes are formed by assemblage of electrons into definite entities, and not merely by electrostatic attractions. Between the absorption spectra of salts and their solutions and the spectra of free ions of equal charge no relationship exists, and absorption in the visible region is conditioned by large units which owe their existence to the peculiar configuration of electronic shells in the transition elements which favours complex formation. The paramagnetism is likewise not consistent with simple ions as the effective unit. Magnetic susceptibility affords a means of investigating the structure of the complexes. The method of interpretation is illustrated with reference to cobalt compounds (cf. A., 1920, ii, 301, 366; 1923, ii, 750; 1924, ii, 372). R. A. MORTON.

Born's dipole theory of anisotropic liquids. G. SZIVESSY (Z. Physik, 1926, **40**, 477—478).—Polemical (cf. Kast, A., 1926, 1194). E. B. LUDLAM.

Molecular diameters at the b. p. P. WALDEN (Z. anorg. Chem., 1926, **157**, 41—44).—The value $0{\cdot}885\times10^{-8}\times V^{1/3}$ cm. (V=mol. vol. at the b. p.) has been derived for the diameter of molecules at the b. p. This is in much better agreement with the values deduced by means of the kinetic theory than is Mokruschin's expression (A., 1926, 780).

R. CUTHILL.

Size of the iodine molecule. B. TOPLEY (Nature, 1926, **118**, 802—803).—The agreement between Mack's value for the cross-section of the iodine molecule (A., 1925, ii, 1124) with that of Rankine is fortuitous; Mack's value for the diffusion coefficient is too large, and the method of calculation is invalid. The mean value of the diffusion coefficient of iodine vapour in air at 25° and 760 mm. is 0·0815(±1%), whence the effective radius of the average iodine molecule, $\sigma_{I_2}=2{\cdot}923\times10^{-8}$ at 25°, Rankine's value being $3{\cdot}656\times10^{-8}$.

A. A. ELDRIDGE.

Changes in the surface of freshly-pulverised crystalline salts [on keeping]. D. BALAREV (Z. anorg. Chem., 1926, **158**, 103—104).—If powdered crystalline neutral salts such as potassium chloride are heated at 300—400° in a vacuum, they acquire an alkaline reaction, presumably because the free acid formed by hydrolysis by the surface layer of water has been volatilised. This alkaline reaction is more pronounced if the salt has been powdered immediately before heating than if it has been kept for some time before heating. This is taken to mean that the surface of a freshly-powdered crystalline solid rapidly becomes less, *i.e.*, smoother, on being kept in air.

R. CUTHILL.

Search for the sixth alkali [metal]. E. MURMANN (Oesterr. Chem.-Ztg., 1926, **29**, 226—227).—In the course of the unsuccessful search for a sixth alkali metal, the cæsium line 3861·5 was detected in cigar ash, North Sea water, commercial magnesium chloride, rubidium alum, hay ash, and fungi, but not in cæsium alum, potash from beet molasses, and the mother-liquors from oxalic acid and lithium salt preparations.

J. W. BAKER.

Laue-photograph taken with a long slit. U. YOSHIDA and K. TANAKA (Nature, 1926, **118**, 912—913).—Divergent X-rays starting from the focus on the molybdenum target of a Coolidge tube are passed through a long, narrow slit, and then illuminate a long, thin crystal. The Laue spots thus become an assemblage of lines, each point on any one of which corresponds with a certain part of the specimen. Such correspondence may be observed by the shadows cast by thin lead wires across the slit very near to the specimen. The orientation of the atomic plane of the crystal which causes a diffraction line, and the glancing angle of the beam of X-rays to the atomic plane can then be calculated at each corresponding point on the specimen, and the indices of an atomic plane responsible for a diffraction line can readily be found. Measurements with single-crystal aluminium wires are recorded; the angles between the axis of the wire and the three edges of the elementary cubic lattice of the crystal are nearly the same for six specimens, and one of the (100) planes of the crystal is situated nearly parallel to the axis of the wire.

A. A. ELDRIDGE.

X-Ray method of determining coefficient of expansion at high temperatures. K. BECKER (Z. Physik, 1926, **40**, 37—41).—The Debye-Scherrer method was used and the preparation was heated by means of an electric current through a tungsten wire. For tungsten, the linear coefficient from 18° to 2200°= $7{\cdot}5\times10^{-6}$, from 18° to 1750°=$6{\cdot}6\times10^{-6}$, from 18° to 1380°=$5{\cdot}8\times10^{-6}$. For zircon, silicon, silicon carbide, and the Nernst filament the values are 4·5, 3·55, 6·25, and $10{\cdot}7\times10^{-6}$, respectively, to the temperatures 1300°, 950°, 1200°, and 2000°.

E. B. LUDLAM.

Intensity of reflexion of X-rays by powdered crystals. I. Sodium chloride, and sodium, lithium, and calcium fluorides. II. Effect of crystal size. R. J. HAVIGHURST (Physical Rev., 1926, [ii], **28**, 869—881; 882—890).—I. Structure factor curves for fluorine in the three fluorides are almost identical, but for sodium in the fluoride and chloride there is a difference.

II. An examination of the necessity for extinction corrections in single crystal measurements.

A. A. ELDRIDGE.

Atomic radii. II. M. L. HUGGINS (Physical Rev., 1926, [ii], **28**, 1086—1107).—The atomic radius is defined as the distance between the nucleus and a point midway between the positions" of the single electrons constituting a valency electron pair. The interatomic distance is then equal to the sum of the two atomic radii only when there is a valency pair on the straight line joining their centres. Further, the radii of the same element in different crystals are the same only when the atoms of the element are structurally similar and are similarly surrounded in the two crystals. Hence many crystal structure determinations are valueless for the calculation of accurate atomic dimensions; new values which the author obtains depend on certain approximations and assumptions. Comparable values of atomic radii have been calculated for a number of elements, and approximate values have been obtained for others. Diameters of the hydrogen atom vary from 1·02 Å. in potassium hydrogen fluoride to 1·7 Å. in ammonium bromide.

A. A. ELDRIDGE.

Relation between lattice constants and densities in nickel steels. A. ŌSAWA (Sci. Rep. Tohoku Imp. Univ., 1926, **15**, 619—630).—See A., 1926, 564.

Recrystallisation of copper wire. E. SCHMID and C. WASSERMANN (Z. Physik, 1926, **40**, 451—455).—Copper wire hard drawn shows no change in X-ray photographs until heated at about 100°, when recrystallisation begins, a simple thread-like structure being formed with the (112) direction parallel to the axis of the wire. Such wire possesses no elastic recoil.

E. B. LUDLAM.

Arrangement of micro-crystals in silver deposited by electrolysis. H. IRATA and H. KOMATSUBARA (Mem. Coll. Sci. Kyoto, 1926, **10**, 95—109, and Z. anorg. Chem., 1926, **158**, 136—152).—Silver was deposited electrolytically on rolled silver plates from solutions of the nitrate containing free nitric acid. The crystals tend to take up a fibrous arrangement, in which the axis of the fibre is parallel to the diagonal of a cube face in the cubic

lattice, but in which the orientation about this axis is haphazard. *X*-Ray photographs taken before and after treating the deposit with nitric acid showed that the above structure exists through the whole fibre, and not merely on the surface. Some specimens showed grains oriented at random as well as those in the fibrous arrangement. W. HUME-ROTHERY.

Atomic structure of AgMg and AuZn. E. A. OWEN and G. D. PRESTON (Phil. Mag., 1926, [vii], **2**, 1266—1270).—The crystal structure of the compound AgMg has been determined both by means of an *X*-ray spectrometer and by the powder method, using a Müller camera. Both methods show a simple cubic structure for the compound, the parameters being 3·28 and 3·27 Å., respectively, by the two methods. The density of the material was determined as 6·2, which leads to the result that one atom of silver and one of magnesium are associated in the unit cell. When the material was etched before examination with the spectrometer, a spectrum was obtained corresponding with a face-centred cube of side 4·076 Å. This is in fair agreement with the value obtained by McKeehan (A., 1923, ii, 428) for the parameter of the silver lattice, and indicates that the etching medium dissolved out the magnesium from the body-centred lattice and that the silver atoms recrystallised at the ordinary temperature on a face-centred lattice. The compound AuZn shows a simple cubic structure of parameter 3·19 Å., there being one atom each of gold and zinc in the unit. Both structures are therefore of the cæsium chloride type.
A. E. MITCHELL.

Crystal structure of beryllium, zinc, cadmium, and mercury tellurides. W. ZACHARIASEN (Z. physikal. Chem., 1926, **124**, 277—284).—The crystal structure of these substances was investigated by means of the powder method. All four tellurides crystallise regularly, with the zinc-blende structure. The lengths (in Å.) of the sides of the unit cells, as determined by precision measurements, and the densities are as follows: BeTe, 5·615±0·006, 5·090; ZnTe, 6·089±0·002, 5·639; CdTe, 6·464±0·002, 5·866; HgTe, 6·434±0·003, 8·123 (cf. Hartwig, A., 1926, 664; de Jong, *ibid.*, 996). L. F. GILBERT.

Form and energy of crystalline sodium nitrate. J. TOPPING and S. CHAPMAN (Proc. Roy. Soc., 1927, **A**, **113**, 658—673; cf. A., 1926, 664).—Calculations of the kind made by Lennard-Jones and Dent (following abstract), of the energy in various configurations corresponding with the "intrinsic" repulsive forces between the atoms of a crystal of the calcite type have been used, in conjunction with the values of the electrostatic energy given previously (*loc. cit.*), to determine the total energy of the sodium nitrate crystal in various possible configurations, this total energy being reckoned from a state of infinite dispersion of the sodium ions and nitrate ionic groups. If a slight change in the repulsive force data given by Lennard-Jones and Dent is made, the series of possible stable configurations is found to pass through the actual measured configuration. The corresponding value of b (the distance between the nitrogen ion and the force-centres of the asymmetric oxygen ions of a nitrate group) is 0·96 Å. The source of discrepancy between this value and the value 0·72 Å. given previously (*loc. cit.*) is probably due to a slight variation, during the special type of virtual displacement of the crystal in which the size of the nitrate group is assumed fixed, in the energy of the repulsive forces between oxygen atoms not of the same nitrate group. Similar considerations explain the discrepancy found by Lennard-Jones and Dent with calcium and magnesium carbonate crystals.
L. L. BIRCUMSHAW.

Theoretical determinations of the structure of carbonate crystals. I and II. J. E. LENNARD-JONES and (MISS) B. M. DENT (Proc. Roy. Soc., 1927, **A**, **113**, 673—689, 690—696).—I. From a knowledge of the intrinsic repulsive forces between all the constituent ions, the potential energies of calcium and magnesium carbonate crystals are calculated for all possible configurations. The function passes through a minimum, which corresponds with the most stable arrangement. For a carbonate group of given size, this direct method determines the size and angle of the rhombohedral cell, and also furnishes an absolute value for the crystal energy, a quantity not yet determined by any other method. The potential energy per mol. of the crystal is given by $W=W^{(c)}+W^{(n)}$, where $W^{(c)}$ is the energy due to the electrostatic forces (cf. Chapman, Topping, and Morrall, A., 1926, 664), and $W^{(n)}$ the contribution of the repulsive forces. A detailed description is given of the method of calculation. The distance b between a carbon ion and the force centre of an oxygen ion in the same carbonate group is regarded as an adjustable parameter to be determined theoretically. The value 1·08 Å. gives the best agreement between theory and experiment, for both calcium and magnesium carbonate. The values of the crystal parameters, corresponding with this value of b, are: for magnesium carbonate, rhombohedral angle 102° 24′ (calc.), 103° 21·5′ (obs.); distance between carbon ions 4·66 (calc.), 4·61 Å. (obs.); crystal energy per g.-mol. 771 kg.-cal.; and for calcium carbonate, rhombohedral angle 102° 18′ (calc.), 101° 55′ (obs.); distance between carbon ions 4·96 (calc.), 4·96 Å. (obs.); crystal energy per g.-mol. 701 kg.-cal. It is found that no improvement is obtained in the agreement between the theoretical and experimental values on the assumption that the centre of the repulsive forces of the oxygen ion does not coincide with that of the electrostatic forces.

II. On the assumption that b=1·08 Å. for the crystals of calamine, chalybite, rhodochrosite, and cadmium carbonate, and that the repulsive forces operating between the ions of these crystals are represented by inverse power laws, the numerical values of the force constants may be calculated, provided that the indices of repulsion are known. A formula is given for calculating the work required to separate one g.-mol. of a crystal of the calcite type into its metallic ions and carbonate groups (U), which is a function of two unknowns only, μ_{12} and n_{12}, the force constant and index, respectively, which determine the repulsive forces between the metallic ions and the carbonate groups. For calamine and chalybite, two sets of values are given for U, corresponding with the two alternative cases n_{12}=10 and n_{12}=11.

Thus, for calamine, if $n_{12}=10$, $U=772$ g.-cal./g.-mol., if $n_{12}=11$, $U=777$ g.-cal./g.-mol.; for chalybite, if $n_{12}=10$, $U=759$ g.-cal./g.-mol., if $n_{12}=10$, $U=765$ g.-cal./g.-mol. For manganous and cadmium carbonates, $n_{12}=11$, and $U=750$ and 719 g.-cal./g.-mol., respectively. L. L. BIRCUMSHAW.

Crystal structure of ammonium hexachloroplumbate, $(NH_4)_2PbCl_6$. R. W. G. WYCKOFF and L. M. DENNIS (Amer. J. Sci., 1926, [v], **12**, 503—509).—*X*-Ray powder photographs of ammonium chloroplumbate indicate that it forms a face-centred cubic lattice with odd order reflexions only from planes with all odd indices. The length of the edge of the unit cube containing four molecules is 10·14 Å. The experimental value for the density obtained by using benzene as the wetting liquid is 2·6; $d_{calc.}$ is 2·89. The structure is similar to that of the platinum, tin, and silicon analogues. M. S. BURR.

Crystallographic investigations on certain heteropoly-compounds. F. RODOLICO (Atti R. Accad. Lincei, 1926, [vi], 4, 471—475).—Compounds of the series $(NH_4)_6H[X(W_2O_7)_x(V_2O_6)_y],nH_2O$, in which X is either P or As and x and y are variable but have the sum 6 for any one compound, crystallise in the tetragonal system. For the one limiting (α) compound of the phosphorus series, containing 40·06% WO_3 and 32·86% V_2O_5, the axial ratio is $a:c=1:0{\cdot}9932$, and for the other (ω), containing 64·22% WO_3 and 12·09% V_2O_5, $a:c=1:1{\cdot}0011$. The corresponding values for the arsenic series are, for the α-compound, with 40·26% WO_3 and 31·60% V_2O_5, 1 : 0·9994, and for the ω-compound, with 63·28% WO_3 and 13·06% V_2O_5, 1 : 1·0011. Hence, geometrically these crystals may be regarded, within the limits of experimental error, as possessed of monometric symmetry. The two series of crystals are isomorphous, and as, moreover, the radical W_2O_7 may be partly replaced by Mo_2O_7, arsenophosphomolybdotungstovanadates, containing five acid radicals, are obtainable; these compounds exhibit almost unchanged the crystalline characters of the simpler ones.

The crystals of the silicotungstates, studied by Wyrouboff (A., 1897, ii, 173), exhibit marked morphological analogy with those described above.

T. H. POPE.

Symmetry of sylvine and the nature of its etching figures. K. F. HERZFELD and A. HETTICH (Z. Physik, 1926, 40, 327—330; cf. A., 1926, 889; Valeton, *ibid.*, 1085).—The right and left groups of the six-faced octahedron are stereochemically different and would behave differently towards optically active impurities. It is claimed that the plagihedry of potassium chloride has not been proved.

E. B. LUDLAM.

Structure of phenacite, Be_2SiO_4. W. L. BRAGG (Proc. Roy. Soc., 1927, **A**, **113**, 642—657).—Twenty-one parameters are required to define the structure of phenacite. An attempt has been made to measure the fifteen parameters determining the positions of the silicon and oxygen atoms. Knowledge of other structures is used to suggest a series of possible configurations of the crystal, the SiO_4-group being assumed to be distinct, and to have the same form as in other orthosilicates. These configurations are tested by their capacity to explain the reflecting powers of the crystal planes. All experimental observations of reflecting power are expressed as absolute values, and interpreted by means of Darwin's formula for reflexion by an imperfect crystal, which for phenacite is $F=11{\cdot}65\sqrt{\{\sin 2\theta/(1+\cos^2 2\theta)\}(\rho\times 10^6)}$, ρ being the integrated reflexion $E\omega/I$, measured by rotating the crystal at constant angular velocity, ω. It is believed that the method of using absolute measurements leads directly to a close approximation of the structure. The following measurements were made on the crystal: (*a*) a rotation photograph with the trigonal axis vertical; (*b*) an absolute determination of intensity of reflexion by the planes (111), (11$\bar{0}$), (11$\bar{2}$), (110), (100) for a number of orders; and (*c*) a relative determination of intensity for about fifty planes round the trigonal axis. The crystal belongs to the space-group C_{3i}^2; the space lattice is rhombohedral, with $a=7{\cdot}17_8$, $b=7{\cdot}66_4$, $c=8{\cdot}22_6$ Å.; the unit cell contains six molecules, each occupying a volume of 61 Å.^{3} The proposed structure is built up as follows: four parallel rows of oxygen atoms at intervals of 2·74 Å. are placed together so that a column of Y-shaped section results; two sets of these composite columns are packed together, one set being displaced 1·37 Å. parallel to its length relatively to the other; the silicon atoms lie at the centres of tetrahedral groups of oxygen atoms, similar positions being probably occupied by the beryllium atoms.

L. L. BIRCUMSHAW.

Formation of mixed crystals by precipitation. G. LUNDE (Ber., 1926, 59, [*B*], 2784—2786; cf. Barth and Lunde, A., 1926, 895).—Addition of potassium iodide to a cold solution of silver nitrate and copper sulphate causes the precipitation of homogeneous mixed crystals of silver and cuprous iodides. With potassium bromide and iodide, silver nitrate gives mixed crystals of the silver bromide type if 50% or less of silver iodide is present, whereas if the proportion of silver iodide exceeds this amount, two forms of mixed crystals (silver bromide and zinc sulphide types) are simultaneously produced. The mixed crystals obtained by addition of thallium carbonate to potassium iodide and bromide are of the cubic or rhombic type, according to the relative proportion of thallous bromide and iodide. The double *salt*, 2AgCl,3TlCl, is described. H. WREN.

X-Ray analysis of crystal structures and its relation with chemical constitution. W. L. BRAGG (Deuxième Cons. Chim. Inst. Intern. Chim. Solvay, 1926, 44—65). CHEMICAL ABSTRACTS.

Organic crystals. W. H. BRAGG (Deuxième Cons. Chim. Inst. Intern. Chim. Solvay, 1926, 21—27). **Tables [of cleavage spacings] relating to long-carbon-chain derivatives.** A. MULLER (*ibid.*, 27—29). G. SHEARER (*ibid.*, 29—38). **Succinic acid etc.** (MISS) K. YARDLEY (*ibid.*, 38—41). **General list of organic crystals.** W. T. ASTBURY (*ibid.*, 41—43). CHEMICAL ABSTRACTS.

Orientation in solids. G. SHEARER (Trans. Faraday Soc., 1926, **22**, 465—468).—See A., 1926, 1195.

X-Ray evidence for the existence of different modifications of fatty acids. G. M. DE BOER (Nature, 1927, **119**, 50).—Stearic acid, obtained by slow crystallisation from acetone, alcohol, or petroleum, shows a long spacing of 43·95 Å., whilst a thin layer obtained by fusion or by the evaporation of an alcoholic solution gives a spacing of 39·75 Å. Thus the existence of different modifications of stearic acid is indicated. The long spacing of undecoic acid is 25·4 Å. at 20°, and 30·1 Å. at 12·5°, supporting the results of Garner and Randall (A., 1924, ii, 385) and Garner and Ryder (*ibid.*, 1925, ii, 355). A. A. ELDRIDGE.

Various crystalline forms of long-chain organic compounds. Difficulties in the interpretation of their X-ray spectra. J. THIBAUD (Compt. rend., 1927, **184**, 24—26).—Measurements of the X-ray spectra of pure stearic acid indicate that it can crystallise in various forms having carbon chains of different lengths (cf. Piper, Malkin, and Austin, A., 1926, 1083). Similar measurements with mixed fatty substances (such as butters), with the mixed fatty acids obtained by hydrolysing them, and with their lead soaps, indicate that the method may be used to distinguish between the various types of butter. The analytical interpretation of the results is complicated by the variation of the value of the crystal spacing according to the origin, method of preparation, and purity of the substance. This is especially true for mixtures, particularly of substances of similar nature and having the same number of carbon atoms in the molecule. When heavy atoms are introduced into the chain (as in the case of lead soaps), the variations are less. J. GRANT.

X-Ray examination of the crystal structure of certain compounds. A. N. SARKAR (Phil. Mag., 1926, [vii], 2, 1153—1165).—Examination of the crystal structure of pyrocatechol by the powder method indicates that the basic lattice is Γm, there being 2 molecules per unit cell. The space-group is C_{2v}^4. The molecules should thus possess an element of symmetry which can be either a centre of symmetry or an axis of binary symmetry; the data are not sufficient to differentiate between the alternatives. The translation of the glide plane parallel to itself is $c/2$, so that the molecules are most densely packed in the (100) plane, thus accounting for the fact that the direction of cleavage is parallel to the (100) plane. Examination of a crystal of potassium ferricyanide by Laue's method shows that the basic lattice is Γm, that the molecules are asymmetric, and that the space-group is either or C_{2h}^3, according as the axis of symmetry is a simple or a screw axis. The Laue photograph of aluminium acetylacetonate, together with some measurements of Astbury, shows that the space-group is , with a screw-axis of symmetry and 4 molecules per unit cell. A. E. MITCHELL.

X-Ray study of isomorphism in simple organometallic series. I. Tetraphenyls. W. H. GEORGE (Proc. Roy. Soc., 1927, **A**, **113**, 585—593).—Crystals of carbon, silicon, germanium, tin, and lead tetraphenyl, examined by the rotating and oscillating single-crystal methods, using the $K\alpha$ radiation from a copper anticathode, and employing Bernal's method of interpretation (this vol., 9), yield X-ray photographs which are identical, except for intensity and small dimensional variations. The unit cell contains 2 molecules, having a tetrad alternating axis of symmetry parallel to the c axis of the crystals. The dimensions of the unit cell are: for the carbon compound, a=10·86, c=7·26 Å.; for the silicon compound, a=11·32, c=7·03 Å.; for the germanium compound, a=11·60, c=6·85 Å.; for the tin compound, a=11·83, c=6·42 Å.; and for the lead compound, a=12·06, c=6·50 Å. Thus the size of the square base of the cell increases with increase of atomic number of the grouping element, whilst the height of the cell decreases. The molecules lie very nearly in the (110) planes, consistent with the marked development of the (110) faces, and although the space-group is D_{2d}^1, the structure approximates very closely to that of the space-group which has a plane of symmetry parallel to the (110) plane. The grouping atoms of the molecules lie at the corners and at the centre of the cell, and the phenyl groups are very nearly bisected by the (110) planes, and probably lie near the direction of the shortest distance between the metallic atoms. L. L. BIRCUMSHAW.

Space-group and molecular symmetry of β-benzene hexabromide and hexachloride. S. B. HENDRICKS and C. BILICKE (J. Amer. Chem. Soc., 1926, **48**, 3007—3015).—X-Ray examination of the cubic β-(or *cis*-)modifications of the hexachloride or hexabromide of benzene showed them to have the atomic arrangement of the space-group T_h^6, the molecular symmetry being that of the point-group C_{3i}. The unit cubes contain 4 molecules, the edge being 10·07 for the chloride and 10·42 Å. for the bromide. These structures do not eliminate the possibility that the carbon or the halogen atoms are coplanar, but, neglecting this specialisation, the arrangement of 4, 5, or 6 atoms on the same side of the plane of the molecule would not give the correct symmetry. The structures given by Friedel (A., 1891, 1196) are considered to be incorrect. The conclusions are not in agreement with Mohr's theory of strainless rings as applied to *cyclo*hexane and its derivatives (*ibid.*, 1919, ii, 229). S. K. TWEEDY.

Crystalline forms of 5-nitrosalicylic acid and of related compounds. F. D. CHATTAWAY and W. R. C. CURJEL (J.C.S., 1926, 3210—3215).—By cooling slowly, to the ordinary temperature, a hot, saturated, aqueous solution of 5-nitrosalicylic acid, a hitherto unrecognised *monohydrate* has been separated as very slender, strongly doubly-refracting, elongated, and almost colourless prisms, which readily lose water on exposure to air. Dilatometric and solubility measurements indicate that the transition point is in the neighbourhood of 42·5°. Details of the crystalline structure of the anhydrous form are given, but do not agree with those observed by Fels (Z. Krist., 1903, **37**, 486). No measurable crystals of the hydrated form have been obtained, but they are probably orthorhombic. Crystallographic details are also given for ethyl 5-nitrosalicylate, m. p. 96°, d^{19} 1·429, and for the stable modification of 5-nitro-2-ethoxybenzaldehydesemicarbazone. The crystals of the labile form, which are unsuitable for

measurement, are slender, strongly doubly-refracting prisms. M. S. BURR.

The crystal as a homogeneous polyhedron and the relations between the physical properties of crystals and the various groups of geometrical crystallography. J. BECKENKAMP (Z. Physik, 1926, **40**, 237—254).—Crystal nomenclature, types of symmetry, electrical polarity, enantiomorphy, transmission of light, and elastic deformation are discussed from the point of view of the space lattice. E. B. LUDLAM.

Magneto-spectroscopic investigations on nickel wires with short Hertzian waves. H. ISRAEL (Z. Physik, 1926, **39**, 841—857).—Waves from 30 cm. to 2 metres in length were produced by means of a quenched spark and measured by means of Lecher wires. By a comparison of the decrement of the oscillations in nickel wire, magnetised and unmagnetised, with that of copper, the permeability of the nickel wires could be calculated for the different wave-lengths; these are given in tables and the curves are plotted; they are complicated, but less so for the thinner of the two wires used than for the thicker. E. B. LUDLAM.

Apparent doubling of the optic axis of calcite by means of Federov's plate. (MISS) M. PHILIBERT (Atti R. Accad. Lincei, 1926, [vi], **4**, 376—381).—This phenomenon (cf. this vol., 10) is shown to be due to the anisotropy of the spherical segments of Federov's plate, which behave like a biaxial doubly-refracting substance. Far from being negligible, this double refraction of the segments gives axial angles of 11° and 14° in the two cases considered. T. H. POPE.

Increase of tensile strength of single crystals by plastic deformation. E. SCHMID (Z. Physik, 1926, **40**, 54—74).—The increase of strength of the main faces of slip in zinc crystals caused by plastic extension has been investigated; after passing the elastic limit, the strength increases linearly with the extension. The shape of the extension curve for single crystals depends on the angle between the slip and the direction of the applied force. The group of curves relating the force in the main plane of slip to the extension can be represented by a single line, almost straight. A comparison is obtained for the increase in strength along the actual planes of slip and the latent planes (which cut the former) for crystals of zinc and tin; if the two planes are crystallographically identical, the increase of strength is less in the actual than in the latent planes; for zinc, in which the planes are not the same, the increase is greater in the main actual plane of slip. E. B. LUDLAM.

Variation of mol. wt. of lead with temperature. A JOUNIAUX (Bull. Soc. chim., 1926, [iv], **39**, 1680—1686).—It is shown that, above 450°, the molecule of lead is monatomic, and that below it is associated somewhat. The mol. wt. was determined cryoscopically at a number of temperatures between 450° and 1850° by using various metals as solvents, and the values are distributed irregularly about the atomic weight of lead, the anomalies being explained by the formation of mixed crystals. The mol. wt. at the b. p. deduced from latent heat data, and also the vapour-density values, indicate a monatomic molecule above 450°. The mol. wt. below 450° was obtained both ebullioscopically, using mercury as solvent, and also from surface-tension data, using the Eotvös–Ramsay equation. Thence, on the assumption that lead is monatomic at high temperatures, its critical temperature is calculated to be approximately 2200°; by inserting this value in the equation, the mol. wt. is calculated at lower temperatures, and is found to increase from 207·2 at 500° to 285·7 at 327°. S. J. GREGG.

Mol. wt. of egg-albumin. I. In electrolyte-free condition. T. SVEDBERG and J. B. NICHOLS (J. Amer. Chem. Soc., 1926, **48**, 3081—3092).—The method of determining atomic weights by the ultra-centrifuge (A., 1926, 340, 677) is adapted so as to be applicable to colourless proteins. By this modified method, the mol. wt. of egg-albumin, purified by electro-dialysis, is found to be 34,500±1000 in electrolyte-free solutions. Moderately pure egg-albumin contains a small amount of a substance of mol. wt. 170,000, probably unprecipitated globulins. S. K. TWEEDY.

Influence of pressure on electrical conductivity of platinum. A. MICHELS and P. GEELS (Proc. K. Akad. Wetensch. Amsterdam, 1926, **29**, 1106—1112).—A platinum-resistance thermometer was used and its resistance determined at 15·57°, 21·95°, and 34·75° at pressure intervals up to 251·5 kg./cm.^{2} The results differ from previously published data in that the pressure coefficients vary more considerably with the pressure, and at lower pressures the coefficient varies to a greater extent with the temperature. The importance of this for the measurement of temperature by means of the platinum-resistance thermometer is pointed out. E. S. HEDGES.

Hall effect in bismuth sputtered films. T. F. HARGITT (Physical Rev., 1926, [ii], **28**, 1034—1037).

Determination of optical constants of metals in the visible and ultra-violet. G. PFESTORF (Ann. Physik, 1926, [iv], **81**, 906—928).—A method of examining the light polarised by reflexion from metallic surfaces has been described which enables the refractive index and absorption coefficient to be evaluated. These constants have been determined over the range 250—600 for copper, gold, zinc, silicon, manganese, nickel, and a steel. Considerable discrepancies found between the results of earlier workers are traced to variations in the degree of polishing and alterations in the chemical condition of the metallic surface. Adsorption of liquid films has been investigated in relation to the reflexion of light by nickel and copper mirrors. The high polish necessary for trustworthy results was obtained by a process, not disclosed, due to the firm of Zeiss. The effect of high polish is much greater than that due to adsorption. R. A. MORTON.

Applicability of discharge tubes containing noble gases as photometers. H. KNIEPKAMP (Z. Physik, 1926, **40**, 12—36).—The method consists in counting the number of flashes per sec. produced when the light to be measured falls on the discharge tube. The mean number of flashes is proportional

to the intensity of the light. A dark effect was traced to impurities, probably remains of water vapour or air in the bulb. The method is described in detail. Comparison showed that the method of counting flashes was several thousand times more sensitive than using the bulb as a photo-electric cell in the ordinary way, *e.g.*, a normal candle produced one flash per sec. at a distance of 5 metres; a mercury vapour lamp would produce one per sec. at about 150 metres distance. E. B. LUDLAM.

Deviation from Lambert's law and polarisation of light emitted by incandescent tungsten, tantalum, and molybdenum, and changes in the optical constants of tungsten with temperature. A. G. WORTHING (J. Opt. Soc. Amer., 1926, **13**, 635—649).—The deviations from Lambert's cosine law for the light emitted by tungsten, molybdenum, and tantalum are of the same order. The brightness increases from the normal value at normal emergence gradually with increase in emergence angle to about 75° by 20%, and then decreases rapidly to 0 at grazing emergence. Straight filaments of circular cross-section have average brightnesses, viewed normal to their axes, which are greater than the normal brightness by 2·8% for tungsten, 3·6% for molybdenum, 2·7% for tantalum. The average brightness of a filament considering all directions is about 5% greater than the normal brightness. The polarisation of the light emitted, which is zero for normal emergence, increases with angle of emergence to about 95% at grazing emergence, and, for straight circular filaments viewed normal to their axes, is about 20%. The values of the optical constants n and k for tungsten were found to be 3·86 and 0·81 at 300° Abs., and 3·85 and 0·89 at 1900° Abs. C. J. SMITHELLS.

Polishing of surfaces. F. W. PRESTON (Nature, 1927, **119**, 13).—In the polishing of glass, the amount of material removed corresponds with a solid layer of the order of ten wave-lengths in thickness. The efficiency of the operation, on the assumption that the energy is required for liquefying a thin surface layer, is not more than about 0·5%. The process is regarded as primarily one of abrasion (cf. Macaulay, A., 1926, 998). A. A. ELDRIDGE.

High-temperature thermometer. [Properties of gallium.] S. BOYER (J. Opt. Soc. Amer., 1926, **13**, 117—122).—Details are given for constructing a thermometer in which the glass and mercury of the ordinary type are replaced by fused quartz and gallium, respectively. Temperatures up to 1000° may be measured; the position of the lower limit depends on the fact that liquid gallium is easily undercooled below the m. p. (29·7°); undercooling to −20° was often observed. The removal of gas from liquid gallium and the effect of impurities on the amount of undercooling and on the tendency to wet quartz have been investigated. The ease of surface oxidation of gallium is greater than is reported in the literature. L. F. GILBERT.

Determination of high temperature by the effusion and transpiration of gas. Y. YAMAGUCHI (Bull. Chem. Soc. Japan, 1926, **1**, 209—215).—For the measurement of high temperature, three methods are given, depending on the rate of flow of gases. The first requires the measurement of t, the time of effusion of a given volume of gas through a quartz tube, and from the relation $t=a+b\sqrt{T}$ (where a and b are constants) temperatures up to 1000° can be determined. In the second method, also applicable up to 1000°, the temperature is found from the expression $\log T=a+b\log t+c(\log t)^2$, where t is the rate of transpiration of gas through a quartz capillary tube and a, b, and c are constants. The temperature of the transpiring gas may also be determined by observation of the increase of pressure p required to maintain a constant rate of flow with elevated temperature. In this case, the relation $\log p=a\log T+b$ (where a and b are constants) obtains up to 1200°. A. S. CORBET.

Method for obtaining very low temperatures. F. SIMON (Physikal. Z., 1926, 27, 790—792).—The liquefaction of gases would be easy if the less volatile gas (*e.g.*, hydrogen) could be so far removed by pumping that the temperature would fall below the critical point of the more volatile gas (*e.g.*, helium). The lowest point attained by pumping off hydrogen (9°) is still well above the critical temperature (5·2°) of helium. This and similar gaps can be bridged by a new device. A vessel containing gas-free carbon is connected to a vessel containing helium. The preliminary cooling is carried out by means of liquid hydrogen and the temperature reduced as far as possible by pumping off hydrogen. Helium is then passed into the cold charcoal under a few atm. pressure. The considerable heat of adsorption is taken up by the hydrogen in the surrounding Dewar flask. On bringing the vessel into thermal isolation and pumping off the adsorbed helium, the temperature of the charcoal falls. Using 17 litres of helium, 15 g. of charcoal, 8 litres of helium were adsorbed, and in a few seconds after beginning to pump off the gas the temperature fell to 7° Abs. and in a few minutes to below 4° Abs. The high degree of cold can be maintained for a few hours. There are serious difficulties in the way of making a continuous process employing the new principle. R. A. MORTON.

Measurement of true specific heats at high temperatures. H. KLINKHARDT (Z. Elektrochem., 1926, **32**, 534—535).—The substance, preferably in the form of a short cylinder, is made the anode in an evacuated glass vessel and subjected to bombardment by electrons from a neighbouring cathode consisting of platinum foil coated with an alkaline-earth oxide or a tungsten wire coated with thoria. A cage around the electrode system minimises energy losses due to reflexion of the electrons. The current may be a few milliamps. at 100—200 volts, but it is important that the pressure should be at least as low as 10^{-4} mm. Under these conditions, the kinetic energy of the electrons is converted almost entirely into heat in the anode. The rise in temperature of the latter due to the transfer of a measured amount of energy during a short period of bombardment is measured by a thermocouple in contact with the anode. Data obtained for nickel over the range 100—450° are recorded on a graph; the accuracy is about 0·5%. Materials which are insulators or have

high vapour pressures can be dealt with if sealed in a metal container, but the accuracy is less than with metals. Values for the specific heat and the heat of transition of ammonium chloride are recorded.

H. J. T. ELLINGHAM.

Specific heats of a highly cooled, non-condensed phase. N. PERRAKIS (Compt. rend., 1927, **184**, 28—30).—Starting from the revised form of Trouton's rule, the author has confirmed, by means of simple thermodynamical considerations, Perrin's conclusion that all gases cooled sufficiently have molecular heats equal to those of monatomic gases.

J. GRANT.

Six-place tables of the Debye energy and specific heat functions. J. A. BEATTIE (J. Math. Phys. Mass. Inst. Tech., 1926, **6**, 1—32).—The values of $\frac{1}{3}UR^{-1}T^{-1}$ and of $\frac{1}{3}C_vR^{-1}$ have been computed as functions of the argument x ($=h\nu_m k^{-1}T^{-1}$, where ν_m is a frequency characteristic of the substance) in the range 0—24 in increments of 0·1. For values of x greater than 24, an error of less than one in the sixth significant figure is introduced by using $\frac{1}{3}UR^{-1}T^{-1}=19{\cdot}481818x^{-3}$, and $\frac{1}{3}C_vR^{-1}=77{\cdot}92727x^{-3}$.

R. W. LUNT.

Latent heat of fusion. N. VON RASCHEVSKY (Z. Physik, 1926, **40**, 214—219).—Proceeding from the assumption that the liquid state is reached when the distance between the atoms becomes so great that the elastic modulus becomes zero, the second differential of the lattice energy in respect to lattice constant becoming zero, the value of the latent heat of seven metals is calculated and is in satisfactory agreement with experiment. E. B. LUDLAM.

Determination of the latent heat of vaporisation of liquid helium. L. I. DANA and H. K. ONNES (Proc. K. Akad. Wetensch. Amsterdam, 1926, **29**, 1051—1060).—A simple method is described by means of which the latent heat of vaporisation of liquid helium has been measured for pressures at and below 1 atm. The results show that the curve representing the heat of vaporisation as a function of temperature shows a maximum near 3° Abs. and descends again at lower temperatures. This agrees with the values of latent heat derived by application of the Clapeyron–Clausius formula to the data of other workers. The behaviour of the saturated vapour deviates appreciably from the ideal gas laws. An anomaly was noticed at the temperature of maximum density. E. S. HEDGES.

Determination of the specific heat of liquid helium. L. I. DANA and H. K. ONNES (Proc. K. Acad. Wetensch. Amsterdam, 1926, **29**, 1060—1068).—An apparatus is described for measuring with an accuracy of about 3% the specific heat of liquid helium and its variation with temperature for saturation pressures at and below 1 atm. The method of following the rise in the temperature of the liquid on heating was to determine the rise in vapour pressure. A table is given showing the specific heats at different temperatures; these values, when plotted, tend to lie on a straight line. E. S. HEDGES.

Heats of vaporisation of condensed gases at low pressures. A. EUCKEN and E. DONATH (Z. physikal. Chem., 1926, **124**, 181—203).—A method of determining heats of vaporisation or sublimation is described which depends on the measurement of heats of condensation and is applicable at pressures as low as 1 mm. Liquid and solid ammonia, solid carbon dioxide, nitrous oxide, and hydrochloric acid were investigated. Giacomini's value for the heat of vaporisation of ammonia (A., 1925, ii, 757) was not confirmed. The heats of vaporisation of carbon dioxide and nitrous oxide accord with the hypothesis that the molecules of these gases have open structures (cf., for carbon dioxide, A., 1922, ii, 349, 805). The data obtained for ammonia and carbon dioxide allow the integration constant i in the vapour-pressure formula to be directly calculated (cf. *ibid.*, 1925, ii, 98); for carbon dioxide, the value is the same as previously obtained (*loc. cit.*), but for ammonia it is somewhat less.

L. F. GILBERT.

Degree of polymerisation of vapours at the b. p. V. KIREJEV (Z. anorg. Chem., 1926, **157**, 138—140; cf. A., 1926, 1088).—Reasons are given for supposing that the molecular heat of vaporisation in the usual expression for Trouton's constant K is that of the vapour, not that of the liquid. Hence by comparing the observed values with those calculated by means of the equation $K=f(T_s)$, where T_s is the b. p., the mol. wt. of the vapour can be calculated. For a number of liquids, the results are in good agreement with the values obtained from the ebullioscopic constant and vapour pressure. In some instances, the opposing effects of association of the liquid and polymerisation of the vapour may cause Trouton's constant to have its theoretical value. R. CUTHILL.

Heat of formation of cementite. G. H. BRODIE, W. H. JENNINGS, and A. HAYES.—See B., 1927, 14.

Influence of pressure on the crystallisation temperature of *p*-azoxyanisole and α-naphthylamine. N. A. PUSHIN and I. W. GREBENSCHTSCHIKOV (Z. physikal. Chem., 1926, **124**, 270—276; cf. Hulett, A., 1899, ii, 468).—The influence of pressure on the m. p. and transition point (temperature of change from liquid-crystalline to isotropic state) of *p*-azoxyanisole and on the m. p. of α-naphthylamine has been investigated; the maximum pressures employed were 1088, 2645, and 2995 kg./cm.², respectively. In each case, pressure is an approximately linear function of temperature. Ostwald's opinion that with increase of pressure the range of existence of liquid crystals decreases, *i.e.*, that the critical point isotropic liquid–solid may be realised experimentally, is contradicted by the data obtained for *p*-azoxyanisole.

L. F. GILBERT.

Trouton's quotients. W. HERZ (Z. anorg. Chem., 1926, **157**, 382—384).—There appears to be no corresponding temperature above the b. p. at which the ratio of the molecular heat of vaporisation of liquids to their b. p. (Abs.) is any more nearly constant than it is at the b. p. R. CUTHILL.

Rule of the three temperatures. E. VAN AUBEL (J. Chim. phys., 1926, **23**, 823).—A correction of Prud'homme's paper (A., 1921, ii, 376).

R. CUTHILL.

Relation between temperature of incipient increase in size of granules and m. p. of metals. A. A. BOTSCHWAR (Z. anorg. Chem., 1926, **157**, 319—

320).—For a number of metals the ratio of the temperature (Abs.) at which new granules commence to be formed in the metal, worked as far as possible in the cold, to the m. p. (Abs.) tends to increase with decrease in the latter temperature, but usually lies between 0·35 and 0·45. R. CUTHILL.

Temperature of commencement of internal diffusion in crystals. G. TAMMANN (Z. anorg. Chem., 1926, **157**, 321—325).—The sintering together of powders on heating is most probably due to the molecules commencing to change their places. If T is the m. p. (Abs.), the average temperature at which this change commences is for metals $0{\cdot}33T$, for salts $0{\cdot}57T$, and for organic compounds $0{\cdot}90T$. The more complicated the molecule is, the nearer does this temperature approach the m. p. R. CUTHILL.

[Temperatures of] equal internal pressure. W. HERZ (Z. anorg. Chem., 1926, **157**, 326—328).—The temperatures at which the internal pressure is 800 and 1500 atm., respectively, have been calculated for a number of liquids. The quotient of these temperatures and also that of the corresponding densities are roughly the same for all the liquids. With substances of a similar structure, the difference of the two temperatures tends to rise with rise in mol. wt. R. CUTHILL.

Transformation of the theoretical chemical constants. E. WERTHEIMER (Physikal. Z., 1926, **27**, 771—773).—Theoretical. R. A. MORTON.

Absolute density and coefficient of expansion of silicon tetrachloride. P. L. ROBINSON and H. C. SMITH (J.C.S., 1926, 3152—3153).—After the application of a correction for the coefficient of cubical expansion of the glass floats employed in determinations of the relative densities and coefficients of thermal expansion of silicon tetrachloride, prepared from siliceous material from different sources (A., 1926, 771), the absolute density of this liquid is found to be $1{\cdot}481475\pm0{\cdot}0_5 6 8$ and the absolute coefficient of thermal expansion $0{\cdot}0014044\pm0{\cdot}0_6 87$. The results do not affect the previous conclusion that silicon, in the samples obtained, shows no greater variation in atomic weight than 0·005 unit. M. S. BURR.

Gaseous methyl chloride. T. BATUECAS (Anal. Fís. Quím., 1926, **24**, 528—551; cf. A., 1925, ii, 753).—The mean value of twenty-three determinations of the weight of a normal litre of methyl chloride, obtained by the thermal decomposition of tetramethylammonium chloride, is 2·3075, compared with 2·3084 previously given by the author and 2·3045 given by Baume. The weight of the normal litre is a linear function of the pressure, and the value obtained by extrapolation to zero pressure is 2·2527. The deviation from Avogadro's law is therefore 1·0243. The author discusses the divergence between the relationships obtained from measurements of compressibility and those obtained from measurements of density at low pressures. G. W. ROBINSON.

Determination of gas density with the gas-density balance. II. Ethylene as a comparison gas. A. STOCK and G. RITTER (Z. physikal. Chem., 1926, **124**, 204—216; cf. A., 1926, 669).—Ethylene is a convenient comparison gas for density determinations, as it is easily prepared in the pure state and is almost quantitatively condensed by liquid air, a necessary property during the manipulation. Its density at 0° and 760 mm., and the necessary data concerning its deviations from Boyle's law, have been determined by means of type IV of the gas-density apparatus previously described, using oxygen as the comparison gas. The preparation of pure oxygen is discussed. L. F. GILBERT.

Dependence of density on temperature. A. PREDVODITELEV (Z. Physik, 1926, **40**, 474—476).—Polemical (cf. A., 1926, 669, 999). E. B. LUDLAM.

Recording small pressure differences. I. B. SMITH (J. Opt. Soc. Amer., 1926, **12**, 655—657).—A pair of parallel wires constituting, together with parts of the slide-wire, one arm of a Wheatstone bridge was placed in each limb of a U-tube containing a solution of an electrolyte. A difference of level of 0·00003 inch of the liquid in the limbs of the U-tube could be detected by the disturbance of the bridge equilibrium. It is suggested that the principle be applied to the recording of small pressure differences. L. F. GILBERT.

High-temperature investigations. O. RUFF and M. KONSCHAK (Z. Elektrochem., 1926, **32**, 515—525).—The previously described method for the measurement of vapour pressures at high temperatures (A., 1919, ii, 265; 1925, ii, 579) has been further tested by new measurements on copper and gold. A slight modification in the method of obtaining b. p. from the graphs of experimental data produces almost no change from previously recorded values for these metals. In an atmosphere of pure argon, trustworthy vapour-pressure data have now been obtained for alumina and silicon, crucibles of tantalum and carborundum, respectively, being used; values for silica in an iridium crucible are regarded as less accurate. The factors governing the choice of crucible materials are discussed. The following b. p. at 760 mm. are recorded: copper, 2360°; gold, 2677°; alumina, 2980°±60°; silicon, 2392°±50°; silica, 2590° (estimated minimum). Plotting $\log p$ against $1/T$ gives straight lines. The latent heats of vaporisation of alumina and silicon are estimated from the data obtained. The behaviour of carborundum was investigated in a graphite crucible glazed externally with a mixture of vanadium carbide and oxide. Examination of the residue left in the crucible showed that the vapour from carborundum contains free silicon. The total vapour pressure was measured at various temperatures and the corresponding partial pressures of silicon were calculated from analytical data. On a $\log p$–$1/T$ graph, two parallel straight lines are thus obtained. At 2717°, the total vapour pressure is 764 mm. and the partial pressure of silicon 193 mm. By the aid of the van 't Hoff reaction isochore, the heat of dissociation is calculated: $SiC=C+Si(vapour)-106{\cdot}6$ kg.-cal. whence $SiC=C+Si(solid)-25$ kg.-cal. No carbide other than SiC was recognised (between 2400° and 2700°). From the calculations of Pollitzer on the basis of the Nernst theorem, the equilibrium temperature of the system $SiO_2+3C=SiC+2CO$(1 atm.) is

1462°, whereas the experimental result obtained by heating silica and lampblack in a carbon crucible is 1635° when the carbon monoxide pressure is 1 atm. It is concluded that $SiO_2+2C=Si+2CO$ is the primary process in the formation of carborundum, for, on this basis, the equilibrium temperature is calculated to be 1612°. The formation and decomposition of carborundum in technical furnaces and the significance of data recorded in the literature for the operation of these furnaces are discussed.

H. J. T. Ellingham.

Vapour pressures and m. p. of sodium and potassium. W. Edmondson and A. C. G. Egerton (Proc. Roy. Soc., 1927, **A**, 113, 520—533; cf. A., 1923, ii, 491).—The vapour pressures of otassium between 100° and 200° and of sodium etween 220° and 300° have been measured by the effusion method previously used (*loc. cit.*). Pyrex glass vessels were used, and the action of sodium on these was found to be mainly due to metal absorbed by the glass at the temperatures of the experiments. The effect on the results was negligible. A new type of air regulator is described, involving the use of a wireless valve. The results are compared with those of previous investigators, and it is found that the equation $\log p$ (mm.)$=-4507{\cdot}0/T+7{\cdot}3447$ represents the results for potassium with sufficient accuracy, whilst the equation $\log p=-5573{\cdot}2_7/T+9{\cdot}7255-0{\cdot}6794\log T$ is in close accord with the results for sodium obtained by the authors and by previous workers. The purity of the sodium and potassium used was tested by measurements of the m. p.; for sodium, the m. p. is 97·7°, for potassium, $63{\cdot}6_5°\pm0{\cdot}05°$.

L. L. Bircumshaw.

Chemical and other thermal constants of sodium and potassium. W. Edmondson and A. C. G. Egerton (Proc. Roy. Soc., 1927, **A**, 113, 533—541).—The chemical constant of potassium was calculated from the vapour pressure and specific heat data by three slightly different methods: (1) from the $\log p$–$1/T$ curves (cf. preceding abstract); (2) from the equation $\log p=-4607{\cdot}2/T-0{\cdot}68\log T+9{\cdot}3678$; and (3) from data given by Ladenburg and Minkovski (Z. Physik, 1922, 8, 137). The values obtained by the three methods were 0·918, 1·008, and 0·970, respectively. The value for sodium was calculated from the equation $\log p=-5573{\cdot}2_7/T+9{\cdot}7255-0{\cdot}6794\log T$. The values finally given are $C_K=0{\cdot}92\pm0{\cdot}04$ and $C_{Na}=0{\cdot}63\pm0{\cdot}03$, which are higher than the values on the basis of the Sackur theory by an amount greater than the probable error, and less by an amount greater than the probable error than the theoretical value of the constant $+\log 2$. They are, however, within the possible error. The latent heats of vaporisation at 0° Abs. are computed to be 21,460 g.-cal. for potassium and 25,800 g.-cal. for sodium.

L. L. Bircumshaw.

Vapour-pressure equation at low temperatures. V. Fischer (Z. Physik, 1926, **39**, 879—882).—The vapour-pressure equation is obtained without neglecting the change in space content for the liquid or solid.

E. B. Ludlam.

Vapour-pressure curves. F. Schuster (Monatsh., 1926, **47**, 341—351).—A discussion of the variations, with varying values of $T_r=T/T_c$ for a number of substances, of the "constant" f of the relation $\log p_c/p=f(T_c/T-1)$ due to van der Waals. Except for hydrogen and helium, the value of f passes through a minimum at the reduced temperature B, and the variation of f is given by the expression: $f=a-(T_r+B)^2(2B-T_r)$.

G. M. Bennett.

Equilibrium pressure of certain hydrated salts. F. J. Norton and J. Johnston (Amer. J. Sci., 1926, [v], 12, 467—476).—The equilibrium vapour pressure of the system S_2–S_1–V, at different temperatures, where S_2 and S_1 are a pair of adjacent hydrates, can be determined by measuring the equilibrium pressure of the system S_2–S_1–L'–V, where L' is a solution saturated with both S_2 and S_1, and contains sufficient of a third solute to lower the transition temperature to the temperature required. Some of the technical difficulties of the ordinary method are thus overcome. This method has been found to be satisfactory for the system $Na_2SO_4,10H_2O$–Na_2SO_4–water vapour, using sodium chloride, sodium nitrate, and sulphuric acid, respectively, as the third solute. The vapour-pressure measurements were made by both a static (cf. Johnston, A., 1908, ii, 358) and a dynamic method (cf. Schumb, *ibid.*, 1923, ii, 219). At temperatures down to 0°, the equilibrium pressure is represented by the equation $\log p=-2710/T+10{\cdot}370$, where p is expressed in mm. Values for the vapour pressure of saturated solutions of sodium chloride, at temperatures from 20·4° to 50·4°, are also given.

M. S. Burr.

Magnitude of internal pressures, especially that of mercury. T. W. Richards (J. Amer. Chem. Soc., 1926, **48**, 3063—3080).—A more satisfactory mathematical treatment of internal pressures is given. The rate of increase of intrinsic cohesive pressure with decreasing volume for mercury is 1·98; some of the derived equations are verified for this element. Very great internal pressures must be supposed in order to account for the observed coefficients of expansion and compressibility. The approximate behaviour of these coefficients under pressure is calculated to within the limit of experimental error.

S. K. Tweedy.

Relation between coefficients of expansion and compressibility of liquids. V. S. Vrkljan (Z. Physik, 1926, 40, 270—277; cf. A., 1926, 786).—A continuation of the former work. The experimental values for water, alcohol, acetone, and ether are in good agreement with the formula.

E. B. Ludlam.

Theory of state of matter. VII. Molecular volume at the b. p. F. Schuster (Z. Elektrochem., 1926, **32**, 550—552).—It has previously been shown (A., 1926, 670) that for normal organic substances, $V_b=0{\cdot}79b$, where V_b is the mol. vol. at the b. p. and b van der Waals' constant. Van Laar has shown ("Die Zustandsgleichung," 1924) that the value of b for a substance is made up of definite contributions by each of the constituent atoms, although the mode of combination has an effect with some atoms. From these atomic contributions, values of the atomic volumes at the b. p. have been obtained from the above relation and are tabulated beside those of Kopp.

Tabulation of values of molecular volume for various organic substances obtained (1) by direct measurement, (2) from Kopp's atomic volumes, and (3) from van Laar's atomic volumes, shows better agreement between (1) and (3) than between (1) and (2). The ratio v_c/T_b, where v_c is the critical volume, is not a general constant, but increases with increasing critical temperature. The increment of molecular volume between successive members of a homologous series increases on ascending the series and, in general, the difference of molecular volume between two substances of high b. p. is greater than between two similarly constituted substances of lower b. p.

H. J. T. Ellingham.

Correction to the equation of state for nitrogen. L. B. Smith and R. S. Taylor (J. Amer. Chem. Soc., 1926, 48, 3122—3123).—The correction of a small error in the measurements recorded previously (A., 1923, ii, 755) gives the following revised equation of state for nitrogen: $p=[2\cdot9286/(v-\delta)]T-1650\cdot5/(v+0\cdot313)^2$, where $\log_{10}\delta=0\cdot2174-(0\cdot4307/v)$. Verschoyle's inference that impure gas was used is shown to be unfounded (A., 1926, 894).

S. K. Tweedy.

Surface tension of insulating liquids in an electric field. G. Bruhat and M. Pauthenier (Compt. rend., 1926, 183, 1272—1274).—It is shown theoretically by two independent methods, involving the application of thermodynamics and mechanics, respectively, that the surface tension of an insulating liquid in an electric field is independent of the strength of the field. This is in agreement with most experimental results. J. Grant.

Occurrence of helium and neon in vacuum tubes. R. W. Lawson (Nature, 1926, 118, 838—839).—A consideration of the conditions leading to diffusion of helium and neon into vacuum tubes. The precautions taken by Baly and Riding (A., 1926, 1191) appear insufficient to exclude the possibility that the helium and neon obtained were of atmospheric origin. A. A. Eldridge.

Experimental contributions to the theory of [liquid] diffusion. E. Wilke and W. Strathmeyer (Z. Physik, 1926, 40, 309—321).—Glass capillary floats of exactly the desired specific gravity were obtained by making a very large number (5000) and picking out those which floated horizontally and had a specific gravity inside the desired range. The behaviour of these indicated change of concentration with an accuracy of 0·1%. It was found that the influence of vibration from machinery etc. had been much exaggerated, but the effect of temperature changes was very great. The diffusion coefficient for concentrated solutions of the halogen acids rises and sinks periodically with the increase of concentration. E. B. Ludlam.

Densities and vapour pressures of aqueous solutions of ammonia and of liquid nitrogen tetroxide for the temperature interval 0—60°. A. Mittasch, E. Kuss, and H. Schlueter (Z. anorg. Chem., 1926, 159, 1—36).—A method has been devised for the simultaneous determination of densities and vapour pressures. Two types of tension pyknometers, (i) with mercury manometer, (ii) with a glass spring manometer, and also a compression pyknometer for the measurement of higher pressures, are described. The densities and vapour pressures of 20, 30, 40, and 50% solutions of ammonia and of liquid nitrogen tetroxide were determined between 0° and 60° and the results represented graphically.

For ammonia solutions up to 35% at 0—50°, the vapour density results agree with those of Mollier (Forsch-Arb. Ing., 1909, Heft 63/64); above 50° and with ammonia concentrations up to 50%, there is a maximum deviation of about +7·5%. For nitrogen tetroxide, the results agree with the values of Scheffer and Treub (Z. physikal. Chem., 1913, 81, 300) between 0° and 40°; above this to 60°, the maximum deviation is +1·5%. M. Carlton.

Composition of hydrochloric acid of constant b. p. W. D. Bonner and B. F. Branting (J. Amer. Chem Soc., 1926, 48, 3093—3095).—The compositions of hydrochloric acid solutions of constant b. p. are recorded between 620 and 660 mm. Under a pressure of 640 mm., the constant-boiling acid has b. p. 104·1°, d 1·0983, and contains 20·504% of hydrogen chloride. The composition of the acid solution is not a linear function of pressure. S. K. Tweedy.

Determination of the b. p. and condensation curves of mixtures of hydriodic acid and water under a pressure of 746 mm. of mercury. E. Carriere and Ducasse (Compt. rend., 1926, 183, 1281—1282).—The hydriodic acid was purified by distillation over calcium iodide and collected in hydriodic acid which had been similarly treated. This then contained 70% of the acid. The b. p. of mixtures containing from 15·1 to 64·9% of the acid were determined with the thermometer immersed in the liquid, a maximum value (126·5°) being obtained for 56·7% of acid. Two cases are distinguished in the determination of points on the condensation curve, according as the hydriodic acid–water mixture contains more or less than 56·7% of the former. The curves conform to the Gibbs–Konovalov rule. Both the mixture distilled and the distillate contained traces of iodine. J. Grant.

Electrical properties of copper–nickel resistance alloys. S. Kimura and Z. Isawa (Res. Electrotechn. Lab. Japan, 1926, 171, 1—10).—The resistivity–temperature curve (from −200° to 800°) for a certain range of nickel content has one maximum and one minimum, and thus corresponds with certain nickel–chromium and copper–manganese alloys. The negative character of the temperature coefficient of copper–nickel alloys is believed to be closely related to the A2 transformation of nickel. For alloys poor in nickel there is, however, a considerable discrepancy between the temperature at which the lowering of the temperature coefficient becomes conspicuous and the Curie point. The question whether copper–nickel alloys form a series of continuous solid solutions is discussed.

Chemical Abstracts.

Properties of saturated salt solutions at 100°. M. Prudhomme (Bull. Soc. chim., 1926, [iv], 39, 1703—1708).—The depression d of the vapour pressure at 100° of a saturated solution is a function of the molecular fraction of the solute, the generalised

form of the relationship being $M(760-d).g/d(100-g)$, where g is the solubility in g. referred to 100 g. of solution and M is the mol. wt. of the solute. In any individual case, however, one or more of the factors of the formula may be suppressed or inverted. S. J. GREGG.

Diffusion of zinc in the α-series of solid solutions in copper. J. S. DUNN (J.C.S., 1926, 2973—2979).—The measurement of the rate of evaporation of zinc from a brass surface forms a simple method of measuring the diffusion of zinc through copper. The sample of brass was heated under vacuum in a silica tube, and weighed after a definite time, and the rate of zinc loss was found to vary with the square root of time, as demanded by the equation used in calculating the diffusion coefficient. This calculation is analogous to that used by Rayleigh in his estimation of the age of the earth from the temperature gradient at the surface. The loss of zinc per sq. cm. in a given time and the diffusion coefficient increase approximately exponentially with zinc content; their variation with the temperature is also exponential, as demanded by Hevesey's view that diffusion is due to loosened patches in the crystal lattice. The temperature coefficient of diffusion is in fair agreement with the Rideal–Dushman equation for a unimolecular reaction. S. J. GREGG.

Solubility rule. F. CROTOGINO (Z. Elektrochem., 1926, **32**, 558—561).—An attempt to find a rule stating the way in which the solubility of various salts of the alkali metals changes in passing along the series, sodium, potassium, rubidium, cæsium. H. J. T. ELLINGHAM.

Effect of addition of less volatile substances on the solubility of non-electrolytes. G. TAMMANN (Z. anorg. Chem., 1926, **158**, 25—32).—Addition of a less volatile substance to water affects its physical properties in much the same way as does an increase in external pressure, *e.g.*, the temperature of maximum density is depressed. It seems likely that this effect is due to a change in the molecular constitution of the water, resulting from an increase in the internal pressure. If, with increase in the concentration of water-I molecules (this vol., 93), the solvent power of water for non-electrolytes increases proportionately, then neglecting the solvent power of the other water molecules and assuming that the volume change in the transformation of water-I into the other kinds of water molecules is independent of the pressure, Setschenov's formula, $s=s_0e^{-kc}$, follows. Here s_0 is the solubility of a non-electrolyte in pure water, s the solubility in water containing a concentration c of an added substance, and k is a constant. This formula is not valid for high concentrations of foreign substance, on account of the approximations used in deducing it. If the added substance lowers the solubility of the non-electrolyte by increasing the internal pressure, then the value of k should be proportional to the increase in internal pressure per g.-mol. of added substance. Data for the solubility of gases in solutions of salts approximately confirm this deduction. Since the concentration of water-I diminishes with rise in temperature, and water-I increases the solubility of non-electrolytes, the solubility depression produced by the foreign substance must decrease with rising temperature, until at 50° it corresponds with the effect of the foreign substance alone. R. CUTHILL.

Influence of temperature on solubility of gases. G. TAMMANN (Z. anorg. Chem., 1926, **158**, 17—24).—If the heat of solution of a gas in its saturated solution corresponds with the work done against the osmotic pressure, the solubility, s, will be related to the temperature (Abs.), T, by the equation $1/\log_e . d\log_e s/dT = \mp 1/T$, according as s is greater or less than 1. Many solutions of gases in liquids fulfil this equation, but in other cases deviations occur on account of thermal effects accompanying the formation of new molecular species, such as compounds of solvent and solute. Thus with aqueous solutions of gases, except those of helium and neon, the solubility first decreases with rise of temperature, even when s is less than 1, and afterwards increases again. This abnormal behaviour is probably due to hydrate formation (cf. this vol., 93), and as the concentration of these molecules diminishes with rise in temperature, the relation between the temperature and the solubility ultimately becomes normal. R. CUTHILL.

Adsorption. XI. Kinetic theory of gas adsorption. A. MAGNUS (Z. anorg. Chem., 1926, **158**, 67—83; cf. A., 1926, 1001).—Lorenz and Lande's derivation of an equation for the amount of gas adsorbed by a surface (A., 1923, ii, 13) is corrected. A value is deduced for the "critical adsorption temperature," this being the temperature at which the heat of adsorption is zero and above which adsorption cannot occur. For adsorbed carbon dioxide at high concentrations, an equation of state analogous to that of van der Waals is deduced. This is supported by new experimental data, which do not accord with Langmuir's equation (*ibid.*, 1918, ii, 430). The results also show that adsorbed gases cannot be in the liquefied state unless the external pressure is such that the gas would be liquefied in absence of the adsorbent. If the dipole theory of adsorption is correct, the experimental evidence makes it necessary to assume that the dipoles are not rigid. This removes certain difficulties in Eucken's theory of the configuration of the carbon dioxide molecule (*ibid.*, 1926, 882). R. CUTHILL.

Adsorption of nitrogen at low pressures by activated charcoal. R. CHAPLIN (Phil. Mag., 1926, [vii], **2**, 1198—1207).—The adsorption isotherm for nitrogen and charcoal at 25° has been determined between the pressures 2×10^{-4} and $1{\cdot}3\times10^{-2}$ mm. Under these conditions, the quantity of nitrogen adsorbed is a linear function of the pressure, being given by the expression $q=0{\cdot}023p$, where q is in mg. of nitrogen per g. of charcoal and p is in mm. Thus for this region the value of n in Freundlich's adsorption formula is 1. Provided that pure nitrogen is employed, equilibrium is rapidly attained and the adsorption is completely reversible. A modified form of McLeod gauge for use in this type of investigation is described. A. E. MITCHELL.

Vanadium, titanium, and hydrogen. H. HUBER, L. KIRSCHFELD, and A. SIEVERTS (Ber.,

1926, 59, [*B*], 2891—2896).—Vanadium which has been heated in a vacuum at 1100° readily absorbs hydrogen, and equilibrium is rapidly and certainly attained from either side. The pressure–volume curves are recorded at 300°, 400°, 600°, and 800°. There is no evidence of ageing in the behaviour of the metal. Titanium, after being pre-heated at 800—1100° in a vacuum, absorbs hydrogen with noticeable rapidity at 375°. At higher temperatures, equilibrium is attained with speed and certainty, but with repeated use the absorptive capacity of the element decreases. The pressure–volume curves are recorded at 500°, 600°, 800°, and 1000°. For the metals of the fourth and fifth groups of the periodic system, the following regularities are observed. The form of the isobars is similar for all elements; the rapid decline in the isobars is displaced towards higher temperatures as the absorptive capacity of the metal for hydrogen increases; the power of absorbing hydrogen increases with increasing atomic weight of the metal in each group; of two neighbouring elements that with the lower atomic number has the greater absorptive power. H. Wren.

Adsorption on solids. W. E. Garner (Trans. Faraday Soc., 1926, 22, 459—464).—See A., 1926, 1091.

Hydrolytic adsorption on platinum-black. A. Frumkin and A. Obrutscheva (Z. anorg. Chem., 1926, 158, 84—86).—If a hydrogen electrode is immersed in a solution of a neutral salt, *e.g.*, sodium sulphate, in which the osmotic pressure of the hydrogen ions is less than the electrolytic solution tension of the electrode, a small amount of hydrogen ions will pass into solution, and the resulting negative charge on the surface of the electrode will attract sodium ions from the solution, which will therefore become acid. This has been confirmed by experiment. The alkali can be removed from the electrode by destroying its charge of hydrogen with a current of air.

R. Cuthill.

Adsorption of metal complexes on charcoal. B. V. Nekrasov (J. Russ. Phys. Chem. Soc., 1926, 58, 207—214).—The hitherto uninvestigated phenomenon of adsorption of complex metallic salts on active charcoal was studied with double salts, metal ammines, and stable complexes (cobalt). Solutions of these salts were treated with highly purified active charcoal and analysed. Eight double sulphates of the type $M''(NH_4)_2SO_4.6H_2O$ gave a constant adsorption for the ammonium salt, but an increasing value for the metal according to the series Ni, Zn, Mg, Mn, Cd, Co, Fe, Cu, which is in the reverse order of the decrease in solubility of their sulphates due to complex formation, thus showing that selective adsorption of the complex-forming metal had taken place.

The metal ammines gave results completely analogous to the series of tervalent cobalt compounds, from $[Co(NH_3)_6]Cl_3$ to $Na_3[Co(NO_2)_6]$. It is concluded that during adsorption the complexes are destroyed, and tervalent cobalt is reduced to the bivalent state. Groups containing NH_3 are adsorbed in the form $M(NH_3)_2$, any excess of ammonia remaining in solution. Of the anions, chlorine is not at all, nitrite slightly adsorbed. Un-ionised complexes are more adsorbed than ionised, and, in the case of isomerides, the asymmetrical *cis*-isomerides more than the symmetrical. Other metal complexes are being studied, to determine whether the same regularities persist. M. Zvegintzov.

Adsorption of hydrogen and hydroxyl ions by animal charcoal. I. Isoelectric point of animal charcoal. H. Bohn (Biochem. Z., 1926, 178, 119—138).—Phosphate buffer solutions treated with animal charcoal undergo an alteration in hydrogen-ion concentration, the magnitude of which varies with the p_H of the buffer present and with the isoelectric point of the charcoal (cf. Silberstein, A., 1922, ii, 452). This observation is made the basis of determinations of the isoelectric points of various charcoals. Conductivity measurements of pure water after treatment with charcoal show that the impurities present influence the value of the isoelectric point. The adsorption of hydrogen and hydroxyl ions by charcoal follows a typical adsorption isotherm.

J. Pryde.

Adsorption of solids by fibres from aqueous suspensions. M. A. Iljinski, A. A. Balandin, M. V. Gaverdovskaja, and B. Tourova Poliak (J. Russ. Phys. Chem. Soc., 1926, 58, 241—248).—The kinetics of adsorption by cotton, wool, and silk fibres from aqueous suspensions were studied. Clean, dry fibres were immersed for a definite time in suspensions of ferric hydroxide, barium chromate, manganese dioxide, lead carbonate, lead sulphate, nickel carbonate, copper ferrocyanide, indigo, and ultramarine (which had been washed free from electrolytes), pressed out, and the solid adsorbed determined gravimetrically. The amount adsorbed was in all cases a linear function of the initial concentration, suggesting a distribution of the solid between the liquid and the fibre according to the partition law. The process, however, was irreversible, as treated fibres, when immersed in pure water, did not obey the law. Microscopical observation showed the existence of a dynamic equilibrium of the solid particles between the fibre and the suspension.

M. Zvegintzov.

Adsorption of sols and ions by precipitates and its influence on the formation of periodic precipitates. A. C. Chatterji and N. R. Dhar (Z. anorg. Chem., 1927, 159, 186—196; cf. A., 1924, ii, 158; 1925, ii, 865).—Quantitative measurements of the adsorption of various sols by the corresponding freshly-precipitated substance show that sols of lead chromate, silver chromate, ferric hydroxide, and arsenious sulphide are strongly adsorbed, the percentage adsorption increasing with increasing values of the ratio of precipitate to sol. Sols of cadmium sulphide, antimony trisulphide, and manganese dioxide are not adsorbed under these conditions, and in fact the precipitated substance has a marked tendency to pass into the colloidal state. Substances which adsorb their sols give Liesegang rings in which consecutive rings are separated by a clear space. Those substances which do not adsorb the corresponding sols form periodic precipitates consisting of alternate layers of precipitated substance and the sol. Only small amounts of silver ion are adsorbed

by silver chromate, whilst the adsorption of chromate ion by silver chromate and lead chromate is practically zero. J. S. CARTER.

Adsorption of dyes on silver halides. S. E. SHEPPARD (Nature, 1926, 118, 913—914).—Experimental curves indicate that the dye is first adsorbed until the surface is saturated. The dye disperses in water to form colloidal as well as true solution, and the last ascending portion of the curve corresponds with mechanical adsorption. A modification of Langmuir's formula for the unimolecular adsorption of gas molecules on a plane surface is in good agreement with the data. At p_H 5·5, 1 mol. of dye is computed to be adsorbed for 20 ions of the lattice surface. Possible explanations of the low adsorption density of the dye are considered. The solubility of the dye in water is greatly diminished in the presence of small amounts of soluble halides. A. A. ELDRIDGE.

Mists from chemical reactions. IV. Absorption of mists by liquids and solids. H. REMY and H. FINNERN (Z. anorg. Chem., 1927, 159, 241—255; cf. A., 1925, ii, 107).—When mists of ammonium chloride or sulphur dioxide are passed through water or aqueous solutions of alkalis or through tubes packed with coarse pumice, gas-mask charcoal, etc., relatively little absorption occurs. Absorption is, however, almost complete on passing the mists through tubes packed with fibrous material such as glass wool, filter-paper, etc. As an example of the orders of magnitude encountered, the following numbers give the mean percentage absorption for moist mists under the author's experimental conditions by water (Winkler absorption coil), 10 cm. of tube containing gas-mask charcoal, and 10 cm. of tube packed with glass wool, respectively, the figures in parentheses are the corresponding numbers for the dry mists: ammonium chloride: 58 (39); 27 (93); 99 (98); sulphur trioxide: 37 (7); 30 (82); 99 (90). The behaviour of an absorbent towards a mist depends primarily on the size and mobilities of the suspended particles. With decreasing size and increasing mobility (*e.g.*, on drying or filtering) the mists more closely resemble gases; the efficiency of purely filtrational absorbents diminishes, whilst that of absorbents for gases, *e.g.*, charcoal, increases. Water, however, absorbs moist mists more readily than dry, since the dry mists take up water to form particles larger than those existing in moist mists. A dried, filtered mist of ammonium chloride consisting of very fine particles was, however, almost completely freed from the salt on passing through a Winkler coil containing water. Experiments in which a moist mist of sulphur trioxide was passed through solutions of gelatin of concentrations ranging up to N show that the percentage absorption decreases with increasing gelatin content (*i.e.*, increasing viscosity). Mists of sulphur trioxide are more completely absorbed by water at low temperatures than at high temperatures. J. S. CARTER.

Stabilising ions and their adsorption. G. ROSSI and V. OSTI (Gazzetta, 1926, 56, 811—816).—The conductivity of solutions of tetramercuriacetanilide acetate containing various proportions of acetic acid shows that, for constant concentration of the acetic acid, the adsorption of this increases with the concentration of the colloid, and that, when the concentration of the colloid is kept constant, the adsorption of the acetic acid by the disperse particles increases to a maximum and then diminishes as the concentration of the acid rises continuously. These results are discussed in relation to the authors' views (A., 1924, ii, 330, 459). T. H. POPE.

Action of silica on electrolytes. A. F. JOSEPH (Nature, 1926, 118, 878).—Polemical against Mukherjee (A., 1925, i, 488, ii, 383; 1926, 1112). The author holds that silica does not adsorb acids. A. A. ELDRIDGE.

Interaction between hydrated silica and neutral electrolytes in its relation to the nature of hydrolytic adsorption. J. N. MUKHERJEE, B. C. GHOSH, K. KRISHNAMURTI, G. N. GHOSH, S. K. MITRA, and B. C. ROY (J.C.S., 1926, 3023—3033).—The usual conceptions of chemical equilibrium fail to explain the reaction between silica and solutions of neutral electrolytes. By treating hydrated silica with saturated potassium chloride solution, 50 c.c. of the solution being removed daily and replaced by fresh, the hydrogen-ion concentration gradually diminished to a definite limit, leaving a residue which was inactive to potassium chloride. According to the ordinary equation, however, $2n\text{KCl}+\text{H}_{2n}\text{SiO}_{n+2}=2n\text{HCl}+\text{K}_{2n}\text{SiO}_{n+2}$, the hydrogen-ion concentration should remain constant and then suddenly fall when no more silica remains. Also, a solid residue remains which contains much hydrogen partly replaceable by washing with solutions of certain other neutral electrolytes. From *E.M.F.* measurements, the hydrogen-ion concentration for solutions in contact with silica was found to be greater for barium chloride than for calcium chloride; whereas since the silicate of calcium is less soluble than that of barium, the opposite order would be predicted from ordinary chemical theory. Further, the hydrogen-ion concentration of potassium chloride solution in contact with silica depended on the relative weights of silica and potassium chloride present. The above facts can be explained by Mukherjee's theory of ionic adsorption (A., 1922, ii, 689). Adsorption was confirmed by electro-osmotic measurements, and the adsorption of acids by silica was directly demonstrated by determining the concentration of an acid solution (by *E.M.F.* measurements) before and after contact with silica. S. J. GREGG.

Adsorption in its relation to catalysis and enzyme actions. J. DUCLAUX (Deuxième Cons. Chim. Inst. Intern. Chim. Solvay, 1926, 630—645).—The hypothesis that molecules and atoms exist either completely independently or in chemical combination is extended to all liquid, gaseous, and solid systems. Adsorption is but a particular case of the formation of additive compounds, which proceeds spontaneously, either without activation or by autoactivation. These compounds are considered to be capable of spontaneous internal transposition, followed by dissociation. Catalysis is defined in these terms. CHEMICAL ABSTRACTS.

Physical phenomena at interfaces. E. K. RIDEAL (Trans. Faraday Soc., 1926, 22, 434—439).—See A., 1926, 1093.

Arrangement of molecules on the surface of pure liquids. S. SUGDEN (Trans. Faraday Soc., 1926, 22, 486—490).—See A., 1926, 1094.

Physical properties of composite surfaces. W. RAMSDEN (Trans. Faraday Soc., 1926, 22, 484—485).—See A., 1926, 1094.

Electrification at interfaces. H. FREUNDLICH (Trans. Faraday Soc., 1926, 22, 440—451). R. K. SCHOFIELD (*ibid.*, 452—458).—See A., 1926, 1094.

Insoluble films on liquid surfaces. N. K. ADAM and G. JESSOP (Trans. Faraday Soc., 1926, 22, 472—476).—See A., 1926, 1093.

Spreading of proteins. E. GORTER and F. GRENDEL (Trans. Faraday Soc., 1926, 22, 477—483).—See A., 1926, 1094.

Ring method for the determination of surface tension. W. D. HARKINS, T. F. YOUNG, and L. H. CHENG (Science, 1926, **64**, 333—336).—The ring method for the determination of surface tension may yield results in error by 25% or more, unless the ring is large. A correction factor has been introduced into the equation employed, and preliminary values for the factor have been obtained by a comparison of the surface tension of various liquids by the ring, capillary height, and drop-weight methods. Certain essential experimental precautions are enumerated.

A. A. ELDRIDGE.

Absolute measurement of the average size of droplets of the disperse phase of an emulsion. W. P. DAVEY (Science, 1926, **64**, 252—253).—If one drop of a permanent oil-in-water emulsion is deposited on the surface of clean water so as not to break the surface film, it spreads on the water like an oil. Assuming that the layer is one particle deep, and that the droplets are small enough to retain their shape, the average diameter of the particles can be measured by Langmuir's method for measuring the cross-section of oil molecules. This involves a knowledge of the total volume of the droplets of the disperse phase as they exist in the emulsion; so far, this volume has been found to be the same as that of the same mass of undispersed material.

A. A. ELDRIDGE.

Surface tension and heat of vaporisation. J. E. VERSCHAFFELT and F. DE BLOCK (Z. anorg. Chem., 1927, **159**, 265—268).—The relation, $\log L = a + b \log \gamma$, where L is the heat of vaporisation, γ the surface tension, and a and b are constants, put forward by Herz (A., 1926, 1008), is discussed, and it is shown that a relation of this type will hold between any two magnitudes which become zero at the critical point. The relation $L/a^2 = 18$, where a is the capillary constant, deduced by de Kolossovski (*ibid.*), is valid only for normal liquids at the b. p. and is not independent of temperature. J. S. CARTER.

Preparation of colloidal manganese dioxide. II. A. STEOPOE (Bul. Soc. Romana Stiinte, 1926 29 11 15, cf. A., 1926, 676).—Colloidal manganese dioxide is prepared by reducing a neutral solution of potassium permanganate with acetylene in presence of colloidal silica. The stability increases with rising concentration of the silica; it is decreased in presence of sodium hydroxide. The precipitation by electrolytes of a manganese dioxide sol (prepared with ethylene as a reducing agent) does not proceed in accordance with the Hardy–Schulze law; immediate precipitation occurs, except in the case of cobalt and silver nitrates, when the precipitation is preceded by coagulation. The presence of electrolytes does not modify the true colours of colloid particles (Dhar, A., 1926, 24). The latter are covered with a thin layer of metal hydroxide, produced by interaction of the added electrolyte with the potassium hydroxide adsorbed on the particles. The true colours are thus masked. S. K. TWEEDY.

Synthesis of colloidal tungstic acid. A. B. DUMANSKI and A. P. BUNTIN (J. Russ. Phys. Chem. Soc., 1926, **58**, 107—112).—The problem whether colloidal tungstic acid is formed directly or is built up in successive stages from complexes, as is the case with vanadium pentoxide (A., 1923, ii, 771), was investigated.

The electrical properties of the solutions indicate that the reaction takes place in stages: $Na_2WO_4 + 2HCl = H_2WO_4 + 2NaCl$ and $H_2WO_4 + Na_2WO_4 = Na_2O,2WO_3 + H_2O$. This process is repeated, until a colloidal particle of the composition Na_2O,nWO_3 or $H_2[WO_4,nWO_3]$ is obtained. Numerous complexes of tungstic acid are known which confirm this view. One of these, $Na_2O,4WO_3$, was prepared, and gave results in agreement with the theory. Experiments on the viscosity of the tungstic acid sols were also carried out. M. ZVEGINTZOV.

Thermal colloid syntheses. III. Colloidal mercury. A. GUTBIER [with R. KOHLER and W. SCHIEBER] (Z. anorg. Chem., 1926, **158**, 99—102; cf. A., 1926, 1003).—Nordlund's work on the preparation of mercury sols by thermal dispersion (A., 1920, ii, 376) has been confirmed, using the apparatus previously described (*ibid.*, 1926, 574). The sols so obtained contain negatively-charged particles, and up to 2·5% of mercury; they are very unstable, decomposition commencing within 24 hrs. after preparation, and being much accelerated by electrolytes or changes in temperature. Addition of the usual protective colloids to the freshly-prepared sols does not increase their stability, but the products obtained by using a 1% solution of gum arabic instead of pure water as the dispersive medium can be kept, with care, for more than a week. The residue obtained by evaporating such sols over sulphuric acid gives, on treatment with water, a secondary sol, which coagulates within 24 hrs. R. CUTHILL.

Dispersion in sulphur suspensions. G. I. POKROWSKI (Z. Physik, 1926, **40**, 368—377).—The dispersion of sulphur particles produced by the action of sulphuric acid on aqueous solutions of sodium thiosulphate is shown to be in agreement with Rayleigh's theory. The variation of the diameter of particles, η, as a function of the time, t, and the thiosulphate concentration c is given by an empirical equation $\eta = \eta_0(1 - e^{-\alpha ct})$, where α and η_0 are constants. R. W. LUNT.

State and stability of colloid solutions. K. LINDERSTRØM-LANG (Compt. rend. trav. Lab. Carlsberg, 1926, **16**, [6], 1—47).—Theoretical. Solutions of colloid electrolytes, regarded as one-phase systems in internal equilibrium, are discussed from the point of view of the thermodynamic principles developed by Lewis, Bjerrum, and Brønsted. On the basis of Gibbs' conditional equation for stability of a phase, it is shown that the behaviour of the so-called osmotically abnormal colloid electrolytes must be explained on the assumption that the activity of the large ion is a diminishing function of the concentration. This can be due only to the presence of strong van der Waals cohesive forces between the large ions, which may or may not result in micelle formation. The bearing of these views on the interpretation of the experimental data of Hammersten (A., 1924, i, 456, 1139; ii, 386) and of McBain and Salmon (*ibid.*, 1920, ii, 234; J.C.S., 1920, **117**, 530) is discussed. M. S. BURR.

Charge on the particles in colloids. R. WINTGEN (Kolloid-Z., 1926, 40, 300—302).—The amount of colloidal substance deposited by one Faraday of electricity may be regarded as the electrochemical equivalent of the colloid, and colloids may therefore be expressed in terms of normality, according to the number of electrochemical equivalents of colloid per litre. This value may be determined by measuring the electrical conductivity of the system before and after ultrafiltration, the difference representing the conductivity due to the charged colloid particles. Results are given for sols of ferric oxide and for dialysed and undialysed gold sols. E. S. HEDGES.

Emulsions. II, III. H. LIMBURG (Rec. trav. chim., 1926, 45, 854—874, 875—880).—II. The influence of potassium, barium, and aluminium chlorides, hydrochloric acid, potassium carbonate, and thallium nitrate on the rate of cataphoresis of the particles in paraffin oil emulsions has been examined. Measurements of the interfacial tension oil–water in presence of potassium chloride, hydrochloric acid, and potassium carbonate were made by the drop-weight method and the stability of the emulsions was examined in presence of potassium, barium, and aluminium chlorides, hydrochloric acid, potassium carbonate, and thallium nitrate, sedimentation of the emulsion being prevented by means of slow rotation. With univalent cations, the rate of cataphoresis increases to a maximum with increasing electrolyte concentration, and then decreases. Barium chloride in moderate concentration is without effect on the cataphoresis. With tervalent cations, the velocity decreases to zero and changes its direction. This reversal of charge is ascribed to the products of hydrolysis of the salts. From a consideration of the effects of electrolyte addition on the stability of the emulsions, it is shown that, in addition to such factors as the charge on the particles, the interfacial tension, and the presence of protective films, the stability is largely determined by the electrical conductivity of the continuous phase. A theoretical explanation is given.

III. Using emulsions of paraffin oil containing 0·5 and 5% of oleic acid, in water, a study has been made of the influence of electrolytes (potassium chloride, hydrochloric acid, and potassium carbonate) on the velocity of cataphoresis of the particles, the stability of the emulsion, and the interfacial tension, oil–water. The fact that the rate of cataphoresis is practically the same as in the absence of oleic acid is explained on the basis of the Langmuir–Harkins orientation theory. From the course of the curves showing the influence of electrolytes on the stability of the emulsions, it is seen that, whilst the stability is greater in presence of oleic acid, the general character of the curves remains unaltered. The increased stability is ascribed to a lowering of surface tension caused by a film of oriented oleic acid molecules, which opposes the combination of the particles. Similar measurements have been made on oil–water emulsions containing 0·089 g. of saponin per litre, in presence of potassium chloride, hydrochloric acid, potassium carbonate, and aluminium chloride. The stability is greatly increased by saponin, which is assumed to form a highly resistant film round the particles. On the other hand, the relation between the charge on the particles and the electrolyte concentration is the same as if no saponin were present. The surface tension appears to be only slightly lowered by saponin, but it is suggested that this may be due to difficulties in the exact measurement of the property. The addition of gelatin to oil–water emulsions has a marked effect on the rate of cataphoresis, dependent on the degree of acidity of the emulsion. The curves showing the influence of gelatin on the stability of emulsions of varying p_H (2·8—9·6) all have a minimum, which is the more pronounced the greater is the acidity. L. L. BIRCUMSHAW.

Polarised fluorescence of dyes in colloidal solutions. W. L. LEVSCHIN (J. Russ. Phys. Chem. Soc., 1926, 58, 177—183).—See A., 1925, ii, 13, 629, 1117.

Relation between viscosity and molecular complexity of cellulose nitrate. N. YAMAGA (Cellulose Ind., Tokyo, 1926, 2, 357—362).—Decrease in viscosity of cellulose nitrate is brought about by the action of heat; light also has a similar action. Change of viscosity does not depend on the decomposition of the cellulose nitrate, but accompanies decrease of molecular complexity. This has been measured by determining the coefficient of diffusion by Schaffer's method. The coefficient of diffusion in acetone solution for a heated sample was found to be 0·8070 cm. per day, as against 0·5962 cm. per day for the original sample. Thus the sample with lower viscosity has also the smaller molecular diameter. Calculations from the experimental data gave for the molecular radii (P) $9{\cdot}838\times10^{-8}$ cm. for the original and $9{\cdot}148\times10^{-8}$ cm. for the heated cellulose nitrate. Assuming the molecular formula $[C_{24}H_{29}O_9(NO_3)_{11}]_n$ for a cellulose nitrate containing 13·32% N, the molecular volume can be calculated by Traube's method from the sum of the atomic weights, $V=n\times 2{\cdot}62\sqrt{A}=M/d$ and from the molecular radii $V=\frac{4}{3}P^3\times6{\cdot}5\times10^{23}$. From these two equations the real mol. wt. M may be calculated, taking the density of cellulose nitrate as 1·655. These calculations gave mean values for M of the original guncotton 8751;

n=about 8, and for the heated sample M=3329, n=about 3. J. F. BRIGGS.

Optical properties of sols and gels containing cellulose. O. FAUST (Ber., 1926, 59, [B], 2919—2920).—The double refraction of artificial silk threads and films is due to tension or pressure during production, and disappears when they are nitrated unless the tension has been very great. Threads prepared in the absence of pressure do not exhibit double refraction. H. WREN.

Effect of anions on the physical, chemical, and colloidal properties of aluminium hydroxides. L. B. MILLER (Third Colloid Symposium Monograph, 1925, 206—215).—The " floc " obtained with sulphate settles rapidly and is compact, thus being suitable for water clarification. The effective p_H range for aluminium sulphate is 5·3—8·7 (max. 5·5), and for chloride 7·8—8·6. The precipitate from a dilute solution (except perhaps at high p_H values) is not aluminium hydroxide, but a complex substance containing varying proportions of the anions. CHEMICAL ABSTRACTS.

Behaviour of silicic acid gel during the drying-up process. J. B. FIRTH and H. A. FELLS (Nature, 1927, 119, 84—85).—A question of priority (cf. Krishnamurti, this vol., 19). A. A. ELDRIDGE.

Effect of acids on hydrophobic colloids, particularly gold. W. PROSCH (Kolloid-Z., 1926, 40, 318—321).—A lecture on the influence of hydrogen-ion concentration on the precipitation of colloidal gold and on the inhibitive effect of protective colloids. E. S. HEDGES.

Deformation of titration curves of proteins in presence of strong electrolytes. L. REINER (Kolloid-Z., 1926, 40, 327—332).—A discussion of the effect of strong electrolytes on the acid- and alkali-fixing power of proteins. The high valency of the protein ions strongly influences the activity of the other ions present. E. S. HEDGES.

Structure of organic acids and protein coagulation. I. N. A. ISGARISHEV and M. I. BOGOMOLOVA (J. Russ. Phys. Chem. Soc., 1926, 58, 156—163).—The coagulation of casein and edestin by different organic acids was investigated in order to determine the physical or chemical nature of the mechanism. Alkaline solutions of the proteins were titrated with the acids, the amount in excess of neutralisation needed to cause precipitation being an inverse measure of the activity of the acid. The results with casein were accurate and reproducible.

No direct connexion was found between the dissociation constant of the acids or the Lorenz ionic volume of the anions and the activities of the acids. Differences of chemical structure, however, were important. Increase of CH_2 groups in the fatty series slightly increased the activity. Hydroxyl groups increased it in aliphatic, but decreased it in aromatic series. A second carboxyl group was ambiguous, whilst halogens when present singly were highly active.

From these results a possible chemical mechanism is suggested. The alkaline proteins are capable of combining with salts of the acids to form complexes analogous to the known silver complexes, which have different solubilities; in consequence the excess of common ion required for precipitation varies considerably. M. ZVEGINTZOV.

Effect of organic acids on the imbibition of gels. II. N. A. ISGARISHEV and A. L. POMERANZEVA (J. Russ. Phys. Chem. Soc., 1926, 58, 164—169; cf. preceding abstract).—The effect of the structure of organic acids on the imbibition of gels was determined by the increase in volume of pure, dry casein, when treated with dilute solutions of the acids. It was found that the dissociation constant has no direct effect, and, consequently, the main factor was the nature of the anion. The presence of hydroxyl or a second carboxyl group, especially in close juxtaposition, enhances the activity up to a point, but such acids as citric and tartaric acids show a reverse effect. Chlorine is very active, and the amino-group acts as an inhibitor, whilst double linkings give ambiguous results. The adsorption of active acids by the casein, the formation of ion complexes, and the possible specific effects of ions are also discussed. M. ZVEGINTZOV.

Electrical endosmose with sulphur. A. F. GUERASIMOV (J. Russ. Phys. Chem. Soc., 1926, 58, 201—206).—The phenomena of electrical endosmose have been examined to ascertain whether octahedral sulphur, like colloidal, adsorbs anions in suspensions in hydrochloric acid (cf. Perrin, A., 1905, ii, 138). The formula employed was Smoluchowski's: $P_1-P_2=CE(\varphi_l-\varphi_s)/4\pi w$, where P_1, P_2 are the pressures at the two ends of the tube, φ_l, φ_s the potentials of the liquid and the diaphragm, and C and w are constants depending on the nature of the latter. An apparatus was devised in which powdered sulphur acted as a diaphragm and P_1, P_2 were measured by changes of level of the liquid.

The results are affected by electrolysis of the chloride and the changes in the condition of the diaphragm, for which a correction must be applied. In all cases, and at all concentrations, the negative charge of the sulphur decreases, *i.e.*, there is no preferential adsorption of anions. M. ZVEGINTZOV.

Rapid dialysis of solutions of sodium silicate. A. GUTBIER and H. BRINTZINGER (Z. anorg. Chem., 1927, 159, 231—240).—The results of experiments on the dialysis of solutions of sodium silicates of varying composition and concentration show that, although the major portion of the silica present passes through the membrane, considerable quantities are retained, together with a little sodium. For example, a solution originally containing 0·3224 g. Na_2O and 0·7160 g. SiO_2 per 100 c.c. contained after dialysis 0·0006 g. Na_2O and 0·2320 g. SiO_2 per 100 c.c., the p_H value falling from 12·47 to 10·20. Solutions of sodium silicate contain ions of the type SiO_3'', Si_2O_5'', etc., which are readily diffusible if the concentration of hydroxyl ions is sufficiently high. As the concentration of sodium and hydroxyl ions decreases, hydrolysis occurs according to the schemes: $SiO_3''+nH_2O \rightarrow SiO_2,(n-1)H_2O+2OH'$; $Si_2O_5''+nH_2O \rightarrow 2SiO_2,(n-1)H_2O+2OH'$. The silicic acids are initially present in a highly dispersed state, but they immediately commence to form large aggregates

incapable of diffusion, especially when the concentration of hydroxyl ion further diminishes.

J. S. CARTER.

Rapid dialysis of solutions of silicic acid. H. BRINTZINGER (Z. anorg. Chem., 1927, **159**, 256—264; cf. Mylius and Groschuff, A., 1906, ii, 160; Willstatter, Kraut, and Lobinger, *ibid.*, 1926, 36; Gutbier and Brintzinger, preceding abstract).—Since aqueous solutions of sodium silicate contain colloidal silicic acids produced as a result of hydrolysis, in addition to the ions, SiO_3'', Si_2O_5'', etc., the relative quantities of which depend on the ratio $[Na_2O]:[SiO_2]$, a rather complex mixture of silicic acids results on acidification. On dialysis, the molecularly dispersed silicic acid will pass through the membrane, whilst the colloidal acid originally present, and that resulting from the agglomeration of the molecularly dispersed particles, remain behind. Hence if the solution obtained on acidification is kept for some days before dialysis, there is a considerable decrease in the percentage of diffusible silica as a result of this aggregation. It is probable that the rate of agglomeration is proportional to the number of collisions between particles, and hence dependent on concentration and temperature. There should therefore be a greater proportion of diffusible silica in dilute solutions, and at low temperatures, provided that the ratio $[Na_2O]:[SiO_2]$ of the solution of sodium silicate acidified is maintained constant. The results of experiments in which solutions of a sodium silicate of the composition, $Na_2O,2{\cdot}3SiO_2$, of varying concentration, were acidified at various temperatures with a slight excess of hydrochloric acid and dialysed, either at once or after some days, are in entire agreement. In all cases, the value of the resulting solution was about 4·6. J. S. CARTER.

Ionic volume and hydration. N. R. DHAR (Z. Elektrochem., 1926, **32**, 596—598).—Theoretical. The view has been put forward (A., 1913, ii, 916) that the ions of an electrolyte occupy a smaller volume than the corresponding undissociated molecule. Also Eddington has expressed the view that when an atom loses an electron, the positive ion remaining may be much denser than the original atom. This explains the marked decrease in molecular volume accompanying the dissolution of electrolytes such as sodium or potassium chlorides in water. But with lithium chloride this decrease in molecular volume is very small; this is ascribed to the considerable hydration of the lithium ion. Hence, degree of hydration might be deduced from molecular volume data. The conclusion that strongly hydrated ions have a smaller charge per unit surface than weakly hydrated ions is applied to the explanation of certain properties of colloidal solutions. H. J. T. ELLINGHAM.

Nature of the solution of strong acids from the point of view of the salt effect. System: nitric acid–sodium nitrate. L. H. ANGUS and H. M. DAWSON (Proc. Leeds Phil. Lit. Soc., 1926, **1**, 104—107).—According to previous work (Carter, A., 1926, 236), the solubility of iodine in water is depressed by salts, such as sodium nitrate and sodium sulphate, with which it does not form a complex ion, and the salting-out effect may be expressed by the formula $s=s_0e^{-kc}$, where s_0 is the solubility of iodine in pure water, s the solubility in the same quantity of water containing c g.-mol. of salt, and k a constant depending on the nature of the salt. The behaviour of free acid varies, *e.g.*, nitric acid raises, whilst sulphuric acid lowers the solubility. To determine whether or not the behaviour of nitric acid is due to incomplete ionisation, the solubility of iodine in $1{\cdot}3N$ and $2{\cdot}7N$ solutions of nitric acid in the presence of varying quantities of sodium nitrate has been examined. The behaviour is similar to that with water and sodium nitrate alone, the value of k in the formula increasing very slightly from 0·0533 for water to 0·0577 for the weaker acid and 0·0593 for the stronger. The results suggest that the condition of the acid is not much affected by the addition of the salt, and therefore that the proportion of non-ionised acid is probably very small. M. S. BURR.

Determination of vapour pressures of aqueous solutions. R. WHYTLAW-GRAY and H. WHITAKER (Proc. Leeds Phil. Lit. Soc., 1926, **1**, 97—103).—The rate of evaporation of a droplet of a solution can be followed by attaching to a silica spring, suspended on a micro-balance, and following the change in weight. The diffusion gradient round the droplet can be fixed by surrounding it by a hollow vessel the inside of which is covered with a suitable absorbent material. If s is the surface at any time t, vapour pressures may be calculated from the ds/dt values for different concentrations by Langmuir's method (Physical Rev., 1918, **12**, 368). By a second comparative method, a solution of known vapour pressure may be used to wet the inside of the vessel surrounding the droplet, which is then allowed to evaporate until equilibrium is reached, when its vapour pressure will be the same as that of the surrounding liquid. The composition of the droplet can then be calculated by weight. By the second method, the vapour pressures of about 65% and 19% sulphuric acid solutions have been determined, using in the first case a mixture of oxalic acid and its dihydrate to cover the inside of the surrounding vessel, and in the second a solution of sucrose of known vapour pressure. The values obtained for the lower concentrations are in good agreement with those of Grollman and Frazer (A., 1925, ii, 398), and for the higher with those of Daudt (Z. physikal. Chem., 1923, **106**, 255). M. S. BURR.

Binary liquid mixtures. XXIV. G. WEISSENBERGER and R. HENKE (J. pr. Chem., 1927, [ii], **115**, 75—77).—The fact that the partial pressures of methyl alcohol in many binary mixtures (cf. Weissenberger, Henke, and Sperling, A., 1926, 787) calculated on the van Laar formula are greater than those of methyl alcohol alone led the authors to redetermine the values of the van der Waals constants for a number of substances, and so to detect many inaccuracies in the recorded data. The new values, determined between 20° and 30°, for a (litre-atm.) and b (litre), respectively, are as follows: tetrahydronaphthalene, 20·9 and 0·1147; *cyclo*hexanone, 15·7 and 0·0873; anethole, 8·5 and 0·0825; *cyclo*hexanol, 14·4 and 0·0869; methyl alcohol, 7·4 and 0·0349; monochloroacetic acid, 5·9 and 0·0462; dichloroacetic acid, 14·3 and 0·0709; trichloroacetic acid, 31·8 and 0·0985; pentachloroethane, 16·3 and 0·0992; benzaldehyde, 16·4 and

0·0864; phenetole, 18·1 and 0·1051; phenyl acetate, 32·4 and 0·1138. When these values are employed, the deviations from the calculated curve vanish. J. W. BAKER.

Binary liquid mixtures. XXV. G. WEISSENBERGER (J. pr. Chem., 1927, **115**, 78—80).—A summary of conclusions concerning the nature of residual fields which have resulted from the study of binary mixtures (cf. A., 1926, 787). All organic compounds possess a residual field which is polar in character and depends on the constitution of the compound, the formation of molecular compounds being only an extreme case. J. W. BAKER.

Phase-rule study of the zinci-, cadmi-, mercuri-, and nickelo-cyanides of potassium. A. S. CORBET (J.C.S., 1926, 3190—3202).—Potassium cyanide forms compounds of the type $K_2M(CN)_4$ with the cyanides of zinc, cadmium, and mercury, respectively. Aqueous solutions of the double compound dissolve increasing amounts of the heavy metal cyanide on passing from zinc to mercury. Hence, in the cyanometric determination of zinc, the potassium cyanide solution must not be too strong, about 0·2*N* being suitable. With nickel cyanide, a compound, $K_2Ni(CN)_4,H_2O$, is formed, and solutions which are in equilibrium with solid nickel cyanide contain the simple cyanides in the stoicheiometric ratio required for the double salt. S. J. GREGG.

Stability of iron carbide at high pressures. E. SCHEIL (Z. anorg. Chem., 1926, **158**, 175—180).—From the data of Sauerwald for the changes in volume of white and grey cast iron on solidifying (B., 1926, 131) it is deduced that at high pressures iron carbide probably possesses a region of stability, and the p–t–x diagram is discussed. R. CUTHILL.

Double sulphates of rare-earth and alkali metals. VII. Lanthanum ammonium sulphates. F. ZAMBONINI and (MISS) A. STOLFI (Atti R. Accad. Lincei, 1926, [vi], **4**, 424—429; cf. A., 1926, 1113).—The isotherms for the system $La_2(SO_4)_3$–$(NH_4)_2SO_4$–H_2O at 25° reveal the existence of the compounds 1 : 1 : 2, 1 : 3 : 0, 1 : 5 : 0, and 1 : 6 : 0 (cf. Marignac, "Oeuvres," I, 393; Cleve, A., 1875, 337; Kraus, *ibid.*, 1901, ii, 453, and Barre, *ibid.*, 1911, ii, 42). T. H. POPE.

Thermal analysis of binary systems of anhydrous beryllium chloride with various metallic chlorides. J. M. SCHMIDT (Bull Soc chim., 1926, [iv], **39**, 1686—1703).—The beryllium chloride was prepared by passing carbonyl chloride over beryllium oxide at 750—800°; it contained 98·5% $BeCl_2$, the remainder being water. The binary mixture was prepared in each case by fusing the two substances together and allowing to cool with constant stirring. The f.-p. diagrams so obtained showed that the chlorides of silver, lead, and cadmium give no compounds with beryllium chloride; those of sodium, lithium, and thallium give compounds of the type $BeCl_2,2MCl$, whilst thallium chloride gives in addition $2BeCl_2,TlCl$ and barium chloride gives $BeCl_2,BaCl_2$. In no case were mixed crystals obtained. S. J. GREGG.

Double decomposition in absence of solvents. VI. Irr ersible alt pair $\longrightarrow$ $Ag_2Cl_2+HgI_2$. A. G. BERGMAN and T. A. HENKE (J. Russ. Phys. Chem. Soc., 1926, **58**, 80—112; cf. A., 1923, ii, 568, 636, 764, 1761; 1924, ii, 178).—The several binary systems involved were studied by the synthetic method and both liquidus and solidus curves were traced. The system Ag_2Cl_2–Ag_2I_2 has eutectic m. p. 264°, 46·5% AgI, polymorphic, transition point AgI 129—130°; $HgCl_2$–HgI_2 has eutectic m. p. 145°, 47% HgI_2, transition point 73°; Ag_2Cl_2–$HgCl_2$ has eutectic m. p. 272°, 16·5% AgCl, no solid solutions; HgI_2–Ag_2I_2 both solid solutions and compound formation ($2AgI,HgI_2$, incongruent), eutectic m. p. 245°, 5·5% Ag_2I_2. Steger's work (A., 1903, ii, 482) is criticised. Ag_2Cl_2–HgI, has eutectic m. p. 137°, 32·5% Ag_2Cl_2.

The salt pair, $HgCl_2+Ag_2I_2 \longrightarrow Ag_2Cl_2+HgI_2$, is shown in a three-dimensional diagram. One diagonal (Ag_2Cl_2–HgI_2) cuts it into two ternary systems, the other is a section through them. Diagrams for both are given. The ternary system Ag_2Cl_2–HgI_2–$HgCl_2$ has eutectic m. p. 121°, 14% Ag_2Cl_2, 56·5% HgI_2, 29·5% $HgCl_2$, HgI_2 transition point 80—82°. The system Ag_2Cl_2–HgI_2–Ag_2I_2 has eutectic m. p. 136°, 31% Ag_2Cl_2, 68% HgI_2, 1% Ag_2I_2. The diagrams are complicated by the compound $2AgI,HgI_2$. M. ZVEGINTZOV.

Independent components and univariant systems. R. WEGSCHEIDER (Z. anorg. Chem., 1927, 159, 161—185; cf. A., 1904, ii, 17).—Theoretical. J. S. CARTER.

Reaction regions. XII. Reaction space Fe–Mg–Al–S. W. P. JORISSEN and B. L. ONGKIEHONG (Rec. trav. chim., 1926, 45, 849—853; cf. A., 1926, 246, 690).—The upper limit of the reaction region iron–aluminium–sulphur lies approximately at a mixture of 43% Fe and 57% of a mixture of 62·5% Al and 39·5% S. For the region magnesium–aluminium–sulphur, the top of the curve lies at approximately 80% Al, 20% S, and 25% Mg. The space models are discussed. L. L. BIRCUMSHAW.

Equilibrium of heterogeneous systems including electrolytes. II. Equilibrium at interfaces and the theory of electrocapillarity. J. A. V. BUTLER (Proc. Roy. Soc., 1927, **A**, **113**, 594—604; cf. A., 1926, 908).—The conditions of equilibrium at the interfaces in a heterogeneous system including electrolytes may be obtained by the general method of Gibbs. A critical survey is made of previous theories held with regard to the mechanism of the changes produced by electrolytic polarisation at the interface between mercury and solutions of electrolytes. On the basis of the equilibrium equations, a theory of electrocapillarity is developed, including the effect of capillary-active substances. The integration of the equations requires the introduction of kinetic considerations, and a kinetic theory is developed for the adsorption of ions and the effect on the electrocapillary curves. The equations are in good agreement with the data given by Smith (Phil. Trans., 1899, **A**, **193**, 48) for potassium iodide solutions. L. L. BIRCUMSHAW.

Activity coefficients of sodium and potassium bromides and iodides in concentrated aqueous solutions. H. S. HARNED and S. M. DOUGLAS (J. Amer. Chem. Soc., 1926, **48**, 3095—3101).—From

E.M.F. measurements at 25° of cells of the type $Ag|AgX|MX(m_1)|M_xHg(0{\cdot}01\%)|MX(m_2)|AgX|Ag$, where X=Br or I, and M=Na or K, the above activity coefficients are calculated. For each metal the iodide has a higher coefficient than the bromide at a given concentration. The activity coefficients of the alkali metals decrease and those of the halide ions increase with the number of electron layers in their structure, from which it is deduced that the specific action of the ions in deforming the water molecules plays an important role in determining the free energy of an ion in concentrated solution.

S. K. TWEEDY.

Calculation of activities from f. p. C. R. BURY (J. Amer. Chem. Soc., 1926, **48**, 3123—3124).—The plot of j/m against m (cf. A., 1926, 1207) can be regarded as having zero slope at $m=0$ only in the case of aqueous solutions of non-electrolytes. A deduction of the limiting value of j/m from the graph of θ/m (which is less susceptible to experimental error than j/m) against θ, the f.-p. depression, is of more general applicability. If θ/m can be written $\lambda+\alpha\theta+\beta\theta^2+..$ then $j/m=-\delta(\theta/m)/\delta\theta$. The curve can be extrapolated readily and, for those cases in which the method is applicable (aqueous solutions of non-electrolytes; nitrobenzene solutions of alcohols and phenols) is almost a straight line in dilute solution. S. K. TWEEDY.

Specific heats of the systems sulphuric acid–water, ferrous sulphate–water, and sulphuric acid–ferrous sulphate–water. G. AGDE and H. HOLTMANN (Z. anorg. Chem., 1926, **158**, 316—320).—The specific heats of the above systems determined at 25—45° show some deviation from those calculated on an additive basis. A. S. CORBET.

Electrical resistance of concentrated sulphuric acid and theory of hydration. M. H. FISCHER and M. O. HOOKER (Kolloid-Z., 1926, **40**, 305—307).—The electrical resistance of sulphuric acid–water mixtures decreases with rise of temperature. For a given temperature the resistance decreases with increasing concentration of sulphuric acid, there being a minimum when the mixture contains 50 c.c. of concentrated sulphuric acid (d 1·84) and 200 c.c. of water. Above this concentration, the resistance increases rapidly, a second inflexion indicating the presence of excess of sulphuric anhydride. The mode of variation of properties with composition indicates a change from a solution of sulphuric acid in water to a solution of water in sulphuric acid, and the analogy with solvated colloids is discussed. E. S. HEDGES.

Conductivity of phosphoric acid solutions at 0°. A. N. CAMPBELL (J.C.S., 1926, 3021—3022).—The specific conductivity κ_0 of phosphoric acid solutions at 0° was determined for a number of dilutions, the maximum value being 1408×10^{-4} mho. The values of $1/\kappa_0 . (d\kappa/dT)_9$ were calculated by using Kohlrausch's data for 18°, and since these are larger than Kohlrausch's values for $1/\kappa_{18} . /(d\kappa/dT)_{22}$, it is inferred that the temperature coefficient will eventually become negative. S. J. GREGG.

Conductivity of acetic acid in acetone. N. SATA (Bull. Chem. Soc. Japan, 1926, **1**, 245—247).—The variation of conductivity with dilution has been investigated, and the results fit an equation of the Ostwald form. Since the constants of the equation give the high value 0·77 for the degree of dissociation at 500 litres dilution, it is suggested that the undissociated molecules also transport electricity. Great difficulties were experienced in purifying the materials.

S. J. GREGG.

Hydration of ions and variation in equivalent conductivity of salts on dilution. N. R. DHAR (Z. anorg. Chem., 1926, **159**, 57—64).—The equivalent conductivity of a salt solution on dilution increases with the degree of ionic hydration. The order of degree of hydration is Li>Na>K>Rb,Cs and Mg>Ca>Sr>Ba.

Under similar conditions, the higher the degree of hydration, the higher is the viscosity and the smaller the electric charge on the substance. M. CARLTON.

Polished platinum electrodes in conductivity work. A. F. GUERASIMOV (J. Russ. Phys. Chem. Soc., 1926, **58**, 197—200).—The catalytic action of platinum-black on organic substances, when the latter are employed as solvents, has necessitated the use of the hitherto imperfectly investigated polished platinum electrodes. Kohlrausch has dealt with the subject theoretically, but the specific influence of a solution at different dilutions on the cell constant can be determined only by experiment. From experiments with potassium chloride and magnesium sulphate at different dilutions, it is found that the relation between W, the cell-constant, and R, the resistance, is given by: $W=a+b/R$. Within certain limits, the linear relation $W=c-dR$ holds.

M. ZVEGINTZOV.

Conductivity of organic compounds and certain elements in the solid and liquid state. M. A. RABINOVITCH (J. Russ. Phys. Chem. Soc., 1926, **58**, 229—239).—The conductivity of organic compounds and halogens was investigated under a constant *E.M.F.* of 125 volts to determine the coefficient of loosening (α) of the crystal lattice, *i.e.*, the ratio of the conductivities of the solid and liquid at the m. p., with the view of elucidating the mechanism of electrical dissociation. The individual conductivities of the halogen-substituted acetic acids and the nitroparaffins are not in the same order as their conductivities in aqueous solution. The results show that symmetrical molecules with small dipole moments have little tendency to dissociate. This is confirmed by the values of α for the chloromethanes. The values of α for benzene, naphthalene, anthracene, and substituted hydrocarbons are in the order of their polarity. The behaviour of such substances in a non-polar solvent, such as ether, is analogous to the behaviour in it of acids (palmitic, stearic) of the same individual solid and liquid conductivity. Finally, the halogens were investigated by themselves and in solution, and a dynamic theory of the internal ionisation of the halogen molecule is discussed. M. ZVEGINTZOV.

Electrolytic conductivity of solids. E. FRIEDERICH (Z. Elektrochem., 1926, **32**, 576—577).—In a solid electrolyte, the ion which migrates under a potential gradient is the one carrying the smaller charge; when both ions have the same charge, the ionic diameter seems to be a determining factor (under

these conditions it is generally the metallic ion which moves). This rule covers all cases which have been investigated, but they are too few to ensure generality. H. J. T. ELLINGHAM.

Electronic conductivity of solid halides. E. FRIEDERICH and W. MEYER (Z. Elektrochem., 1926, 32, 566—576).—The type of electrical conductivity exhibited by solids can be determined from the form of the current–voltage curves obtained from measurements of the direct current flowing through a rod of the substance when various voltages are applied. For electronic conductors, the current–voltage curve is a straight line through the origin, and at given voltage the current does not change with time. For electrolytic conductors with increasing voltage, the current remains practically zero until a definite decomposition voltage is exceeded, when it increases rapidly; at given voltage, the current changes with time. Substances showing mixed electronic and electrolytic conductivities give curves of composite character. A substance to be examined was prepared as a pure, dry powder, compressed into a rod, and then caused to sinter by heating in an indifferent gas. Silver bromide and iodide showed simple electrolytic conductivity, the decomposition voltages being 0·55 volt at 270° for the bromide, 0·507 at 110°, and 0·373 volt at 230° for the iodide. Silver chloride gave a more complex curve, but this was due to the presence of traces of finely-divided silver depolarising anodic deposition of chlorine. After prolonged electrolysis at high voltage, a simple curve with decomposition voltage at 0·733 at 230° was obtained. Cuprous iodide exhibits simple electronic conductivity at the ordinary temperature, and the statement by previous workers that this is true only when excess of iodine is present is definitely refuted. Cuprous bromide behaves like the iodide at the ordinary temperature. Cuprous chloride at 120° gives a complicated current–voltage curve, the conductivity being essentially electronic at low voltages, whilst above 0·1 volt cuprous chloride begins to depolarise anodic chlorine deposition (electrolytic conductivity). The true decomposition voltage lies at 0·466 volt, but can be obtained only by decreasing the voltage after electrolysis at above 1 volt. No other halides have been reported to show electronic conductivity. Those of univalent gold, mercury, and thallium might be expected to do so, but thallous iodide at 270° showed simple electrolytic conductivity (decomposition voltage 0·6), whilst results obtained with mercurous iodide were inconclusive. Reasons for the electronic conductivity of cuprous halides are discussed. The phenomenon may be connected with the facility with which the copper atom loses two valency electrons, although it is in group 1 of the periodic classification. H. J. T. ELLINGHAM.

Electrical transport in solutions in fused aluminium bromide. W. ISBEKOV (Z. anorg. Chem., 1926, 158, 87—93).—The following values have been obtained for the transport number of the cation in solutions of bromides in fused aluminium bromide: 11·97% solution of potassium bromide at 110°, 1·14; 14·33% solution of silver bromide at 130°, 0·837; 31·09% solution of antimonious bromide at 130°, 0·953. The results are ascribed to the presence and ionisation in solution of polymerised solute molecules and solute-solvent complexes, and to solvation of the bromide ion. R. CUTHILL.

Contact *E.M.F.* between any two solutions. I. Simpler derivation of Planck's and Johnson's formulæ for solutions with equivalent cations and anions. Some considerations and formulæ for more complex cases. E. DENINA (Gazzetta, 1926, 56, 798—810).—A mathematical paper in which Johnson's expression (Ann. Phys., 1904, 14, 995) is obtained by a new method of integrating the differential equations of Nernst and of Planck as applied to the contact of two solutions having equivalent ions. The more general case of ions of any valency is discussed, and a formula is derived for the contact *E.M.F.* in a case involving three ions of any valency, provided that the total ionic concentration is equal for the two solutions. This formula includes as a special case the expression deduced by Guyot (A., 1908, ii, 656). G. M. BENNETT.

Rate of maximum activation by collision for complex molecules with applications to velocities of gas reactions. R. H. FOWLER and E. K. RIDEAL (Proc. Roy. Soc., 1927, A, 113, 570—584).—Theoretical. Homogeneous unimolecular reactions are considered from Arrhenius' point of view, *i.e.*, an equilibrium between active and inactive molecules, where the active molecules are all those which contain internal energy greater than ϵ_0. The rate of decomposition is then proportional to the total molecular concentration as long as the rate of activation and deactivation is large compared with the rate of decomposition. If x and y are the concentrations of active and inactive molecules at any time, then from the two equations $dx/dt=Z'y-(Z+B)x$, and $dy/dt=-Z'y+Zx$, where $Z'ydt$ is the total number of activations in time dt, and $Zxdt$ the total number of deactivations, it is shown that $x=X_0e^{-BZ't/(Z+Z')}$, $y=Y_0e^{-BZ't/(Z+Z')}$, which is of the unimolecular form. The value of ϵ_0 is known from Arrhenius' equation and from observations on the effect of temperature, and from ϵ_0 x can be calculated from statistical theory, and B is then determined from observations of the absolute rate of decomposition. The fraction of molecules with energy greater than ϵ, and the total number of collisions with available energy greater than ϵ_0 are calculated, and on the basis of these results the decomposition of nitrogen pentoxide and the dissociation of bromine are discussed. The calculation on the above basis for the decomposition of the former leads to a rate which is more than twenty times as large as the observed reaction rate at low pressures, and it is considered that the possible rate of activation may still be several hundred times the rate of decomposition at the lowest pressures, and that the real rate of activation by collision can be easily great enough to account for the observed unimolecular rate and law. Similar results are obtained in the case of bromine.

L. L. BIRCUMSHAW.

Thermal reactivity of ozone in presence of hydrogen. J. W. BELTON, R. O. GRIFFITH, and A. MCKEOWN (J.C.S., 1926, 3153—3166).—Reaction velocity measurements have been made in mixtures

of ozone, oxygen, and hydrogen at 78° and 100°. The deozonisation process $2O_3 \longrightarrow 3O_2$, and a water-forming reaction (probably $H_2+O_3 \longrightarrow H_2O+O_2$) occur. The values of k_2 and k_1, the respective bimolecular velocity coefficients, both increase markedly with increasing partial pressure of hydrogen, but decrease with increasing partial pressure of oxygen. The catalytic effect of hydrogen is very much stronger than that of the inert gases helium and argon (A., 1925, ii, 1168). The ratio k_2/k_1 varies relatively slightly with the composition of the gas mixture, lying between 22 and 17 at both temperatures. Conditions which favour an increase in k_2 have a similar effect on k_1, and the two reactions are probably coupled in some way. The temperature coefficient of k_2 in the absence of hydrogen is 2·9; in the presence of excess of hydrogen, it is 2·4. The average value of E from the Arrhenius equation is 27,700 g.-cal. The mechanism of the reactions is discussed. W. THOMAS.

Ignition point of gases at different pressures. H. B. DIXON and W. F. HIGGINS (Mem. Manchester Phil. Soc., 1925—1926, 70, 29—36).—A preliminary account of experiments on the ignition points of hydrogen and of methane in air and in oxygen at various pressures from 100 mm. to 7 atm. The gases were brought into contact in an improved form of concentric cylinder device, and the time elapsing, or lag, between the moment of mingling of the combustible gas with air or oxygen and that of the appearance of the flame has been observed as a function of the temperature of the mingling gases and of their pressure. The differences between the values obtained for the ignition temperatures, corresponding with experiments using an open-ended, and (the same) closed ignition tube (in which the preheating was more uniform), as a function of the lag show a maximum for hydrogen and an increase for methane as the lag is increased from 0·5 to 15 sec. The effect of increasing pressure for mixtures of hydrogen and air for values of the lag from 0·5 to 3·0 sec. show a maximum for the ignition point at 1000 mm. in the range 75—1520 mm. In the range 100—5320 mm., methane–air mixtures show a progressive diminution; methane–oxygen mixtures, however, reach a maximum at 200 mm. The existence of these maxima is held to be a general property of combustible gases.

R. W. LUNT.

Supposed law of flame speeds. A. G. WHITE (Nature, 1927, **119**, 51).—Wheeler and Payman's speed generalisation must obviously break down when one of the combustible gases in a complex mixture interferes with the burning of another, as is the case with carbon monoxide–hydrogen–air mixtures (cf. Bone, this vol., 26). By mixing suitable carbon disulphide–air and ether–air mixtures having the same flame speed, mixtures can be obtained which do not propagate flame. A. A. ELDRIDGE.

Ignition of gases by an explosion-wave. I. Carbon monoxide and hydrogen mixtures. C. CAMPBELL and D. W. WOODHEAD (J.C.S., 1926, 3010—3021).—A photographic investigation has been made of the behaviour of the flame in certain gaseous mixtures ignited by the explosion-wave in a hydrogen–oxygen mixture. An apparatus is described allowing of the photographing of a flame as it travels from one explosive mixture into another. When the igniting and ignited gases are mixtures of hydrogen and oxygen in different proportions, the flame travels in both mixtures at the normal explosion-wave rates, the velocity in the second mixture becoming adjusted after travelling a few cm. in it. When the mixture $2CO+O_2$ is ignited by electrolytic gas, the flame velocity falls rapidly to less than half the normal rate, and detonation is re-established only after the flame has travelled several metres. A fairly complete drying of the carbon monoxide mixture does not appear to lower the flame speed below a certain limit, although it lengthens the period before detonation. The addition of more than 1% of hydrogen to the carbon monoxide mixture allows the flame to proceed immediately at its full rate; hydrogen is thus more efficient than water vapour in allowing the explosion wave to develop. A flame just previous to the setting up of the explosion-wave in these mixtures tends to show marked discontinuities. The reasons for the temporary damping down of the explosion wave in passing from the hydrogen–oxygen to the carbon monoxide–oxygen mixture have been suggested by Dixon and Walls (J.C.S., 1923, **123**, 1025) and Crussard (Bull. Soc. Ind. Min., 1907, **6**, 257).

W. THOMAS.

Pressure wave sent out by an explosive. II. W. PAYMAN and W. C. F. SHEPHERD.—See B., 1927, 30.

Influence of the reaction on the decomposition of sulphuretted waters by a current of inert gas; hydrological applications. A. DESGREZ, L. LESCŒUR, and (MLLE.) S. MANJEAN (Compt. rend., 1926, **183**, 1244—1247).—The rate of removal of hydrogen sulphide from solutions by a stream of inert gas is modified by the addition of certain salts. In the case of Challes water, 5% of sodium hydrogen carbonate and of potassium monophosphate accelerated the removal of the gas, the latter to the greater extent. Sodium borate (1%) had less influence, a curve being obtained from which the angular point previously found for sulphuretted waters (A., 1926, 1113) was absent. Experiments in which borate and phosphate buffer solutions were added to the sample showed that it is the p_H value which influences the rate of removal of hydrogen sulphide. The curve showed the instability of the gas in an acid medium and its stability in an alkaline medium, a rapid transition taking place at p_H 8—9. Since the mean p_H of the urine is 6·5, the absence from it of hydrogen sulphide, even after considerable quantities of sulphuretted waters have been drunk, is explained.

J. GRANT.

Law of hydrolysis of sucrose by acids. H. COLIN and (MLLE.) A. CHAUDUN (Compt. rend., 1926, **183**, 1285—1286).—The ratio of the velocity of hydrolysis to the weight of crystallisable sugar in the liquor, $1/t \cdot \log a/(a-x)$, has been determined for the hydrolysis of 10% solutions of sucrose by 0·1N-nitric and oxalic acids; it increases with the time. This indicates that the reaction is neither simply unimolecular nor the resultant of two reactions, one of which is instantaneous. Such reactions would be

produced respectively by the hydrogen ions and by the formation of an unstable complex compound between the sucrose and the elements of water, with subsequent decomposition into dextrose and lævulose. In the latter case, the cations and anions of the acid respectively assist in the formation and decomposition of the complex. J. GRANT.

Hydrolysis of α- and β-glycerophosphoric acids by chemical reagents and by enzymes. P. FLEURY and Z. SUTU (Bull. Soc. chim., 1926, [iv], **39**, 1716—1718).—No difference in the rate of hydrolysis of α- and β-glycerophosphoric acids was found with hydrochloric acid, sodium hydroxide, or the enzyme from white mustard as hydrolysing agent. S. J. GREGG.

Irreversible oxidation of organic compounds. I. Oxidation of aminophenols by reagents of definite potential. II. Apparent oxidation potentials of certain phenols and enols. J. B. CONANT and M. F. PRATT (J. Amer. Chem. Soc., 1926, **48**, 3178—3192, 3220—3232).—I. The rates of irreversible oxidation of *o*- and *p*-aminophenol and of 1 : 2- and 1 : 4-aminonaphthols by reversible oxidising agents have been studied in a manner analogous to that previously applied to irreversible reduction processes (cf. A., 1926, 1134). These rates are independent of the dilution, and are related to the oxidation–reduction potential of the reagent employed. By measuring the rate of oxidation of each of the above substances by a series of reagents of graded potentials, the potential of the (hypothetical) reagent which just causes "appreciable oxidation" can be determined, and this potential is called the "apparent oxidation potential" of the substance under examination. These relationships suggest that the rate of the total oxidation process is governed by that of the stage which is itself reversible, a condition which would be fulfilled if the first stage of the oxidation of the aminophenols to the corresponding quinones is a reversible oxidation to the quinoneimine, the subsequent hydrolysis of which is irreversible and relatively slow (cf. Wieland, A., 1910, i, 243). Evidence of the reversibility of the oxidation of *p*-aminophenol to benzoquinoneimine was obtained by the titration method and the method of mixtures in alkaline solutions (p_H 7·8—11·3), in which the quinoneimine is relatively stable. Certain electrochemical equations are developed, and the relative rates of oxidation of each amino-compound with several reagents of different potentials are shown to be of the order of magnitude predicted from these.

II. The rate of oxidation of α-naphthol in acid solution (p_H 2·6—6·9) at 60° by reversible reagents of known potential has been determined, and the rate of oxidation shown to be related to the potential of the reagent employed. The rates of oxidation of phenol, resorcinol, α- and β-naphthols, quinol monomethyl ether, ethyl malonate, and ethyl acetoacetate are practically independent of dilution. It is suggested that the first stage in the oxidation is the reversible formation of a free radical (cf. Goldschmidt, A., 1924, i, 1062), which then undergoes unimolecular isomerisation and polymerisation. Certain electrochemical equations are developed on this assumption, and the above relative rates of oxidation of α-naphthol are of the order of magnitude predicted from these equations. The apparent oxidation potentials of a number of phenolic and enolic substances have been determined in buffer solutions of varying acidity at 25° and 60°. F. G. WILLSON.

Velocities of esterification. P. PETRENKO-KRITSCHENKO, V. BOGATSKY, and N. LOUBMAN, (J. Russ. Phys. Chem. Soc., 1926, **58**, 215—218).—A summary of work already published (A., 1925, ii, 556) on velocities of esterification of primary, secondary, and tertiary alcohols under different conditions with the view of elucidating the mechanism. The theories of Menschutkin and of Michael (*ibid.*, 1909, ii, 219) are only partly true; there is a lack of uniformity in the results, and the variations of rate depend more on the nature of the acid than on the groups attached to the α-carbon atom of the alcohols. M. ZVEGINTZOV.

Decomposition of diacetone alcohol [*iso*hexan-δ-ol-β-one] in alkali hydroxide-alkali salt solutions. G. ÅKERLOF (J. Amer. Chem. Soc., 1926, **48**, 3046—3063).—The velocity of decomposition of *iso*hexan-δ-ol-β-one dissolved in some alkali salt solutions (up to 6*N*) of constant alkali concentration was investigated at 25°. The results obtained were always the opposite to those obtained in an acid–salt solution of corresponding concentration. The velocity–salt concentration curves have the same general form, independent of the nature of the anion of the salt; the curves for salts with a common cation never intersect. Potassium cyanide has a higher activity coefficient than the sodium salt at the same concentration; similar behaviour is shown by the alkali hydroxides (Harned and Åkerlof, A., 1926, 796). The rate of decomposition of a compound by hydrogen and hydroxyl ions in a salt solution is always directly related to the activity coefficients of these ions, an increase in the coefficient increasing the velocity, and *vice versa*. S. K. TWEEDY.

Rate of dissolution of copper in aqueous ferric chloride solutions. E. BEKIER and S. TRZECIAK (Rocz. Chem., 1926, **6**, 483—496).—See A., 1926, 482.

[Oxidising action of iodic acid and its restriction.] O. WARBURG (Ber., 1926, **59**, [*B*], 2705; cf. A., 1926, 1011).—A claim for priority against Fischer and Wagner (*ibid.*, 1215). H. WREN.

Relation between the order of a reaction and its temperature coefficient for reactions of certain organic acids with chromic acid or potassium permanganate. A. N. DEY and N. R. DHAR (Z. Elektrochem., 1926, **32**, 586—596).—Velocity constants of the following reactions have been measured in the dark, at various temperatures, with various concentrations of reactants, and with or without the presence of manganous sulphate as catalyst. From the results are obtained the number of molecules of organic acid (n_1) and of oxidising agent (n_2) participating in the reaction, and the temperature coefficient ($c = k_{T+10}/k_T$) of the reaction. Tartaric acid, $n_1 = 2$, $n_2 = 0$, $c = 2·4$ (25—35°); with addition of manganous sulphate, n_1 = about

1·5, $n_2 = 0$, c = about 5. Lactic acid and chromic acid, $n_1 = 2$, $n_2 = 1$, $c = 2·16$ (25—35°); with addition of manganous sulphate, $= 2$, $n_2 = 0$, $c =$ 2·5 (25—35°). Maleic acid and chromic acid, $n_1 =$ about 2, $n_2 = 1$, $c = 1·96$ (25—35°); with addition of manganous sulphate, $n_1 = 1·5$, $n_2 = 0$, $c =$ 3·9 (25—35°). The reactions of tartaric, citric, and lactic acids with potassium permanganate are all unimolecular with respect to the permanganate, and the temperature coefficients are, respectively, 2·55, 1·8, and 3·2 (10—20°); they are retarded by increasing concentration of manganous salt, but accelerated by sulphuric acid. An increase in the concentration of tartaric acid or of lactic acid causes a slight decrease in the corresponding velocity constant, but change in the concentration of citric acid is practically without influence. The results are claimed to support the "von Halban–Dhar" rule that the lower is the order of a reaction (true, not "apparent" order), the higher is the temperature coefficient. The life-period of activated molecules in three of these reactions is calculated by the Turner equation.

H. J. T. Ellingham.

Acid and salt effects in catalysed reactions. III. Dependence of the characteristics of the minimum-velocity mixture on the concentration of the acid and the application of minimum velocity to the determination of catalytic and ionisation constants. H. M. Dawson and C. R. Hoskins (J.C.S., 1926, 3166—3173).—The reaction velocities (v_i) and hydrogen-ion concentration $[H]_i^+$ characteristic of the minimum-velocity mixture for the catalysis of the acetone–iodine reaction by acetic acid and sodium acetate have been determined for acid concentrations ranging from 0·01N to N. The variations of v_i and of $[H]_i^+$ with the concentration of the acid between 0·01N and 0·50N are in accordance with theoretical predictions. The ratio of the minimum velocity to the corresponding hydrogen-ion concentration is independent of the concentration of the acid. The data for N-acetic acid are not in agreement; this may be connected with a decrease in the ionisation constant of the acid in more concentrated solutions. Minimum velocities may be used for the determination of the catalytic coefficient characteristic of the undissociated acid. A kinetic method for the determination of the dissociation constants of weak acids is described and applied to the experimental data for acetic acid.

W. Thomas.

[Acid and salt effects in catalysed reactions. V.] Isohydric solutions and the velocity of chemical change. H. M. Dawson and C. R. Hoskins (Proc. Leeds Phil. Lit. Soc., 1926, **1**, 108—112).—When the reaction between iodine and acetone is catalysed by a solution containing equimolecular quantities of acetic acid and sodium acetate, and therefore of approximately constant p_H value 4·73, the velocity is not the same for all the solutions, as might be expected by the hydrogen-ion theory of catalysis, but for a N solution is about 160 times as great as for a 0·005N solution. It is shown, however, that these results may be accounted for quantitatively on the assumption that the total catalytic effect produced by an acid, or by a mixture of this with the corresponding sodium salt, represents the sum of effects which are separately produced by the hydrogen ion, the acid anion, the hydroxyl ion, and the undissociated acid.

M. S. Burr.

Catalysis [of decomposition of ethyl alcohol]. D. Balarev [with N. Kolev] (Z. anorg. Chem., 1926, **158**, 105—110; cf. A., 1923, i, 287).—When ethyl alcohol and phosphoric acid are heated together, the reaction with rise of temperature successively assumes the following forms: (*a*) formation of phosphates, (*b*) formation of phosphates and simultaneous partial decomposition with production of ethylene, (*c*) partial adsorption of alcohol on surface of phosphoric acid, and partial combination, and (*d*) adsorption of alcohol, but no combination. In all stages except the first, ethylene is formed.

R. Cuthill.

Heterogeneous catalysis and electrochemical polarisation. E. Spitalsky and M. Kagan (Ber., 1926, **59**, [*B*], 2900—2907).—The catalytic decomposition of hydrogen peroxide in neutral solution at 25° in the presence of smooth and platinised platinum and of platinum foil has been investigated. The activity of the metal depends largely on its previous electrochemical treatment, being greatly increased by cathodic polarisation, but decreased by anodic polarisation. Platinised platinum which has been exclusively treated cathodically exhibits an unusually high catalytic activity, and the reaction, under otherwise identical conditions, follows an unusual course, since the constants, calculated for a reaction of the first order, diminish rapidly during the change. The effect is not due to a metastable condition of the metal, since the original activity of the fatigued metal is restored when the concentration of the hydrogen peroxide is increased. Feeble anodic polarisation destroys this enhanced activity, and the electrode then behaves normally, causing decomposition with smaller and tolerably uniform constants of the first order. Sufficiently drastic anodic polarisation almost destroys the catalytic activity of the metal, which, however, can be restored by cathodic treatment, so that, by alternate use as anode or cathode, the activity of the metal can be varied at will. Electrodes, passive because of anodic treatment, can be activated by treatment in concentrated sulphuric acid or glycerol at 150—165°, or, to a less extent, in boiling water (cf. Teletoff, A., 1908, ii, 95); the effect is due to the temperature used.

H. Wren.

[Catalytic hydrogenation.] W. Traube and W. Lange (Ber., 1926, **59**, [*B*], 2860—2863; cf. Wieland and Fischer, A., 1926, 806).—The application of the dehydrogenation theory to the decomposition of water by chromous salts (cf. Traube and Lange, A., 1926, 257) and to the action of carbon dioxide on water in the presence of palladium, necessitates the adoption of arbitrary subsidiary hypotheses without experimental foundation. The conversion of chromous to chromic salts is accelerated by substances which cannot be regarded as hydrogen acceptors. The production of sodium formate cannot be established when carbon monoxide and water interact at a palladium surface in the presence of alcoholic sodium hydroxide.

H. Wren.

Low-temperature oxidation at charcoal surfaces. III. Behaviour of blood charcoal and the influence of temperature on the reaction rate. E. K. RIDEAL and W. M. WRIGHT (J.C.S., 1926, 3182—3190).—The area of carbon surface active for the oxidation of oxalic acid varies within the limits 30—55% of the total, depending on the method of preparation of the charcoal. The range of promoter action of one iron atom extends to not more than six carbon atoms, and an analogy is sought in the complex iron cyanides. The variation in adsorption of oxalic acid with the temperature is small; the temperature coefficient of oxidation increases with increasing concentration of oxalic acid. From the temperature coefficients, the following critical energy increments are calculated; for autoxidation 11,000 g.-cal. per g.-mol.; for oxidation of oxalic acid on the C–C complex 14,020 g.-cal.; on the –Fe–C– complex 13,030 g.-cal.; and on the Fe–C–N complex 12,290 g.-cal. The nature of the surface adsorption of the oxygen is more important than the surface concentration of the oxalic acid. Sugar and blood charcoals differ in the amount of oxalic acid adsorbed, but are identical in respect of the rates of oxidation of oxalic acid and the temperature coefficients of the rates (cf. A., 1926, 919). W. THOMAS.

Catalytic synthesis of water vapour in contact with metallic silver. A. F. BENTON and J. C. ELGIN (J. Amer. Chem. Soc., 1926, 48, 3027—3046).—The above synthesis was investigated at 50—100° by the method of Pease and Taylor (cf. A., 1922, ii, 701), the results being treated by a new quantitative method. When hydrogen is in excess, the rate of water formation rapidly attains a maximum, and then falls slightly and reaches a steady state after about 40 min.; it rapidly becomes zero on cutting off the oxygen, so that the latter is not continuously taken up and retained by the catalyst, although small quantities are absorbed at the start of a run. With oxygen in excess, the steady state is attained more rapidly, no hydrogen being taken up by the catalyst. No hydrogen peroxide could be detected in the reaction products. The rate of the reaction is proportional to the pressure of hydrogen, and is independent of the oxygen pressure; the reaction is anti-catalysed by the water vapour formed, due to absorption of the latter by the silver, and is retarded by a preliminary heating of the catalyst in oxygen, when large quantities of this gas are adsorbed independently of the temperature (26—110°) and pressure. The reaction depends on collisions of gaseous hydrogen molecules with those adsorbed oxygen atoms which are free from adsorbed water, although possibly the oxygen atoms must be adjacent to bare spaces on the catalyst surface in order to react readily. S. K. TWEEDY.

Catalytic decomposition of ammonia. E. ELOD and W. BANHOLZER (Z. Elektrochem., 1926, 32, 555—558).—The percentage decomposition of ammonia caused by passage through a heated tube containing a catalyst (iron, copper, or alumina) was measured for various rates of flow of the gas. Determinations were made at 700° and 600°. For a mixture of ammonia and nitrogen or argon, the extent of decomposition was simply that corresponding with the rate of flow of ammonia through the tube under the given conditions, but for mixtures of ammonia and hydrogen, the percentage decomposition was notably less than that corresponding with the rate of passage of the ammonia. Hydrogen causes this retardation in the velocity of decomposition of ammonia when other catalysts, such as cerium oxide, are used. With a 50% mixture of ammonia and hydrogen, increasing the rate of flow reduces the extent of decomposition of the ammonia more considerably and relatively more sharply than in the corresponding experiments with ammonia alone. Rise of temperature increases the percentage decomposition in all cases, but the magnitude of this effect depends greatly on the catalyst used and on whether the gas is mixed with nitrogen or hydrogen. H. J. T. ELLINGHAM.

Effect of formaldehyde on the dissolution of iron in acids. G. BATTA (Bull. Soc. chim. Belg., 1926, 35, 393—411).—The presence of formaldehyde greatly reduces the rate of dissolution of powdered cast iron in hydrochloric acid; the extent of the reduction is not proportional to the amount added, but addition of 0·25 c.c. of a 40% solution to 100 c.c. of 17% acid reduces the rate to 0·25 of the normal. The rate varies with the time, about half the metal added being left after 19 hrs. in presence of 0·25 c.c. of the formaldehyde solution, but all being dissolved after that time if none is present. The retardation is less pronounced at higher temperatures. Even 1 mg. of formaldehyde exercises a marked effect, using 100 c.c. of acid. No loss of formaldehyde from the solution occurs in laboratory tests. Similar results were obtained with steel and wrought-iron plates; the addition of 2% by volume of commercial formaldehyde solution to the acid reduced the loss in weight under comparable conditions to one fiftieth. The effects of acetaldehyde and propaldehyde are very similar in nature and extent. S. I. LEVY.

Cathodic sputtering. II. Variations in experimental conditions. E. BLECHSCHMIDT (Ann. Physik, 1926, [iv], 81, 999—1042). **III. Theory of cathode sputtering.** A. VON HIPPEL (*ibid.*, 1043—1075; cf. A., 1926, 1013).—A systematic study has been made of the effect of variations in experimental conditions—dimensions, materials, temperature, etc.; and a general theory of cathodic sputtering has been based on the conception of local vaporisation of the electrode metal under bombardment. The impact-velocity of the cations has been measured directly. The implications of local vaporisation are developed thermodynamically and subjected to experimental test. An expression which gives a complete qualitative formulation of the sputtering phenomena is advanced. The relationships existing between the following variables are discussed: area and thickness of sputtered film, time of sputtering, number of atoms released from electrode. The order of ease with which metals are sputtered is that of decreasing heat of sublimation. The influence of secondary factors and the elimination of some such effects are further discussed. R. A. MORTON.

Use of auxiliary washing electrodes in the preparation of pure hydrogen by electrolysis.

A. MÜLLER (Physikal. Z., 1926, 27, 778—779).—The claim that oxygen-free hydrogen can be prepared by the use of an auxiliary cathode to generate hydrogen for hindering the diffusion of oxygen through the electrolyte (Niese, A., 1923, ii, 314) is contested, and Gaede's method (Ann. Physik, 1913, [iv], 41, 302) is preferred. R. A. MORTON.

Electrolytic preparation and electromotive behaviour of complex cyanides of univalent nickel and cobalt. G. GRUBE [with H. LIEDER and P. SCHÄCHTERLE] (Z. Elektrochem., 1926, 32, 561—566).—Solutions containing the complex cyanide, $K_2Ni(CN)_3$, in which nickel is univalent (cf. Bellucci and Corelli, A., 1914, i, 260), are produced by electrolytic reduction of a cold alkaline solution of potassium nickelocyanide, $K_2Ni(CN)_4$, using a nickel cathode in a diaphragm cell from which air is excluded; the anolyte is a dilute potassium hydroxide solution. Cathode materials of higher hydrogen overvoltage have no advantage, since they soon become coated with nickel. The resulting blood-red solution may have 60—70% of its nickel content in the univalent form. It oxidises in the air and evolves hydrogen on warming. Electrolytic reduction of alkaline solutions of potassium cobalticyanide under similar conditions at cathodes of platinum, cobalt, nickel, or tin produces first an olive-green solution of potassium cobaltocyanide and then a brownish-green solution containing a complex cyanide of univalent cobalt. The latter could not be isolated from the solution, which decomposes with vigorous evolution of hydrogen at the ordinary temperature. Solutions of this substance are also obtained by treating solutions of potassium cobalticyanide or cobaltocyanide with potassium amalgam. It can be determined by measuring the hydrogen evolved on boiling the solution or by titration with permanganate. Potentials of electrodes of the type Pt(platinised)|$K_4Co(CN)_6$,$K_3Co(CN)_6$ in 0·77*N*-KOH were measured and ${}_0\varepsilon_h$ was calculated to be −0·814 at 2°. Similar measurements were made on solutions containing the complex cyanides of univalent nickel and cobalt, *e.g.*, Pt(platinised)|$K_2Ni(CN)_4$ (0·057 g.-mol./litre), $K_2Ni(CN)_3$(0·049 g.-mol./litre) in *N*-KOH, ε_h = −0·880 at 2°; Pt(platinised)|$K_4Co(CN)_6$ (0·057 g.-mol./litre), $K_xCo(CN)_{x+1}$ (0·043 g.-mol./litre), ε_h = −0·846 at 2°. Hydrogen is evolved at the platinum in all cases, and the results may thus be low. Cobaltocyanide can be determined in the presence of cobalticyanide by oxidising with alkaline potassium ferricyanide, acidifying, and titrating electrometrically with permanganate the ferrocyanide produced.
H. J. T. ELLINGHAM.

Mechanism of Kolbe's electrosynthesis. D. A. FAIRWEATHER and O. J. WALKER (J.C.S., 1926, 3111—3121).—Solutions of acetates and propionates have been electrolysed under various conditions, and it is shown that synthesis is not due to the partial oxidation of the acid formed by the action of the discharged ions on water, but to the direct interaction of the discharged ions themselves. The effect on yield of the concentration, temperature, current density, and anode material has been studied. A certain minimum concentration of discharged ions is necessary before synthesis can commence. The yield is increased in non-aqueous solvents where reaction between the discharged ions and the solvent cannot take place, and where, therefore, the oxidation theory is not applicable. The electrolytic oxidation of acetic acid is complete to carbon dioxide and water, and not partial under ordinary conditions.
W. THOMAS.

Anodic oxidation of aluminium and its alloys as a protection against corrosion. G. D. BENGOUGH and J. M. STUART.—See B., 1927, 16.

Decomposition of nitrogen pentoxide. R. G. W. NORRISH (Nature, 1927, 119, 123).—As an alternative to the hypothesis of Fazel and Karrer (this vol., 29) decomposition of nitrogen pentoxide is regarded as taking place as follows: (*a*) $2NO_2$(in light) $\longrightarrow 2NO+O_2$; (*b*) $NO+N_2O_5=3NO_2$. Hence the decomposition of nitrogen pentoxide is not a true photosensitised reaction, but a secondary dark reaction.
A. A. ELDRIDGE.

Quanta measurements of the decomposition of lactic acid in the presence of uranyl sulphate. R. H. MULLER (Biochem. Z., 1926, 178, 77—81).—The photochemical conversion of lactic acid into acetaldehyde and carbon dioxide in the presence of uranyl sulphate gives an energy absorption of 1·05 quanta per mol., the average wave-length of the irradiation being 4025 Å. Using an oxalic acid–uranyl sulphate solution as an actinometer system, 0·99 quantum is absorbed per mol., so that the Einstein equation holds. Oxalic acid–uranyl sulphate solution is well suited to act as an actinometer in systems in which uranyl salts play a catalytic or oxidative part.
J. PRYDE.

Light-distribution between two absorbing media, and the conception of intensity in photochemistry. J. PLOTNIKOV (Z. wiss. Phot., 1926, 24, 305—308).—It is shown that, instead of the usual expression, it is preferable to regard the total absorption of light by a mixture of two absorbing media as the sum of the absorptions of the two components. The question of light intensity, in particular the bearing of the experiments of Lasarev (Ann. Physik, 1907, 24, 661) on the problem, is considered.
W. CLARK.

Panchromatisation of photographic plates for use in the ordinary spectrum. E. VITERBI.—See B., 1927, 61.

Active hydrogen. M. SCANAVY-GRIGORIEVA (Z. anorg. Chem., 1926, 159, 55—56).—Formation of hydrogen sulphide by hydrogenation of sulphur at the ordinary temperature is no longer sufficient evidence that hydrogen is activated by passing it over glowing metals such as platinum, palladium, etc. In experiments on the activation of hydrogen by this method, the presence of hydrogen sulphide was always observed, whether the hydrogen on its emergence from the tube of hot metal was led through sulphur or not. This is due to the tendency of substances, especially when finely divided, to absorb sulphur compounds from the atmosphere.

All the substances examined, amongst which were platinum, palladium, copper, and glazed porcelain, gave up the absorbed sulphur as hydrogen sulphide

at 600—700°. The reduction of nitrates or of tungsten or molybdenum trioxide by this method of activation has not been confirmed, and under the conditions described no activation of hydrogen in the direction of increasing its reducing powers occurs.
M. CARLTON.

Preparation of hydrogen peroxide. M. L. KILPATRICK, O. M. REIFF, and F. O. RICE (J. Amer. Chem. Soc., 1926, **48**, 3019—3021).—Pure sodium peroxide is added in small portions to 20% sulphuric acid solution (which is preferable to phosphoric acid), the temperature being kept below 20°, until 95% of the acid is neutralised. The sodium sulphate decahydrate crystals are filtered off after 1 hr., washed with cold water, and the mother-liquor and washings distilled in a vacuum at 60—65° in 100 c.c. portions, the final solid residue being heated at 85°. In the first of two cooled receivers, 20—23% hydrogen peroxide solution collects (yield 96%), and in the second, colder, receiver, a 2—2½% solution. A second distillation of the concentrated peroxide solution over excess of pure silver sulphate yields pure peroxide solution, which may be concentrated to 88%, with a loss of 12% on yield, by storing in a vacuum over concentrated sulphuric acid for 3 days at the ordinary temperature. S. K. TWEEDY.

Reduction of sodium sulphate to sodium sulphide. P. P. BUDNIKOV.—See B., 1927, 10.

Stability of alkaline solutions of potassium ferricyanide used for etching in microscopy. T. MURAKAMI and K. SOMEYA (Z. anorg. Chem., 1926, **158**, 117—135).—An alkaline solution of potassium ferricyanide may be used for etching steel previously to microscopical examination. Increase in the concentration of either the alkali or the salt accelerates the etching process, but the most suitable concentrations for use depend on the nature of the steel under examination. The effectiveness of the solution gradually increases for some time after it has been made up, then slowly decreases. The ferricyanide, however, decomposes in an approximately linear manner from the time of preparation, whilst the rate of disappearance of the alkali is at first rapid, but later falls off, and tends to zero. Decomposition is promoted by sunlight. The ferricyanide first forms the aquoferricyanide, which is then reduced to the aquoferrocyanide, and so to ferrocyanide. It is probable that the initial increase in the etching power of the solution with its age is due to some very active intermediate product. R. CUTHILL.

Higher oxides of silver. II. Ag_2O_2. F. JIRSA [with J. JELINEK and J. SRBEK] (Z. anorg. Chem 1926, **158**, 33—60; cf. A., 1925, ii, 1182).—Largely details of work of which the chief results have already been published (*ibid.*, 1162). The active oxygen in the oxide, Ag_2O_2, can be accurately determined by Topf and Diehl's method modified as follows. The peroxide is treated with a 57% solution of potassium iodide, and after 3 min. sulphuric acid is added and the free iodine titrated. When the oxide is boiled with water, the amount of decomposition increases in an approximately linear manner with the relative amount of water, the reaction $Ag_2O_2+H_2O=2Ag^{\cdot}+2OH'+\frac{1}{2}O_2$ apparently ceasing when the solution is saturated with silver hydroxide. R. CUTHILL.

Higher oxides of silver. III. Oxidation of silver by ozone. F. JIRSA and J. JELINEK (Z. anorg. Chem., 1926, **158**, 61—66; cf. preceding abstract).—Silver in the form of a rod is oxidised by ozone to Ag_2O, but with the finely-divided metal ternary solid solutions of Ag_2O, Ag_2O_2, and Ag_2O_3 result. Water converts the Ag_2O_3 in these into Ag_2O_2, with liberation of a corresponding amount of oxygen. Pure Ag_2O_2 is not oxidised by ozone, and solid solutions of Ag_2O_3 in Ag_2O_2 seem incapable of existence. R. CUTHILL.

Dehydration of gypsum. J. T. MCCORMACK (J. Geol., 1926, **34**, 429—433).—At the ordinary temperature, and pressures of 600—316,000 lb. per in.^{2}, gypsum is not dehydrated within short periods (0·5 hr.—5 days). Temperature is far more important than pressure in the dehydration of gypsum.
CHEMICAL ABSTRACTS.

Preparation of calcium cyanide. H. H. FRANCK and C. FREITAG.—See B., 1927, 42.

Method of producing molecular mixtures. S. VON BOGDANDY, J. BOEHM, and M. POLANYI (Z. Physik, 1926, **40**, 211—213).—The method consists in depositing at very low pressures on a cooled rotating drum layers of metals etc. together with naphthalene. The metals showed no *X*-ray interference lines; the colour exhibited depended on the proportion of metal to naphthalene; on dissolving out the naphthalene from the metallic deposit and warming, interference lines were obtained. A mixture of cadmium and sulphur was black; when warmed to about 50°, it turned red (cf. Semenov and Schalnikov, A., 1926, 1107). A mixture of zinc with naphthalene exploded violently after several days.
E. B. LUDLAM.

Barium sulphate-potassium permanganate mixed crystals. W. GEILMANN and E. WÜNNENBERG (Z. anorg. Chem., 1927, **159**, 271—272).—Although Balarev (A., 1926, 1195) has shown that the violet mixed crystals of barium sulphate and potassium permanganate obtained by a diffusion process were decolorised by a mixed solution of sulphuric and oxalic acids, large violet crystals containing about 5% of potassium permanganate, which are not decolorised by sulphuric and oxalic acids or by sulphurous acid, are obtained by allowing 2*N*-solutions of sulphuric acid and barium chloride to diffuse slowly into a 10% solution of potassium permanganate.
J. S. CARTER.

Fluoborates. E. WILKE-DÖRFURT and G. BALZ (Z. anorg. Chem., 1927, **159**, 197—225; cf. Funk and Binder, A., 1926, 1015; Lange, *ibid.*, 1112).—The following fluoborates are described: sodium, $NaBF_4$; *thallous*, $TlBF_4$; calcium, $Ca(BF_4)_2,2H_2O$; *silver*, $Ag(H_2O)BF_4$; strontium, $[Sr(H_2O)_4](BF_4)_2$; magnesium, lead, cupric, *manganous*, cadmium, ferrous, nickelous, and cobaltous, $[M(H_2O)_6](BF_4)_2$; *silver-diammine*, $[Ag(NH_3)_2]BF_4$; *zinctetrammine*, $[Zn(NH_3)_4](BF_4)_2$; *nickelous-*, *cobaltous-*, *manganous-*, and *cadmium-hexammine*, $[M(NH_3)_6](BF_4)_2$; *cobaltic-* and *chromium-hexammine*, $[M(NH_3)_6](BF_4)_3$; *chrom-*

ium-hexacarbamide, $[Cr(CN_2H_4O)_6](BF_4)_3$; *magnesium-*, *manganous-*, *nickelous-*, and *cobaltous-hexa-aquohexamethylenetetramine*, $[M(H_2O)_6](BF_4,C_6H_{12}N_4,H_2O)_2$; *silverdipyridine*, $[Ag(C_5H_5N)_2]BF_4$; *silvertetrapyridine*, $[Ag(C_5H_5N)_4]BF_4$; *cuprictetrapyridine*, $[Cu(C_5H_5N)_4](BF_4)_2$; *nitrosyl*, BF_4NO; nitron, $C_{20}H_{16}N_4,HBF_4$, m. p. 227° (uncorr.). J. S. CARTER.

Construction of neutralisation curves. B. ENGLUND (Z. anorg. Chem., 1926, **158**, 359—369).—The subject is discussed theoretically with reference to the neutralisation curves of mono-, di-, and tribasic acids, carbonates, and ampholytes.

A. S. CORBET.

Reactivity of silicon. F. ROLL (Z. anorg. Chem., 1926, **158**, 343—348).—When kept under oxygen-free and oxygen-saturated water for a year, crystalline silicon showed a maximum increase of 2% and 10%, respectively, in the silica content, whilst under similar conditions the amorphous form gave 5—8·2% and 12—20·5%, respectively. Increased silica formation occurred in presence of added impurities and when the two forms remained under boiling water for a month.

Oxidation experiments carried out by heating crystalline silicon in a stream of oxygen showed that no action occurs below 250°, but above this temperature oxidation increases with increased temperature and time of heating and decreased size of grain. Crystalline silicon with a high silica content does not behave very differently. A. S. CORBET.

Acidic properties of silicic acid and certain silicates. H. KAPPEN and J. BREIDENFELD.—See B., 1927, 9.

Preparation of metallic germanium and volatility of the metal in hydrogen and in a vacuum. J. H. MÜLLER, E. F. PIKE, and A. K. GRAHAM (Proc. Amer. Phil. Soc., 1926, **65**, 15—32).—The purest germanium is prepared by the reduction of specially purified germanium dioxide with hydrogen and graphite; the metal has m. p. 959° in hydrogen, 958° in carbon dioxide, 975° in a vacuum; it is volatile in hydrogen at atmospheric pressure below 800°, and in a vacuum below 760°. Molten germanium (1 g.) absorbs hydrogen (0·183 g.) on cooling. When heated with germanium in a vacuum, germanium dioxide is reduced to the monoxide.

CHEMICAL ABSTRACTS.

Germanium. XVII. Fused germanium dioxide and some germanium glasses. L. M. DENNIS and A. W. LAUBENGAYER.—See B., 1927, 42.

Hydrolysis of zirconium chromate. P. KRISHNAMURTI and B. B. DEY (Z. anorg. Chem., 1926, **158**, 94—98).—Addition of a large excess of a saturated solution of potassium dichromate to a concentrated solution of zirconium oxychloride precipitates a *basic zirconium chromate*, $Zr(OH)_4,2Zr(OH)_2CrO_4$. Using a dilute solution of the zirconium salt, the product has approximately the formula $Zr(OH)_4,Zr(OH)_2CrO_4$. With very dilute boiling solutions of the oxychloride and only a slight excess of dichromate, the composition of the product, after washing with boiling water, corresponds with the formula $2Zr(OH)_4,Zr(OH)_2CrO_4$. R. CUTHILL.

Ammoniates of compounds of the rare earths. I. Contraction during the formation of compounds. F. EPHRAIM and R. BLOCH (Ber., 1926, **59**, [*B*], 2692—2705).—Contraction in volume during the formation of compounds is ascribed mainly to the union of the electron sheaths of several atoms to a homogeneous formation and to the deflexion of outer electrons with markedly excentric path. Any deformation of the outer sheath must be followed by a similar change in the inner ring. The vibrations of the electrons must therefore become shorter, and the spectrum must consequently be expected to be displaced towards the violet. This expectation is to some extent realised with the ammines of praseodymium chloride, since the reflexion spectrum of the octammine is sharply displaced towards the region of shorter wave-length in comparison with the anhydrous chloride with respect to all the bands. With the pentammine, however, a non-uniform displacement of the position of the bands is observed. The spectrum of the diammine generally resembles that of the pentammine, but the displacement of the band of greatest wave-length is more marked. In the monammine, fission of two of the bands occurs, probably denoting the presence of two differently placed praseodymium atoms, as indicated by the formula, $[Pr(NH_3)_2]PrCl_6$. The spectrum of the chloride left after complete expulsion of ammonia from the ammines is not completely identical with that of the original chloride.

The sensitiveness of the ammonates to atmospheric air renders it necessary to prepare the anhydrous chlorides, add ammonia, decompose the ammonates thermally, measure the approximate volume of the powder, and observe the reflexion spectrum in the same apparatus, which is figured and described. The following ammines are described, the temperatures of decomposition to the next lower member being placed within parentheses: *lanthanum chloride octammine* (71°), *pentammine* (86°), *triammine* (145°), *diammine* (181°), *monammine* (265°); *cerium chloride octammine* (70°), *pentammine* (115°), *diammine* (198°), *monammine* (281°); *praseodymium chloride octammine* (71°), d^{25} 1·67, *pentammine* (115°), d^{25} 2·18, *diammine* (218°), d^{25} 2·81, *monammine* (290°), d^{25} 3·28; *neodymium chloride octammine* (70°), *pentammine* (114°), *diammine* (219°), *monammine* (293°). For the determination of density, the ammines are prepared in the pyknometer itself, pentane being used as filling liquid. H. WREN.

Oxidations and reductions of ammonium salts, nitrites, and nitrates by iron compounds, insoluble in water. K. BORESCH.—See B., 1927, 10.

Formation of nitric oxide at high temperatures. E. BRINER, J. BONER, and A. ROTHEN (J. Chim. phys., 1926, **9**, 788—807).—See A., 1926, 916. The equilibrium concentration of nitric oxide in air is now given as $0·79 \pm 0·06\%$ at $1600 \pm 10°$.

Allotropic modifications of phosphorus. V. IPATIEV and W. NIKOLAJEV (Chem.-Ztg., 1926, 50. 989—990; cf. A., 1926, 487).—A more detailed account. It is concluded that red phosphorus is probably a mixture of the black and purple varieties.

E. H. SHARPLES.

Oxidation of phosphorus vapour at low pressures. J. CHARITON and Z. WALTA (Z. Physik, 1926, **39**, 547—556).—The reaction between oxygen and phosphorus vapour has been studied at pressures of the order 10 mm. If the oxygen pressure is below a critical pressure, no rapid reaction takes place; the value of the critical pressure is greater the greater the pressure of the phosphorus vapour. Above the critical pressure, the reaction is extremely rapid. If oxygen is admitted until its critical pressure is nearly reached, and then argon is allowed to enter, the luminescence appears; the effect is as though the pressure of the phosphorus had diminished, but the intensity of the light is less. With argon almost at atmospheric pressure, the glow made its appearance immediately oxygen was allowed to enter, but its intensity was very feeble. It is suggested that the reacting molecule is P_2; when this is oxidised, more molecules are formed from P_4 with absorption of heat; this, together with the fact that some of the heat of oxidation is lost as radiation, prevents the rapid action. The higher is the pressure of the phosphorus vapour the greater is the proportion of P_4 molecules and the higher is the critical pressure of the oxygen. The argon diminishes the loss by radiation, receiving energy by collision, which is then communicated to the phosphorus by further collisions and the critical pressure is reduced. E. B. LUDLAM.

Quadrivalent vanadium. E. PARISI (Gazzetta, 1926, **56**, 843—847).—The transformation of the pink vanadyl hydroxide into the olive-green modification (cf. Gain, A., 1908, ii, 284) is a consequence of conversion of part of the vanadium from the quadrivalent to the quinquevalent condition. The pink compound remains unchanged as regards both colour and power to reduce permanganate if kept in a tightly-stoppered vessel filled with water previously boiled and saturated with carbon dioxide (cf. Crow, J.C.S., 1876, **30**, 453). T. H. POPE.

Amphoteric hydroxides, their aqueous solutions and crystalline salts. IV. Antimonic acid and the alkali antimonates. G. JANDER and W. BRÜLL (Z. anorg. Chem., 1926, **158**, 321—342; cf. A., 1925, ii, 988).—Potassium and sodium antimonates contain their component oxides in the ratio 1 : 1 and are probably derived from an orthoantimonic acid. The solubility in water, at 20°, of sodium antimonate, $NaSbO_3,3H_2O$ (the so-called "pyroantimonate"), is $2{\cdot}52$—$2{\cdot}55\times10^{-3}$ mol. per litre, and this value is almost equally depressed by the presence of potassium antimonate or sodium chloride in equivalent concentrations. When a cold 5% solution of potassium antimonate is saturated with carbon dioxide, a white precipitate of the triantimonate, $K_2H_3Sb_3O_{10},5H_2O$, results, and thus freshly-prepared solutions of potassium antimonate should be used when testing for sodium. At 20°, the solubilities in water of sodium and potassium triantimonates are $1{\cdot}3\times10^{-5}$ and $0{\cdot}9\times10^{-3}$ mol. per litre, respectively.

Increasing hydrogen-ion concentration in aqueous solutions of antimonate ions leads to decrease of the diffusion coefficient and increased tendency towards formation of tri- and tetra-antimonates. Antimony cations do not appear to exist in appreciable amount in *N*-hydrochloric acid, and no formation of antimonate from triantimonate appears to occur in dilute alkaline solution. A. S. CORBET.

Sulphurous acid and its salts. V. Behaviour of pyrosulphites when heated. F. FOERSTER and G. HAMPRECHT (Z. anorg. Chem., 1926, **158**, 277—315).—The very complicated course of the decomposition of pyrosulphites when heated is due to the occurrence of several simultaneous reactions, and is affected by the cation combined with S_2O_5'', the nature and velocities of the principal reactions, and the temperature and partial pressure of sulphur dioxide during the experiment. The decomposition of crystalline potassium pyrosulphite has been followed from 150° upwards and three principal reactions are found to occur: $2S_2O_5'' \longrightarrow S_3O_6''+SO_4''$ (i); $3S_2O_5'' \longrightarrow S_2O_3''+2SO_4''+2SO_2$ (ii); $S_2O_5'' \rightleftharpoons SO_3''+SO_2$ (iii). At the commencement (i) is the main reaction and yields a yellow product which dissolves very readily in water to give a trithionate. Above 250° (ii) is exclusively the main reaction, whilst (iii) commences above 200°, but only when the partial pressure of the sulphur dioxide generated by (ii) is kept low. Passage of nitrogen over the heated mixture favours (iii), which is retarded, however, when sulphur dioxide remains over the salt.

In addition, the following side reactions occur: $S_3O_6'' \longrightarrow SO_4''+SO_2+S$ (iv); $2S_2O_3''+SO_2 \longrightarrow 2SO_4''+3S$ (v); $4S_2O_3'' \longrightarrow 3SO_4''+S_{1+4}$ (vi); $4SO_3'' \longrightarrow 3SO_4''+S''$ (vii). Accompanying (i), (iv) commences when the trithionate concentration has reached a definite amount and effects its initial decomposition. Reaction (v) depends on (ii) and at 220°, in closed apparatus, (ii) and (v) dominate the decomposition. Provided all thiosulphate has not been eliminated by (v), (vi) first becomes evident above 400°. The reaction velocity of (vii) first becomes noticeable at 550°.

Combination of (i) and (iv) and of (ii) and (v) gives $2S_2O_5'' \longrightarrow 2SO_4''+SO_2+S$, which completely represents the decomposition after the disappearance of thiosulphate.

Although qualitatively similar, the quantitative decomposition of sodium pyrosulphite is very different, for in this case the heat of dissociation for (iii) is much smaller and, at 150°, (iii) is the principal reaction. A. S. CORBET.

Laboratory preparation of sulphuryl chloride. H. DANNEEL (Z. angew. Chem., 1926, **39**, 1553—1554).—Sulphuryl chloride is easily prepared by the interaction of sulphur dioxide and chlorine in presence of activated carbon if provision is made for removing the heat of reaction, *e.g.*, by allowing the catalyst tube to fill with liquid sulphuryl chloride and cooling externally. The sulphuryl chloride overflows as it is formed through a side tube into a collecting vessel, a yield of 100% being readily obtained. Sulphuryl bromide, if it exists, decomposes at 18° with evolution of sulphur dioxide. The properties of solutions of paraldehyde and metaldehyde in sulphuryl chloride are described. C. IRWIN.

Molybdic acid and molybdates. A. TRAVERS and MALAPRADE (Bull. Soc. chim., 1926, [iv], **39**,

1543—1573).—A more detailed account of work already published (A., 1926, 1114).

Ferric and manganese dichromates. S. HUSAIN and J. R. PARTINGTON (Chem. News, 1926, **133**, 386—387).—The prolonged action of chromic acid solution on excess of precipitated ferric hydroxide at 80—90° yielded a solution which, on evaporation at 90°, gave a residue corresponding with the composition $Fe_2O_3,6CrO_3$, or $Fe_2(Cr_2O_7)_3$, after drying in a vacuum. *Ferric dichromate* is a hygroscopic, brown solid, hydrolysing in aqueous solution on extensive dilution. It decomposes somewhat at 100°; contrary to the results of Calcagni (A., 1925, ii, 891), at 140° the chromate radical is decomposed, a black residue remaining which slowly dissolves to a green solution in boiling concentrated hydrochloric acid. The action of chromic acid solution on excess of solid manganous carbonate yielded a dark red solution probably containing manganese dichromate, $MnCr_2O_7$. Only partly decomposed solid products could be obtained from this solution. Attempts to prepare double salts of this dichromate with potassium chromate failed: the latter was oxidised to dichromate with precipitation of manganese dioxide.

S. K. TWEEDY.

Chemical changes in magnetite when heated in air. E. GREULICH (Z. anorg. Chem., 1926, **159**, 65—77).—For the reaction $4Fe_3O_4+O_2\longrightarrow 6Fe_2O_3$, a temperature of 1385° is necessary. Above this temperature, the reaction is one of dissociation. Magnetite, which was fractionated by a magnetic process and contained about 65% of iron, was heated in a current of air in a special furnace at known temperatures up to 1400° for periods of 0·5, 1, 2 . . . 100 hrs.

Between 400° and 1200°, the magnetite is converted into ferric oxide, the velocity of the reaction being small below 1000° (*e.g.*, in 100 hrs. at 400°, 5·4% was changed; at 900°, 95·9%). For complete oxidation at 900°, 40 hrs.' heating was required; at 1000° 10 hrs., and at 1100° only 2 hrs.; at 1200° less than 1 hr.

Magnetite is no longer oxidised in air above 1380°. Above 1450°, the ferrous oxide content of the roasted product is almost that of the original substance, but measurements of the magnetisability of this product show that a portion of the ferrous oxide is not present as ferrosoferric oxide, but as ferrous oxide. The amount of this is about 2% at 1500° and 3% at 1550°, in agreement with the values obtained by Ruer and Nakamoto (A., 1923, ii, 643).

These results are confirmed by microscopical examination. The oxidation of the magnetite at 1200° is exponential in character, and the kinetics of this reaction are compared with those of other heterogeneous systems. M. CARLTON.

Mechanism of oxidation of iron with steam, air, and carbon dioxide at high temperatures. P. P. FEDOTEEFF [with T. N. PETRENKO].—See B., 1927, 15.

Oxidations with fluorine. VI. Preparation of cobaltic sulphate. F. FICHTER and H. WOLFMANN (Helv. Chim. Acta, 1926, **9**, 1093—1096).—Passage of fluorine into a solution of cobaltous sulphate in sulphuric acid (24 g. of $CoSO_4,7H_2O$ in 125—150 c.c. of 8*N*-sulphuric acid) at 0° yields cobaltic sulphate which is extremely unstable, the analytical data for which do not agree, in confirmation of the observations of Marshall (J.C.S., 1891, 59, 302), exactly with the formula $Co_2(SO_4)_3,18H_2O$. The action of fluorine on a 1·15*N*-solution of cobaltous carbonate in sulphuric acid yields the cobaltic salt only with difficulty. Increase in the concentration of the solvent acid causes the compound $CoF_2,5HF,6H_2O$ to separate, and in one case a 60% yield of cobaltic fluoride was obtained.

J. W. BAKER.

Preparation of salts of bivalent ruthenium. H. GALL and G. LEHMANN (Ber., 1926, **59**, [*B*], 2856—2860).—Ruthenium trichloride is reduced by hydrogen in alcoholic solution in the presence of spongy platinum to *ruthenium dichloride* mixed with metallic ruthenium. The production of the latter is obviated by addition of hydrochloric acid, preferably derived from chloroform, added to the alcoholic solution. The dichloride behaves as a reducing agent. In solution, it does not absorb carbon monoxide at the atmospheric temperature; at 210°, it is converted by dry carbon monoxide into the compound, $RuCl_2,2CO$ (cf. Manchot and König, A., 1925, ii, 149). *Ruthenium dibromide* is prepared by reduction of the tribromide in absolute-alcoholic solution in the presence of bromoform. Indications of the production of ruthenium di-iodide are obtained by reduction of ruthenium tri-iodide dissolved in alcohol saturated with dry ammonia. H. WREN.

Role of carbon monoxide in the preparation of ruthenium trichloride. W. MANCHOT and J. KÖNIG (Z. anorg. Chem., 1927, **159**, 269—270).—The statement of Remy (this vol., 34) that Joly (A., 1892, 658) isolated a carbonyl derivative of ruthenium dichloride is erroneous. J. S. CARTER.

Ternary salts of rhodium [Wilm's chloronitrate]. O. E. ZWIAGINCEV (J. Russ. Phys. Chem. Soc., 1926, **58**, 170—176).—The history and properties of Wilm's rhodium chloronitrate, $Rh_2Cl_6,6NH_4Cl,2NH_4NO_3$ (A., 1884, 660; 1893, ii, 213) are discussed, and its structure is investigated in the light of Werner's theory. An aqueous solution of the pale lilac salt becomes blood-red. Silver nitrate precipitates an amorphous, pale-rose *compound* containing all the rhodium, and hence is formulated $[RhCl_6]Ag_3,NH_4NO_3$. The complex is soluble in ammonia and is slightly decomposed on warming. The *mercury* and *lead* salts are described.

The position of the ammonium nitrate in the molecule was determined by thermal decomposition experiments with Kurnakov's pyrometer and found to be analogous to "water of co-ordination." Such a structure explains the behaviour in solution. The following formula is suggested:

$$\left[\begin{matrix}NH_4\\NH_4\end{matrix}[RhCl_6]\begin{matrix}NH_4\\NO_3\end{matrix}\right]NH_4$$

M. ZVEGINTZOV.

Calculation of the limiting composition of mixed crystals resistant to chemical action. G. MASING (Wiss. Veröff. Siemens-Konz., 1926, **5**, 156—169).—A theoretical and mathematical paper in which a correction is introduced into the equations

of Masing (A., 1922, ii, 37) and of Borelius (Ann. Physik, 1924, [iv], 74, 216) so as to make them agree more fully with the theory of probability in expressing the limiting composition which resists attack of mixed crystals of a metal highly resistant to chemical attack and a less noble metal. The resistance limit of a plane model according to this calculation occurs when two thirds of the atoms in the plane consist of the less noble metal.

A. R. Powell.

Dehydration of salt hydrates by means of acetic anhydride. N. Schoorl (Chem. Weekblad, 1927, 24, 13).—The method of Menke (this vol., 27) may yield only a lower hydrate in place of the anhydrous salt. S. I. Levy.

Spectrographic identification of certain elements and the possibility of quantitative determination by means of the arc spectrum. I. C. Porlezza and A. Donati (Annali Chim. Appl., 1926, 16, 519—555).—Omitting the rare gases, experimental spectral data are lacking for dysprosium, gadolinium, holmium, osmium, praseodymium, samarium, terbium, and thulium. For 62 elements, the spectra at relatively high dilutions are known, at least partly. In spectral analysis, knowledge of the lines of an element of great sensitiveness is of importance, which is, however, not absolute, but relative, since the experimental conditions, particularly the character of the diluent, affect the results.

As regards the possibility of determining elements spectrographically, it is pointed out that the diminution in the intensity of all lines as the concentration of an element diminishes is not uniform for the different lines composing the spectrum, and that quantitative spectral analysis on the basis of the data given in published tables is not possible unless preliminary auxiliary investigations on the relations between spectral variations and concentration are made. Details of the experimental results are to be published later. T. H. Pope.

Improving detections. M. de Jong (Pharm. Weekblad, 1926, 63, 1428).—Very slight precipitates may be detected more readily by localising the solid formed in a ring between the water of the solution and added chloroform or petroleum. S. I. Levy.

Temperature corrections in volumetric analysis. N. Schoorl (Chem. Weekblad, 1926, 23, 581—582; cf. Couvée, this vol., 34).—A further table of expansion coefficients for some fifteen common titration solutions in glass vessels is given. S. I. Levy.

Use of nomograms in analysis. S. Reiner (Z. anal. Chem., 1926, 69, 377—382).—Examples are given of the application of nomograms to the calculation of analytical results. R. Cuthill.

Potentiometric determination of hydrogen-ion concentration at higher temperatures. I. M. Kolthoff and F. Tekelenburg (Rec. trav. chim., 1927, 46, 18—27).—See A., 1926, 1220.

Simplification of electrometric p_H determinations. W. U. Behrens (Biochem. Z., 1926, 178, 181—183).—A sliding bridge is described, adapted for use with the hydrogen and quinhydrone electrodes, which gives direct readings in terms of p_H.

J. Pryde.

Buffer solutions with p_H value between 2·0 and 6·6. I. M. Kolthoff and J. J. Vleeschhouwer (Biochem. Z., 1926, 179, 410—413).—See A., 1926, 1220.

Separation of chlorate from perchlorate. K. Scharrer (Ber., 1926, 59, [B], 2746—2749).—Chlorate may be determined in the presence of perchlorate (and nitrate) by reduction to chloride by magnesium powder in hot, dilute nitric acid solution and determination as silver chloride. If perchlorate is also to be determined in similar mixtures, reduction of it and the chlorate to chloride is effected by cautious addition of copper powder to the molten mixture; chloride is determined in the usual manner.

H. Wren.

Separation of hydrochloric from hydrobromic and hydriodic acids. G. G. Longinescu and (Miss) M. N. Badescu (Bul. Soc. Romana Stiinte, 1926, 29, 17—21).—The solid is boiled with concentrated sodium carbonate solution to remove certain heavy metals and the filtrate is acidified with sulphuric acid; two or three drops of "perhydrol" are added and then pure petroleum oil. The mixture is warmed until the aqueous layer is colourless, and the layers are then separated by filtration. Hydrochloric acid is then detected in the aqueous filtrate in the usual way. In the quantitative procedure, the layers are separated in a funnel, the petroleum layer being thoroughly washed with water and the washings added to the aqueous layer. S. K. Tweedy.

Determination of iodide in presence of chloride or bromide, and determination of each halide in a mixture of the three. R. Berg (Z. anal. Chem., 1926, 69, 369—374).—In presence of acetone, hydriodic acid is decomposed by iodic acid according to the equation $2HI+HIO_3+3C_3H_6O=3C_3H_5IO+3H_2O$, whilst hydrobromic acid and hydrochloric acid are attacked only slowly or not at all. To 50—60 c.c. of the solution, which must not contain more than 2% of potassium bromide, are added 20—30 c.c. of acetone and sufficient dilute sulphuric acid to make the total volume 100 c.c. and the acid concentration 2·0—2·5N. Starch is then added and standard potassium iodate solution run in until the solution is colourless. The chloride or bromide is then determined with silver nitrate. In a mixture of the three halides, iodide is determined as above, chloride by Volhard's method, after destroying the bromide with bromic acid (this vol., 35), and bromide by difference.

R. Cuthill.

Potentiometric titrations. I. Determination of the end-point and potential change. II. Titration of iodide with permanganate. F. L. Hahn and G. Weiler (Z. anal. Chem., 1926, 69, 417—449).—Two methods of determining the end-point of a potentiometric titration are available, the graphical and the differential; the former yields more accurate results when the reacting substances are not in equimolecular ratio, as is the case in the titration of iodides with permanganate (Hahn and Wolf, A., 1926, 1220). This titration gives better results potentiometrically when carbon tetrachloride is added to the solution to remove the iodine from the aqueous layer as fast as it forms; in this way, accurate

results are obtained for iodide when 50 mols. of bromide and 600 mols. of chloride are present for every mol. of iodide. Fuller details are given of the direct titration with permanganate, using ethyl acetate to absorb the iodine; this method is more rapid than the potentiometric method, but does not give such good results in presence of chlorides and bromides. A. R. POWELL.

Micro-titration of iodides with iodate and determination of the iodide and ferrous iron content of syrup of ferrous iodide. I. M. KOLTHOFF (J. Amer. Pharm. Assoc., 1926, **15**, 164—166).—To 10 c.c. of 0·1*M*-potassium iodide solution are added 80 c.c. of water, 20 c.c. of 25% hydrochloric acid, and 4—5 c.c. of 10% potassium cyanide solution. The titration is completed with *M*/60-potassium iodate solution, using carbon tetrachloride or chloroform as indicator. The method is accurate to 1% in solutions containing 0·127 mg. of iodine in 100 c.c. The reversed method, in which the iodine is oxidised to iodate by hypochlorous acid and the iodine titrated with potassium iodide, is used for mixtures containing other substances oxidised by iodate; the accuracy is then 1% for solutions containing 0·1 mg. per 100 c.c. For syrup of ferrous iodide, 10 c.c. are diluted with 80 c.c. of water, 10 c.c. of 25% phosphoric acid, and 5 c.c. of 10% potassium cyanide solution. 0·1*N*-Potassium permanganate solution is added in slight excess, then an excess of potassium iodide, and the iodine titrated with thiosulphate. CHEMICAL ABSTRACTS.

Determination of soluble fluorides. F. L. HAHN (Z. anal. Chem., 1926, **69**, 385—386).—The concentrated solution of the fluoride is made alkaline with sodium hydroxide, and then neutralised with acetic acid, and so much sodium sulphate added that there is at least 0·2 g. or, for large amounts of fluoride, still more of sulphate ion in 100 c.c. Excess of calcium chloride solution is then added, and the precipitate ignited and weighed. Finally, the precipitate is moistened with concentrated sulphuric acid and again ignited and weighed, the increase in weight corresponding with the conversion of calcium fluoride into calcium sulphate. R. CUTHILL.

[Volumetric] determination of sulphates. H. ROTH (Z. angew. Chem., 1926, **39**, 1599—1601).—The sulphate is precipitated by barium chloride and the excess of the latter titrated with excess of potassium dichromate, using as indicator *pp'*-diaminodiphenylamine (0·1 g.) dissolved in a mixture of 0·4 g. of pure tartaric acid, 0·1 g. of salicylic acid, and 20 c.c. of water. It is used on filter-paper, which must be kept in the dark. The slightest trace of chromate gives a blue colour. The back titration is performed in dilute ammonia solution free from carbonate, and the end-point is very precise. The barium sulphate need not be removed. Alkaline sulphate solutions such as are encountered in the analysis of pyrites etc. must be freed from any phosphoric and arsenic acids by precipitation with ammoniacal magnesium chloride. The accuracy is comparable with that of the gravimetric method. C. IRWIN.

Decomposition of thiosulphate solutions. F. L. HAHN (Z. anal. Chem., 1926, **69**, 386—389).—Schulek's tests for sulphide and tetrathionate in thiosulphate solutions (A., 1926, 1017) were inconclusive, since they may have been given by free sulphur. It is suggested that the increase in strength of thiosulphate solutions on keeping, which is occasionally observed, is due to the transformation of some impurity in the thiosulphate into thiosulphate, and, to a small extent, to the conversion of thiosulphate into sulphide by bacteria (cf. Mayr, A., 1926, 814). R. CUTHILL.

Comparison of boric and hydrochloric acids in the determination of nitrogen in leather. R. W. FREY and R. M. HANN.—See B., 1927, 54.

Spectrophotometric determination of nitrites and nitrates by means of diphenylamine sulphate. E. TASSILLY and R. SAVOIRE (Bull. Soc. chim., 1926, [iv], **39**, 1755—1759).—See this vol., 35.

Microchemical determination of nitrates. F. ROGOZINSKI (Rocz. Chem., 1926, **6**, 497—500).—See A., 1926, 813.

Detection of nitrite, nitrate, and sulphite ions. E. EEGRIWE (Z. anal. Chem., 1926, **69**, 382—385).—One part of nitrite in 5,000,000 parts of water can be detected by the reddish-violet colour, due to the formation of a diazo-compound, produced when a mineral acid and a 0·03% solution of safranine-*T* are added to the solution. With larger amounts of nitrite, a blue colour results. Nitrates are detected by first reducing to nitrite with magnesium powder and dilute sulphuric acid. If to a solution containing a sulphite there is added a 0·01% solution of fast-blue-*R* crystals drop by drop, shaking after each addition until the violet colour disappears, a yellow coloration is produced, the sensitivity of the test being about 1 in 175,000. Thiosulphates and thionates do not give this reaction. Sulphides, polysulphides, and hydroxides interfere. R. CUTHILL.

Application of hydrolysis to the study of differential analytical reactions. L. ROSSI (Anal. Asoc., Quím. Argentina, 1926, **14**, 239—242).—By the use of a 5% solution of sodium or potassium nitroprusside in the presence of hydrogen sulphide, it is possible to distinguish between normal, monohydrogen, and dihydrogen salts of orthophosphoric acid. In the case of normal salts, the alkalinity produced by hydrolysis is so great that a considerable concentration of sulphide ions results, and a deep red coloration is formed. In the case of the monohydrogen phosphate, a less intense violet coloration is produced, whilst in the case of the dihydrogen phosphate there is no coloration. G. W. ROBINSON.

Titrations with arsenious acid. O. CANTONI.—See B., 1927, 10.

Analysis of volatile liquids and gases. Determination of arsenic in volatile liquids. O. FAUST and E. FISCHER (Z. anorg. Chem., 1926, **158**, 181—184).—Arsenic in carbon disulphide cannot be determined by the Gutzeit method because some hydrogen sulphide is formed by reduction of the carbon disulphide and blackens the silver nitrate.

The following method of determination, which is applicable to other volatile liquids, has been devised. The carbon disulphide is poured into a Marsh's apparatus, and burnt at the jet, partly as vapour and partly as reduction products, the products of combustion being aspirated through a solution of sodium hydroxide. This is then oxidised with hydrogen peroxide, acidified with sulphuric acid, and examined for arsenic with Lockemann's modification of Marsh's apparatus. R. CUTHILL.

Assay of solution of arsenious and mercuric iodide. W. H. SCHULZE (J. Amer. Pharm. Assoc., 1926, **15**, 464—465).—On keeping the solution the arsenious iodide content rapidly changes, particularly on exposure to light. The assay should consist of a determination of the total arsenic present. CHEMICAL ABSTRACTS.

Determination of carbon dioxide in carbonates. J. R. I. HEPBURN.—See B., 1927, 42.

Alkalimetric determination of the hardness of industrial waters. C. BELCOT.—See B., 1927, 62.

Volumetric determination of magnesium in industrial waters. C. BELCOT.—See B., 1927, 10.

Separation of magnesium from the alkali metals. C. OTTO (J. Amer. Chem. Soc., 1926, **48**, 3016—3018).—An almost quantitative separation of magnesium from sodium and potassium is obtained by igniting the mixed nitrates and extracting the alkali nitrates and nitrites from the residue with cold dilute ammonium hydroxide solution. Magnesium oxide is left, and may be confirmed in the usual way after dissolution in acid. Repeated ignition with nitric acid will not convert sulphates into nitrates, and when the sulphate radical is present, the modified procedure of Precht and Wittjen (Z. anal. Chem., 1883, **22**, 81) is suggested. This method was not tested experimentally, however. S. K. TWEEDY.

Determination of zinc by conductivity titration. G. SANDER and O. PFUNDT (Z. angew. Chem., 1926, **39**, 1557—1558).—The use of a membrane filter solves the difficulty of filtering and washing a precipitate of zinc sulphide, but the determination of the zinc in the precipitate by boiling with a known quantity of hydrochloric acid and titrating the residual acid requires care. An easy alternative is given by determination of the conductivity of the acid solution while adding standard sodium hydroxide solution. During neutralisation, the conductivity falls; it remains stationary during precipitation of zinc, and then rises again. The two discontinuities in the conductivity curve give a measure of the zinc content of the solution, which can be determined with an accuracy of 0·3—0·5%. The acidity of the zinc solution used must be limited if the beginning- and end-points are to be sharp. C. IRWIN.

Determination of zinc by electrometric titration. G. G. REISSAUS (Z. anal. Chem., 1926, **69**, 450—455).—The electrometric determination of zinc by titration with ferrocyanide is conveniently carried out in a 600-c.c. beaker provided with a motor-driven stirrer; one electrode consists of a platinum gauze cylinder, and is connected directly to the milliammeter; the other electrode is a narrow-bore tube filled with saturated potassium chloride solution and closed at each end with a wad of filter-paper. This tube makes connexion between the zinc solution and a saturated potassium chloride solution contained in a small flask; the latter solution is connected by a similar tube to a dilute solution of potassium ferrocyanide acidified with sulphuric acid in which is placed a platinum spiral connected through a variable resistance to the other terminal of the ammeter. The zinc solution, prepared from the ore or other material in the usual way, is acidified with sulphuric acid, treated with 5 c.c. of saturated potassium ferricyanide solution, heated to boiling, and titrated with standard ferrocyanide solution until the maximum deflexion of the ammeter for an addition of 0·1 c.c. is obtained. The normal potassium chloride electrode will last for upwards of 50 titrations without requiring renewal. A. R. POWELL.

Stabilisation of the inflexion-point in potentiometric precipitation reactions. I. ATANASIU (Bul. Soc. Romana Stiinte, 1926, **29**, 7—9).—The irregularities observed in the potentiometric curves obtained in the determination of lead, barium, and mercury with potassium chromate, and of cerium, lead, and zinc with potassium ferrocyanide (cf. A., 1926, 929), are probably due to dissolution and ionisation of the precipitate, and may be eliminated by the addition of 30% ethyl alcohol solution. The titration may still be carried out at 65—70°. The addition of alcohol, besides enabling very dilute solutions to be titrated, also enables the position of the inflexion-point to be readily determined from the readings. S. K. TWEEDY.

Volumetric determination of copper in insecticides containing iron, arsenic, and mercury. J. BODNAR and A. TERENYI.—See B., 1927, 30.

Precipitation of aluminium hydroxide by ammonia, and determination of alumina. L. MURAVLEV and O. KRASSNOVSKI (Z. anal. Chem., 1926, **69**, 389—394).—Blum's method of precipitating aluminium hydroxide (A., 1916, ii, 493), in which precipitation is completed at p_H 7, using methyl-red as indicator, gives better results than the ordinary method in the determination of aluminium. The precipitate is washed with a hot 2% solution of ammonium nitrate, which must be adjusted to p_H 7 with ammonia, as it otherwise exerts a slight solvent action. Addition of filter-paper pulp to the solution before precipitation causes the precipitate to settle better, and, contrary to the statements of Wilke-Dorfurt and Locher (A., 1924, ii, 775), does not introduce error. The alumina so obtained is not appreciably hygroscopic. R. CUTHILL.

Determination of manganese as permanganate. R. LANG (Z. anorg. Chem., 1926, **158**, 370—376; cf. A., 1926, 581).—The quantitative oxidation of manganese to permanganate is effected by nickel dioxide, and is carried out in two stages. The chloride-free solution containing 0·015 g. of manganese and 0·25 g. of nickel as sulphate or nitrate is treated with sodium carbonate until a permanent turbidity results, and the salts are oxidised to dioxides

by addition of potassium persulphate. After 3—5 min., the solution is slowly acidified with 30—50 c.c. of 5*N*-sulphuric or nitric acid, when quantitative oxidation to permanganate occurs. 0·1*N*-Arsenious acid is then added until a sap-green colour is obtained. At this point, 20 c.c. of 1 : 1 hydrochloric acid and a drop of potassium iodide or iodate are added, and titration with arsenious acid is continued to a bright green colour; the solution is then titrated back with 0·1*N*-potassium permanganate.

The procedure is not affected by non-oxidisable bivalent metals, such as calcium, copper, and zinc, provided sufficient alkali be present in the initial stage for their complete precipitation, but in presence of ferric, chromium, and lead salts, and more than 0·005 g. of cobalt, a modification in the procedure is necessary. A. S. Corbet.

Organic phosphoric acid compounds. VI. Determination of iron. III. F. Zetzsche and M. Nachmann (Helv. Chim. Acta, 1926, 9, 979—980).—Small quantities of iron (>0·04 g.) may be directly determined as the bis-*p*-chlorophenylphosphate (A., 1926, 705) if the precipitate is washed with 55 c.c. of *N*-hydrochloric acid, 70—100 c.c. of water, and 60—100 c.c. of 40% alcohol, and dried at 105°. Excess of water readily hydrolyses the precipitate, and more concentrated alcohol causes the precipitate to pass through the filter-paper.
J. W. Baker.

Potentiometric determination of ferrous and ferrocyanide [ions] with potassium bromate. I. M. Kolthoff and J. J. Vleeschhouwer (Rec. trav. chim., 1926, 45, 923—927; cf. A., 1919, ii, 352; Collenberg and Sandved, A., 1926, 140).—Using a bright platinum gauze electrode, rolled into a cylinder, and in presence of hydrochloric acid (3—8%), ferrous solutions can be accurately determined by titration with potassium bromate. Even at the ordinary temperature, and without the addition of a catalyst, the determination may be carried out in about 15 min., and is accurate to 0·2%. The presence of cobalt chloride has scarcely any effect on the rise of potential, but mercuric chloride causes a distinct, although small, increase in the rise. Ferrocyanide solutions may also be determined accurately in this way (hydrochloric acid, 3—5%, potassium bromate, 0·01*N*), provided the concentration of the ferrocyanide does not exceed 0·01*N*. In the titration of 0·1*N*-solutions, about 1% too much bromate is required. The addition of catalysts offers no advantage. L. L. Birckumshaw.

Oxidation-reduction potentials. I. M. Kolthoff (Z. anal. Chem., 1926, 69, 374—377).—It is asserted that for the determination of ferrous and ferric salts in a mixture of the two, electrometric titration gives much more accurate results than do measurements of the oxidation potential (Hirsch and Rüter, A., 1926, 930). R. Cuthill.

Colorimetric determination of minute amounts of nickel. L. T. Fairhall (J. Ind. Hygiene, 1926, 8, 528—533).—Armit and Harden's colorimetric determination of traces of nickel with the aid of dimethylglyoxime (A., 1906, ii, 397) gives erroneous results, since the solution has no true colour, the pink tint being due to crystalline particles of the nickel oxime. A sensitive colorimetric method is described involving the use of potassium dithiooxalate, which imparts an intense magenta colour to acid or neutral solutions of nickel salts. Iron and cobalt must be absent (methods of removal are described), but calcium, magnesium, phosphates, and small amounts of manganese may be present. One mg. of nickel may be determined with an accuracy of 0·02 mg. A modified method of preparing potassium dithio-oxalate is described (Jones and Tasker, J.C.S., 1909, 95, 1904). S. K. Tweedy.

Potentiometric titration of tin with potassium bromate. K. Sandved (Analyst, 1927, 52, 2—14)—Bivalent tin is first oxidised with tervalent iron and the resulting ferrous iron titrated with potassium bromate. A boiling solution of ferric chloride in hydrochloric acid is added in quantities 2—2·5 times the stoicheiometrically calculated amount to the boiling solution of the stannous salt, and the mixture diluted and titrated at 50°, as described by Collenberg and Sandved (A., 1926, 140) with potassium bromate. The ordinary monometallic electrode system is used, and a little 0·25 molar solution of cobaltous chloride added as catalyst. An application of the method to antimony and tin alloys is described, whereby the metallic antimony which is precipitated is removed. The method was not found applicable in the presence of quinquevalent arsenic, and in the case of quinquevalent antimony the reaction between it and bivalent tin is so slow that a sharp break of the curve by potentiometric titration of a mixture of stannous and antimonous salts with potassium bromate cannot be obtained. The use of different electrode systems for the titration of the ferrous iron with potassium bromate is discussed.
D. G. Hewer.

Molybdenum thiocyanate and the qualitative detection of molybdenum. F. C. Krauskopf and C. E. Swartz (J. Amer. Chem. Soc., 1926, 48, 3021—3027).—The solution is preferably carefully evaporated to dryness with nitric acid, the residue extracted with hot ammonia solution (to remove iron), filtered, and the filtrate and ammoniacal washings from the iron residue are neutralised with hydrochloric acid. Five c.c. of 10% potassium thiocyanate solution and a fragment of zinc are added, followed by concentrated hydrochloric acid, drop by drop, until hydrogen is evolved. A red colour (sometimes apparent only after extraction with ether) indicates the presence of molybdenum; the addition of a few c.c. of 10% phosphoric acid solution before the ether extraction destroys any colour thought to be due to iron. The sensitivity is 1 in 10^6, but this is decreased by phosphoric acid, mercuric chloride, and certain organic compounds. Attempts to isolate the red molybdenum thiocyanate were unsuccessful, but a determination of the molybdenum : sulphur ratio in ether solution indicated a formula $Mo(CNS)_3$.
S. K. Tweedy.

Method of covering quartz fibres by cathodic pulverisation. J. H. C. Quelle (Arch. Néerl. Physiol., 1926, **11**, 350—360).—A detailed description is given of a method for drawing quartz fibres, and

subsequently covering them with gold or silver by cathodic pulverisation. The method of attaching such fibres, when required for galvanometers, for which the gold-covered fibres are more suitable than the silver, is also described, as well as the determination of the electrical conductivity of the fibres. M. S. BURR.

Calibration of resistance thermometers at the oxygen b. p. and the carbon dioxide sublimation point. A. G. LOOMIS and J. E. WALTERS (J. Amer. Chem. Soc., 1926, **48**, 3101—3107).—The use of another fixed point besides the b. p. of oxygen in the calibration of platinum resistance thermometers obviates a calculation of the resistance at the f. p. of mercury by means of the Callendar equation; a suitable fixed point is the sublimation point of carbon dioxide, which is $-78{\cdot}51\pm0{\cdot}01°$ on the thermodynamic scale. The most probable value of the oxygen point is $-183{\cdot}00\pm0{\cdot}02°$ on the same scale. Details of experimentation are given, including the preparation of pure oxygen from potassium permanganate and of pure carbon dioxide from sodium hydrogen carbonate. S. K. TWEEDY.

Improvement in Victor Meyer apparatus for measuring vapour densities. A. TIAN (Bull. Soc. chim., 1926, [iv], **39**, 1771—1772).—In order to facilitate sweeping out the apparatus with clean dry air after each experiment, a narrow tube is sealed on to the bottom of the large bulb of the apparatus and is bent twice at right angles, both bends being fairly close to the joint. The bend is filled with a little mercury, and on sucking at the open end of the apparatus, a stream of air is drawn through the mercury, which thus acts as a valve. S. J. GREGG.

Hygrometer. A. ROMBERG and L. W. BLAU (J. Opt. Soc. Amer., 1926, **13**, 717—724).—A sensitive, continuous-indicating hygrometer, based on the difference in density between atmospheric air and air saturated with water vapour, is described. C. J. SMITHELLS.

Apparatus for m.-p. determinations. H. TER MEULEN (Chem. Weekblad, 1927, **24**, 36).—The thermometer with the capillary tube attached is supported in a long test-tube, suspended in a wider tube with a constriction near the lower end. A small burner is placed below the constriction, and a piece of gauze above it. S. I. LEVY.

Continuous extraction. M. WAGENAAR (Chem. Weekblad, 1927, **24**, 36—37).—Diagrams are given of apparatus employed for the extraction of aqueous solutions by means of light and heavy solvents. In the first, the light solvent condensed from the vapour rising through a central tube is carried to the bottom of an outer tube, in which the aqueous solution is contained, surrounding the inner tube through which the vapour ascends, and overflows from the top down the central tube into the distillation flask. In the second, the heavy solvent similarly condensed falls through the aqueous layer and escapes from the bottom into the central tube through a seal tube fused into the latter. S. I. LEVY.

Universal [gas] wash-bottle. W. KOCHMANN (Z. angew. Chem. [Chem. App.- u. Maschinenw.], 1927, **40**, 33).—The tube through which the gas enters the flask terminates at its lower end in an upturned jet through which the gas is injected, together with quantities of wash liquid, into an ascending worm connected at its upper end with a descending worm, from the bottom of which the gas bubbles up through the liquid in the usual way. By this arrangement, the gas and liquid are brought into prolonged intimate contact, so that efficient absorption or washing of the gas is effected in one wash-bottle. A. R. POWELL.

Wash-bottle. W. B. BOLLEN (Ind. Eng. Chem., 1926, **18**, 1290).—The wash-bottle is of the familiar pattern but the liquid is ejected by operating a "scent-bottle" bellows, the flow being terminated when required by opening the end of a third tube passing through the stopper. R. CUTHILL.

Weight burette. G. F. SMITH (Ind. Eng. Chem., 1926, **18**, 1216).—The instrument described has a narrow neck with a graduation mark, and the ground joints at the two extremities are so designed that they do not become wet with the contents of the burette. R. CUTHILL.

Apparatus for dehydrating volatile liquids. P. LORIETTE (Bull. Soc. chim., 1926, [iv], **39**, 1767—1770).—The liquid is dropped into an evaporator consisting of a bulb and coil heated in a water-bath, and the vapour so formed passes successively through three dehydrating tubes connected in series and also heated in the bath. The vapour then passes through a condenser and the liquid is collected. Each dehydrating tube contains eleven perforated plates carrying lumps of calcium oxide, each plate being separated from the one below by small feet. As the first tube becomes vitiated it is removed and a fresh tube placed at the other end of the train. S. J. GREGG.

Apparatus for the rapid determination of the conductivity of liquids. F. GOLDSCHMIDT (Z. angew. Chem. [Chem. App.- u. Maschinenw.], 1927, **40**, 31).—The container for the liquid consists of a small cylindrical flask provided with two insulated metal rings at the upper end, which are engaged by conducting clamps fixed into an ebonite boss, from which emerge the leads connecting with the Wheatstone bridge. The metal rings are each connected by means of glass-covered platinum wires with parallel platinum electrodes securely fixed to the bottom of the flask and each coated with platinum sponge. The four arms of the Wheatstone bridge are made up with a fixed resistance of 700 ohms, a vernier variable resistance of 0—700 ohms, the multiplier for the variable resistance, and the liquid the resistance of which is to be measured. The measurements are carried out by the use of a telephone indicator and condenser across one diagonal of the bridge, energised by high-frequency alternating current from a small transformer placed across the other diagonal. A. R. POWELL.

Micro-sublimation in a vacuum. M. WAGENAAR (Pharm. Weekblad, 1927, **64**, 10—11).—A simple apparatus for sublimation of very small quantities in a vacuum is described. S. I. LEVY.

"Ascarite" as a carbon dioxide absorbent. J. S. Buck (Ind. Eng. Chem., 1926, **18**, 1321).—A simple absorption tube for use with "ascarite" in carbon and hydrogen determinations is described (cf. Marsh, B., 1925, 615). R. Cuthill.

Chinese alchemy. J. R. Partington (Nature, 1927, **119**, 11).—It appears unlikely that Chinese alchemical texts are necessarily derived from Greek or Arabic sources; hence their dates should not be estimated on this assumption. A. A. Eldridge.

Mineralogical Chemistry.

Argon content of the atmosphere. E. Moles (Anal. Fis. Quím., 1926, **24**, 560—566).—The author has calculated the percentage of argon by weight in the air from the values for the litre-weight of crude atmospheric nitrogen and chemically prepared nitrogen, respectively, using the mixture rule. For the atmosphere at sea level, the percentage of argon is 0·909 or 0·946 if the maximum density of nitrogen is assumed in the calculation. G. W. Robinson.

Presence of helium in gases from petroleum wells. D. Butescu and V. Atanasiu (Bul. Soc. Romana Stiinte, 1926, **29**, 43—55).—The natural gases from some Rumanian petroleum wells were examined for helium by a spectroscopic method. Most specimens contained very small quantities of this gas, the richest samples containing two or three times as much as is present in air.

S. K. Tweedy.

Alkali metals in beryl from Ishikawa, Iwaki Province. J. Yoshimura (Bull. Chem. Soc. Japan, 1926, **1**, 239).—The beryl contained Cs_2O 0·085, Li_2O 0·015, K_2O 0·24, Na_2O 0·49%; rubidium was absent S. J. Gregg

Lepidolite from Nagatori, Chikuzen Province, and the lithium content of Japanese mica. S. Iimori and J. Yoshimura (Bull. Chem. Soc. Japan, 1926, **1**, 237—239).—The sample contained SiO_2 56·79 (some present as quartz), Al_2O_3 21·71, Fe_2O_3 0·73, FeO 0·14, MnO 0·46, CaO 0·26, MgO 0·13, K_2O 6·23, Rb_2O 0·96, Na_2O 2·45, Li_2O 1·94, F 4·69, H_2O 4·67, less O for F 1·97, total 99·19%. The percentages of sodium, potassium, and lithium in a number of Japanese micas have been determined.

S. J. Gregg

Potash-bearing horizon of the Malagash salt deposit, Nova Scotia. H. V. Ellsworth (Can. Dep. Mines Summ. Rep., 1926, 1924—C, 181—198).—The average potassium chloride content is more than 2%; the magnesium and calcium (other than sulphate) contents are small. The insoluble residues contain much quartz. Chemical Abstracts.

Spectrographic analysis of tufa from Fiuggi. C. Porlezza and A. Donati (Annali Chim. Appl., 1926, **16**, 457—475; cf. A., 1924, ii, 417).—This tufa is found to contain small proportions of zirconium, strontium, chromium, lead, cobalt, nickel, scandium, yttrium, ytterbium, lanthanum, cerium, neodymium, and, probably, niobium and zinc. T. H. Pope.

Spectrographic analysis of certain eruptive products of Stromboli. A. Donati (Annali Chim. Appl., 1926, **16**, 475—487).—Two products of eruptive explosions of Stromboli and one sample of the percolated lava of the same eruptive period (July, 1916) are found by spectrographic analysis to contain silicon, titanium, aluminium, iron, chromium, manganese, vanadium (traces), calcium, strontium, barium, magnesium, potassium, scandium (traces), ytterbium, lead (minimal traces), and cobalt (traces); analysis by the wet way reveals the presence of traces of copper, nickel, arsenic, lithium, and hydrochloric acid, and also of sulphuric and phosphoric acids.

T. H. Pope.

Noteworthy Vesuvian sublimations. G. Carobbi (Atti R. Accad. Lincei, 1926, [vi], **4**, 382—384).—Microscopic and crystallographic investigation of material from the inner wall of a fumarole in a laval channel of a cupola formed on Vesuvius in April—May, 1924, reveals the presence of boric acid in the form of sassoline and of potassium fluoborate as avogadrite (cf. *ibid.*, 306—311). T. H. Pope.

New minerals of the mosandrite group from the Chibine Mountains E. M. Bonstedt K. A. Nenadkevitsch and I. D. Starynkevitsch-Borne- Sci. Leningrad, 1926, [vi], 1181 1198).—To two yellow, greenish-yellow, or brownish-ye ow minerals of the mosandrite group, with a pale yellow streak, the names *rinkolite* and *lovtchorrite* are given. Their hardness is about 5 and they melt readily in blowpipe flame and are easily dissolved by acids. Rinkolite, $d_4^{17.5}$ 3·40, has a vitreous cleavage surface with a fatty fracture, and lovtchorrite, d 3·32, a fatty lustre. The percentage compositions of the two are as follows:

	SiO_2.	TiO_2.	ZrO_2.	ThO_2.	CeO_2.	Ce_2O_3,(DiLa)$_2O_3$,Y_2O_3.
Rinkolite	27·58	11·15	0·35	—	—	18·02
...	27·61	12·71		0·23	8·79	5·15

						BaO.	
Rinkolite		0·99	trace	24·70	3·30	trace	
Lovtchorrite ...	0·13	—	0·53	27·26	3·56	—	0·80

	Na_2O.	K_2O.	H_2O.	F.	−O for F.	Total.
Rinkolite	6·73	0·16	1·75	5·99	2·47	99·72
Lovtchorrite ...	7·18	0·28	0·51	6·38	2·63	100·00

No crystallographic measurements were found possible. T. H. Pope.

Organic Chemistry.

Effects exerted by atoms and groups of atoms on the reactivity of molecules and on the strength of linkings within the molecules. M. Tiffeneau and Orékhoff (Deuxième Cons. Chim. Inst. Intern. Chim. Solvay, 1926, 247—321).—A review.

Chemical Abstracts.

Field of applicability of classical stereochemistry and Weissenberg's geometrical stereochemistry. W. Huckel (Ber., 1926, 59, [*B*], 2826—2838; cf. Weissenberg, A., 1926, 934; Reis, *ibid.*, 934).—There is no positive reason for the extension of Weissenberg's theory to the gaseous

phase. The number of isomerides is adequately explained by the laws of classical stereochemistry, and the tetrahedral hypothesis in the form of the strain theory renders good indications of the relative stability of the isomerides, although further expansion is desirable. Weissenberg's theory predicts for the gaseous phase many more isomerides than have been isolated, which, if existent, must be very rapidly transformable; it may possibly be useful in explaining the existence of certain labile compounds such as the three *cis*-cinnamic acids. The differences in the conditions of existence of molecules in the crystalline and gaseous states render doubtful the choice of identical principles for the stereochemistry of both phases, and similar considerations explain why a stereochemistry, developed like the tetrahedral hypothesis for the gaseous phase, can in most cases give no adequate explanation for the behaviour of substances when crystalline. H. WREN.

Preparation of synthetic rubber hydrocarbon [dimethylbutadiene]. W. C. CALVERT (India Rubber Rev., 1926, No. 9, 48—50, 52, 54).—It appears almost certain that acetone cannot be reduced to pinacol by ordinary reducing agents. A number of condensation methods were examined. The highest yields (52—55%) in the Holleman method were obtained by Adams' procedure (" Organic Syntheses," 1925, **5**, 87), omitting mechanical agitation, or by doubling the amount of mercuric chloride. The order of mixing the reagents must not be reversed. A number of variations were tried without success. It is probable that a mercury compound with pinacol is formed intermediately. Of several methods which were tested for the dehydration of pinacol, the best yield of dimethylbutadiene (58%) was obtained by the hydrogen bromide method, pure pinacol reacting more slowly than impure. Dimethylbutadiene could not be obtained by the dry distillation of magnesium pinacolate. CHEMICAL ABSTRACTS.

Unsaponifiable matter from the oils of Elasmobranch fish. II. Hydrogenation of squalene in the presence of nickel. I. M. HEILBRON, T. P. HILDITCH, and E. D. KAMM (J.C.S., 1926, 3131—3136).—Complete hydrogenation of squalene using a nickel catalyst at 150° yields dodecahydrosqualene. From the product, 0·2% of an oxygenated neutral *compound*, m. p. 67—68°, was isolated. Hydrogenation of squalene is strongly selective; two of the unsaturated linkings appear to be different from the other four, not only in the rate of hydrogenation, but also in that ring closure does not occur after four double linkings have disappeared. B. W. ANDERSON.

Unsaponifiable matter from the oils of Elasmobranch fish. III. Tetra*cyclo*squalene and the production of a new naphthalene hydrocarbon. J. HARVEY, I. M. HEILBRON, and E. D. KAMM (J.C.S., 1926, 3136—3140; cf. A., 1926, 816).—Dehydrogenation of tetra*cyclo*squalene with sulphur at 200—270° gave chiefly a fraction, b. p. 100—160°/13 mm., yielding a *picrate*, $C_{19}H_{17}O_7N_3$, m. p. 139—140°, from which a *hydrocarbon*, $C_{13}H_{14}$, m. p. 33·5°, d^{20} 1·0103, n_D 1·6110, 58·5°, of naphthalene-like odour, was obtained. The pyrogenetic decomposition of tetra*cyclo*squalene gives rise to a mixture of lower terpenes; the sesquiterpene fraction on treatment with sulphur also yielded the above hydrocarbon. The action on squalene of formic acid which had been already used in the formation of tetra*cyclo*squalene gave rise to an *isomeric tetracyclosqualene*, b. p. 228—230°/3 mm., d^{20} 0·9237, n_D^{20} 1·5098, $[R_L]_D$ 132·7, iodine value 111·3. B. W. ANDERSON.

Chlorobromoiodomethane. M. GARINO and E. TEOFILI (Gazzetta, 1926, **56**, 847—852).—Chlorobromoiodopyruvic acid was obtained, but not isolated, by passing gaseous hydrogen iodide into an aqueous solution containing 50% of chlorobromopyruvic acid (A., 1923, i, 24) and 0·5% of iodic acid. Treatment of its sodium salt with excess of alkali results in the formation of *chlorobromoiodomethane*, m. p. about 5°, *d* 2·932—3·120, which begins, in an atmosphere of carbon dioxide, to emit gas at about 150°, b. p. 180—190° (complete alteration). When pure, it is pale yellow, but in the air it turns violet at once, owing to separation of iodine, carbonyl chlorobromide being also formed. The only solvent in which it remains unchanged is vaseline oil. T. H. POPE.

Action of cyanogen chloride on certain secondary organo-magnesium halides. V. GRIGNARD and K. ONO (Bull. Soc. chim., 1926, [iv], **39**, 1589—1594).—Cyanogen chloride reacts with primary organo-magnesium halides in two stages to give the corresponding nitrile and ketone, whereas with secondary organomagnesium halides the main product is the corresponding chloro-derivative, accompanied by a small quantity of nitrile (cf. A., 1911, i, 292; 1920, i, 235). In the aliphatic series, the yields of chloro-derivative and nitrile are about 70% and 8—10%, respectively; in the aromatic series, the yield of chloro-derivative is barely 50%, partly owing to formation of the hydrocarbon obtained by duplication of the organic radical. The following are described: *γ-bromopentane*, b. p. 116·5—117·5°/742 mm., d_4^{19} 1·1993, n^{19} 1·4403, and *γ-chloropentane*, b. p. 104—105°/753 mm., $d_4^{14\cdot5}$ 0·8967, 1·4163; *ε-bromononane*, b. p. 98—99°/12 mm., d_4^{14} 1·0845, 1·4544, *α-butylhexonitrile*, b. p. 99—101°/11 mm., $d_4^{16\cdot5}$ 0·8110, $n_D^{16\cdot5}$ 1·4034, and *ε-chlorononane*, b. p. 85—87°/14 mm., d_4^{15} 0·8639, n_D^{5} 1·4314; α-chloroethylbenzene, d_4^{13} 1·0598, 1·5337; *α-bromopropylbenzene*, b. p. 112—114°/15 mm., d^{19} 1·3098, n_D^{19} 1·5517, and α-chloropropylbenzene, $d_4^{19\cdot5}$ 1·0335, $n^{19\cdot6}$ 1·5252; chlorodiphenylmethane, $d_4^{19\cdot5}$ 1·1398, $n^{19\cdot5}$ 1·5959. M. CLARK.

Preparation of αβγ-tribromopropane and propadiene. M. W. TAPLEY and P. M. GIESY (J. Amer. Pharm. Assoc., 1926, **15**, 173—174).—αβ-Dibromopropane (200 g.) and bromine (300 g.) are heated with iron (card teeth) in a reflux apparatus until hydrogen bromide is no longer evolved (1—2 hrs.); the yield of tribromopropane, b. p. 219—221°/760 mm., is 78% of the theoretical. The product is converted by the Gustavson–Demjanoff method into dibromopropylene, from which propadiene is obtained in 78% yield by dropping into a mixture of zinc dust and ethyl alcohol and heating in a reflux apparatus. CHEMICAL ABSTRACTS.

Isomerisation of alkylvinylcarbinols to ethyl alkyl ketones. R. DELABY and J. M. DUMOULIN

(Bull. Soc. chim., 1926, [iv], **39**, 1578—1584).—See A., 1925, i, 632.

Isomerisation of alkylvinylcarbinols to β-alkylallyl alcohols. R. DELABY (Bull. Soc. chim., 1926, [iv], **39**, 1575—1578).—See A., 1926, 45.

Catalytic action of reduced copper on pinacols. S. YAMAGUCHI (Mem. Coll. Sci. Kyoto, 1926, **10**, 85—87).—See A., 1926, 727.

Cycle of reactions of erythrene derivatives. C. PRÉVOST (Compt. rend., 1926, **183**, 1292—1295).—When heated with 75% formic acid, inactive erythritol yields β-hydroxy-Δ$^{\gamma}$-butenyl formate, which gives β-hydroxy- -butenyl alcohol when treated with barium hydroxide. The alcohol and phosphorus tribromide in the presence of cold pyridine yield solely *trans*-αδ-dibromo-Δ$^{\beta}$-butene, which, when heated with sodium acetate and acetic acid, gives trans-αδ-*diacetyl*-Δ$^{\beta}$-*butylene glycol*, b. p. 118°/13 mm., m. p. 16°, d_D^{20} 1·08015, n_D^{20} 1·4772, hydrolysed to trans-Δ$^{\beta}$-*butylene glycol*, b. p. 131·5°/12 mm., m. p. 25°, d^{20} 1·0687, n_D^{20} 1·4772. When treated with bromine in ethereal solution, the glycol yields the corresponding *dibromohydrin*, m. p. 132·5—133° (corr.), which, with potassium hydroxide, gives butylene dioxide, $CH_2{\cdot}CH{\cdot}CH{\cdot}CH_2$, which in turn gives inactive erythritol. L. F. HEWITT.

Partial esterification of polyhydric alcohols. IV. Oxidation of allyl esters to α-monoglycerides. V. α-Structure of alleged "β"-monoglycerides. A. FAIRBOURNE and G. E. FOSTER (J.C.S., 1926, 3146—3148, 3148—3151).—IV. Oxidation of allyl *p*-nitrobenzoate (*dibromo*-derivative, m. p. 57—58°), and *allyl* 3 : 5-*dinitrobenzoate*, m. p. 50° (*dibromo*-derivative, m. p. 85°), to the corresponding monoglycerides was effected by treating their solutions in acetone with 1% aqueous potassium permanganate. Glycerol α-mono-2 : 4-dinitrophenyl ether was similarly obtained from allyl 2 : 4-dinitrophenyl ether. *Allyl picrate*, m. p. 90° (*dibromo*-derivative, m. p. 106—107°), resisted oxidation to the corresponding glyceride.

V. The two methods proposed by Grün (A., 1910, i, 356) for the synthesis of β-monoglycerides have been found to give α- and not β-products in both cases. In the first case, a specimen of "β"-monochlorohydrin was converted into its *p*-nitrobenzoate, and the product shown to consist chiefly of *glycerol* α-*monochlorohydrin di*-p-*nitrobenzoate*, m. p. 107—108°, with *glycerol* β-*monochlorohydrin di*-p-*nitrobenzoate*, m. p. 121—122°, as an impurity. In the second case, glyceryl "β"-monolaurate was shown to have the α-structure. *Glycerol* αγ-*dibromohydrin* p-*nitrobenzoate*, m. p. 77—78°, being shown not identical with the αβ-dibromohydrin, the possibility of β-substitution in the glycerol molecule was confirmed. *Glycerol* αγ-*dichlorohydrin* 3 : 5-*dinitrobenzoate*, m. p. 129°, was also prepared. B. W. ANDERSON.

***cyclo*Hexylglycerol.** R. DELABY and M. JANOT (Bull. Soc. chim., 1926, [iv], **39**, 1618—1621).—See A., 1926, 165.

Action of water and of alcohols on ethylene oxides in presence of a catalyst. E. FOURNEAU and I. RIBAS (Bull. Soc. chim., 1926, [iv], **39**, 1584—1589).—The action of catalysts in promoting the hydration of ethylene oxides is reviewed. Glycerol epichlorohydrin reacts vigorously and almost quantitatively with alcohols in presence of a trace of concentrated sulphuric acid, giving compounds of the type $RO{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2Cl$. The action is ascribed to the agency of an intermediate product $SO_2[O{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2Cl]_2$. This substance, formed when sulphuric acid reacts with an excess of epichlorohydrin, is a colourless oil. It can be substituted for the acid as catalyst in the alcohol–epichlorohydrin reaction. The action is formulated thus:

$SO_2[O{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2Cl]_2 + R{\cdot}OH \longrightarrow$
$SO_2(OH)[O{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2Cl] +$
$RO{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2Cl$.

The acid sulphate then reacts with more epichlorohydrin to regenerate the neutral compound. The latter is readily hydrolysed by water at the ordinary temperature, giving the acid sulphate. Complete hydrolysis takes place at 100°. The following are described: α-*chloro*-γ-*methoxypropan*-β-*ol*, b. p. 172°/760 mm.; 95°/20 mm.; α-*chloro*-γ-n-*butyloxypropan*-β-*ol*, b. p. 115°/20 mm.; α-*chloro*-γ-iso*amyloxypropan*-β-*ol*, b. p. 118—120°/20 mm. M. CLARK.

Dioxan as solvent, particularly for determinations of mol. wt. L. ANSCHÜTZ and W. BROEKER (Ber., 1926, **59**, [*B*], 2844—2847).—Dioxan [diethylene dioxide], b. p. 101·2—101·4°/760 mm. m. p. 11°, d_4^{20} 1·0329, is a useful solvent for sparingly soluble substances and particularly valuable in the determination of their mol. wts.; the cryoscopic and ebullioscopic constants are 4950 and 2200, respectively. H. WREN.

Mechanism of chemical transformation. T. M. LOWRY (Deuxième Cons. Chim. Inst. Intern. Chim. Solvay, 1926, 135—178).—A discussion.
CHEMICAL ABSTRACTS.

Mechanism of Kolbe's electrosynthesis. D. A. FAIRWEATHER and O. J. WALKER.—See this vol., 119.

Anhydrides of aliphatic acids. D. HOLDE (Chem.-Ztg., 1926, **50**, 994—996).—A review of the present knowledge of anhydrides and a discussion of their properties, methods of preparation, liability to decomposition, and use for edible purposes.
E. H. SHARPLES.

Reduction with acetic anhydride. J. B. MENKE (Rec. trav. chim., 1926, **45**, 908—913).—Hydrated cupric sulphate and chloride when warmed for a short time with acetic anhydride at 60° lose their water of crystallisation and yield the anhydrous salts, whilst refluxing with this reagent for 8 hrs., with the exclusion of moisture, reduces them to the corresponding cuprous salts. A similar reduction occurs with the corresponding mercuric salts, but in this case a complex mercurous *compound* is formed (cf. Sand and Singer, A., 1904, i, 25) which, in the case of mercuric chloride, is obtained in a crystalline form, m. p. about 136° (decomp.), on evaporation of the solution at the ordinary temperature, but the compound obtained from the sulphate is evidently unstable, and the mercurous sulphate resulting from its decomposition yields mercury and mercuric sulphate. Hence, when mercurous sulphate is heated with

acetic anhydride, mercury is produced, whilst the solution is coloured with the complex salt. When mercurous chloride is heated with acetic anhydride, no reduction to mercury occurs. J. W. Baker.

Monoacetin. H. A. Schuette and P. P. T. Sah (J. Amer. Chem. Soc., 1926, **48**, 3161—3163).—Monoacetin, b. p. 189—191°/60 mm., d_4^{25} 1·19846, n^{25} 1·4481, is obtained in practically quantitative yield by heating together molar equivalents of glycerol and acetic acid in presence of phosphoric acid or oxide at 170° for 2 hrs., the phosphoric acid being removed by the addition of sodium acetate and filtration before fractionation of the mixture. Diacetin and triacetin are converted into monoacetin when heated with excess of glycerol in presence of phosphoric acid. When glycerol and acetic acid are heated with sulphuric acid, the product is chiefly diacetin, whilst a mixture of about equal amounts of monoacetin and diacetin is obtained when zinc chloride is used as the catalyst. F. G. Willson.

Optical resolution of chlorobromoacetic acid. H. J. Backer and H. W. Mook (Proc. K. Akad. Wetensch. Amsterdam, 1926, **29**, 998—999).—The optically active components of chlorobromoacetic acid have been obtained by the method of "cold crystallisation." With brucine, a lævorotatory acid was obtained, whilst quinine gave a dextrorotatory compound. The latter alkaloid gave the best results. The salts show a rotation of about the same magnitude as that of the acid, but of opposite sign. The highest values of $[M]_D$ so far observed are +8° and −8° for the free acid and ammonium salt, respectively. The tendency to racemisation was found to be much less than anticipated. J. S. Carter.

Optical activity and the polarity of substituent groups. V. *sec.*-β-Octyl esters of some substituted acetic acids and their behaviour towards solvents. H. G. Rule and R. K. S. Mitchell (J.C.S., 1926, 3202—3209).—*β-Octyl methoxyacetate*, b. p. 120°/15 mm., *β-octyl chloroacetate*, b. p. 119—120°/15 mm.; *β-octyl bromoacetate*, b. p. 121°/15 mm., and *β-octyl iodoacetate*, b. p. 146—147°/17 mm., were prepared and their $[M]_D^t$ (t=20—90°) values tabulated. Values for $[M]_D^{20}$ of the esters in 5% solution in a number of solvents were also tabulated. The relative effect of substituents on the rotation of the acetic ester is given by H<Me<OMe<Et<Cl<Br<I, the order of polarity being followed except for the reversal of the halogens. The relative order for the esters remained unchanged in the various solvents and the effect of various substituents introduced into the solvent benzene molecule in lowering the $[M]_D$ values was in the order Me<H<OEt<Cl<Br<I. B. W. Anderson.

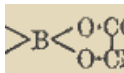
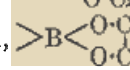
Crotonic acid series. I. Nitrogen derivatives of crotonic acid. M. A. Phillips (J.C.S., 1926, 2979—2983).—Dry carbamide reacts with α-bromobutyryl bromide to form *α-bromobutyrylcarbamide*, m. p. 156°, the action of aqueous sodium hydroxide on which yields the labile *cis*-form of *crotonylcarbamide*, m. p. 207°. The trans-*isomeride*, m. p. 234°, is obtained by the action of carbamide on crotonyl chloride. B. W. Anderson.

Configuration of oleic and elaidic acids. J. Boeseken and A. H. Belinfante (Rec. trav. chim., 1926, **45**, 914—918).—A preliminary note outlining two methods by which it is hoped to determine the configurations of oleic and elaidic acids. In the first method, the ethyl esters are converted into the octadecenols and thence into octadecenes of similar configurations to the original acids. That obtained from elaidic acid has m. p. +2°, and that from oleic acid m. p. about −15°. The second method is based on a comparison of the glycols obtained by oxidation with alkaline permanganate or with peracids and subsequent hydrolysis of the oxido-acid. J. W. Baker.

Condensation of pyruvic acid with paraformaldehyde in the presence of sulphuric acid. W. W. Feofilaktow (Ber., 1926, **59**, [*B*], 2765—2777).—Paraformaldehyde is converted by pyruvic acid in the presence of a little sulphuric acid into an acid, $C_9H_8O_6$, m. p. 234° (Kaltwasser assigns the composition $C_8H_8O_6$), and a *dilactone*, 140—144° when rapidly heated. The *sodium*, *potassium*, *lead*, and *silver* salts of the corresponding acid are described. The lactone is converted by acetic anhydride and a little sulphuric acid with loss of water into the unsaturated *diacetate*, $C_{14}H_{14}O_8$, m. p. 193°, and by chlorine in the presence of chloroform into the *chloride*, $C_{10}H_{11}O_7Cl$, m. p. 226—227°. With sodium ethoxide, it gives the *compound*, $C_{10}H_{10}O_8N_2$, with phenylhydrazine the *substance*, $C_{22}H_{24}O_6N_4$, m. p. 116—118° (decomp.), and with hydroxylamine (with simultaneous loss of water) the *oxime*, $C_{10}H_9O_6N$, m. p. 198—200° (decomp.). Oxidation of the lactone with hydrogen peroxide in alkaline solution affords a *lactonic acid*, $C_9H_{12}O_7$, m. p. 112—113°, and, apparently, a dihydroxybutyric acid of which the *sodium* and *silver* salts are described. The lactone is reduced by hydrogen in presence of spongy platinum to two *compounds*, $C_{20}H_{20}O_{12}$, needles, m. p. 219—220°, and prisms, m. p. 234—235°, whereas with tin and hydrochloric acid the compound, m. p. 219—220°, is alone produced. H. Wren.

Mechanism of Claisen's reaction. F. Swarts (Bull. Soc. chim. Belg., 1926, **35**, 411—416).—Ethyl trifluoroacetate condenses with ethyl acetate in presence of sodium ethoxide; since the mechanism suggested by Geuther and Lapworth for the Claisen reaction could not apply in this case, Claisen's original hypothesis as to the course of the condensation is supported. The trifluoroacetate, in fact, forms an additive product with sodium ethoxide, which is isolated by distilling off the ether and unchanged ester and is stable at 130° under reduced pressure. This intermediate compound forms a colloidal solution in ether, the apparent mol. wt. as determined by b.-p. depression being ±930°; it reacts with ethyl acetate to yield ethyl trifluoroacetoacetate. S. I. Levy.

Optically active borohydroxyisobutyric acid. J. Boeseken, H. D. Muller, and R. T. Japhongjouw (Rec. trav. chim., 1926, **45**, 919—922).—The resolution of asymmetric boron compounds derived from

α-hydroxy*iso*butyric acid,  , and α-hydroxy-α-methylbutyric acid,  , has been effected by means of their brucine salts. A solution of α-hydroxy*iso*butyric acid (2 mols.), boric acid (1 mol.), and brucine (1 mol.) in the minimal quantity of alcohol was heated at 50° in a vacuum desiccator, the vitreous mass dissolved in ether, and the ether evaporated, until the residue after drying over phosphoric oxide was soluble in chloroform. Fractional extraction of this solution with light petroleum yields the l-*brucine* l-*di*(α-*hydroxy*iso*butyryl*)*borate*, $[\alpha]_D^{18}$ −55·8°, whilst the chloroform residue contains the ld-*salt*, $[\alpha]_D^{18}$ −25·6°, both of which slowly change to the constant value, $[\alpha]^{15}$ −42°, of the racemate. By substitution of the appropriate base instead of brucine in the above preparation, the crystalline *aniline*, *o-toluidine*, and *dimethylaniline* salts are obtained. Similar resolution of *brucine di*-(α-*hydroxy*-α-*methylbutyryl*)*borate* yields the *ll*-isomeride, $[\alpha]_D^{18}$ −44·4°, and the *ld*-form, $[\alpha]^{18}$ −16·1°, both changing to the value of the racemate, $[\alpha]_D^{18}$ −28°. J. W. Baker.

***n*-Valerolactone.** H. A. Schuette and P. P. T. Sah (J. Amer. Chem. Soc., 1926, **48**, 3163—3165).—*n*-Valerolactone, b. p. 206—207°, b. p. 125°/60 mm., b. p. 78°/4 mm., n_D^{25} 1·4301, d^{25} 1·04608, is obtained in 60% yield by reducing sodium lævulate, dissolved in 95% alcohol, with metallic sodium (cf. Losanitsch, A., 1914, i, 657). F. G. Willson.

Microchemical differentiation of maleic and fumaric acids. M. Wagenaar (Pharm. Weekblad, 1927, **64**, 6—10).—Fumaric acid can be identified, with the aid of the microscope, by sublimation or precipitation, and from the ease of formation of its lead, mercury, silver, cadmium, and sodium or ammonium uranyl salts. The appearance of the crystals in each case is described. S. I. Levy.

α-Sulpho-*n*-valeric acid. H. J. Backer and M. Toxopeus (Rec. trav. chim., 1926, **45**, 890—907).—The preparation and resolution of α-sulpho-*n*-valeric acid and its derivatives have been effected, and the dispersions of its salts determined. dl-α-*Sulpho*-n-*valeric acid*, $+1{\cdot}5H_2O$, m. p. 65·5° (*barium*, *cobalt* $+2H_2O$, *nickel* $+2H_2O$, *copper* $+1H_2O$, *copper hydrogen* $+5H_2O$, *silver*, *silver hydrogen*, *aniline*, m. p. 146°, *strychnine* $+4H_2O$, *strychnine hydrogen* $+4H_2O$, *brucine* $+6H_2O$, *brucine hydrogen* $+2H_2O$, salts described), may be obtained by the sulphonation of *n*-valeric acid; it is also obtained in 70% yield by the action of sulphur trioxide on propylmalonic acid, and decomposition of the mixed malonic sulphuric anhydride, which is the initial product of the reaction. d-α-*Sulpho*-n-*valeric acid*, $[M]_{625}$ +1·7° (*aniline*, and *aniline hydrogen* salts), is obtained by repeated crystallisation of the brucine hydrogen salt and is isolated as its *barium* salt $+3H_2O$, $[M]$ +37°, whilst conversion of the mother-liquors into the normal brucine salt and fractional crystallisation yield l-α-*sulpho*-n-*valeric acid*, $[M]_{625}$ −1·7° (*barium hydrogen*, *cobalt* $+2H_2O$, *nickel* $+2H_2O$, *copper* $+1H_2O$, *copper hydrogen* $+5H_2O$ salts), isolated as its *barium* salt $+3H_2O$, $[M]_{625}$ −37°, which is also obtained by crystallisation of the strychnine hydrogen salt of the *dl*-acid. The metal hydrogen salts of the active acids have approximately the same rotation as the parent acids, and show very little dispersion, but the normal salts show a much greater rotation and dispersion in aqueous solutions, but no dispersion in alcoholic solution. On heating aniline sulphovalerate with excess of aniline for 5 hrs., *aniline valeranilide*-α-*sulphonate*, m. p. 257° (decomp.) (*barium* $+2H_2O$, *cobalt* $+3H_2O$, *nickel* $+3H_2O$, and *copper* salts), is obtained, which on resolution by means of its strychnine salt yields d-*valeranilide*-α-*sulphonic acid*, $[M]_{625}$ (in water) +2·9°, isolated as its *barium* salt, $+3H_2O$ (*cobalt* $+3H_2O$, *nickel* $+3H_2O$, and *copper* salts). *d*-Sulphovaleric acid heated with excess of aniline yields aniline *l*-valeranilide-α-sulphonate. The metal salts of *d*-valeranilide-α-sulphonic acid in aqueous solution have practically the same rotation as the free acid, but in alcoholic solution the value in each case is increased sixfold, and the cobalt and nickel salts show abnormal dispersion curves in this solvent, due, probably, to the co-ordination of the metal with the nitrogen. The action of *o*-phenylenediamine on α-sulphovaleric acid yields β-benziminazolebutane-α-sulphonic acid (decomp. without fusion) in 70% yield (*barium* $+4H_2O$, *cobalt* $+5H_2O$, *nickel* $+5H_2O$ salts), which is resolved by slow crystallisation in the cold of a mixture of the barium salt and strychnine acetate, which yields the d-*acid* (*barium* salt $+4H_2O$, $\frac{1}{2}[M]_{644}$ 14·8°, *cobalt* salt $+5H_2O$). Treatment of *d*-sulphovaleric acid with *o*-phenylenediamine yields the *l*-benziminazolebutanesulphonic acid, isolated as its *barium* salt. J. W. Baker.

Carbolthionic acids and esters. II. Y. Sakurada (Mem. Coll. Sci. Kyoto, 1926, **10**, 67—77; cf. A., 1926, 950).—The following thionic esters were prepared, using Matsui's method (A., 1912, i, 261): Thionacetates; *methyl*, b. p. 88—91°/atm., d_4^{28} 0·9002, n_D^{28} 1·4212; *propyl*, b. p. 125—130°/atm., d_4^{28} 0·8952, n_D 1·4283, η^{28} 0·7823; iso*propyl*, b. p. 119—122°/atm., d_4^{22} 0·8901, n_D^{22} 1·4501, η^{22} 0·7052; *butyl*, b. p. 146—149°/atm., d_4^{29} 0·8883, n^{28} 1·4196, η^{29} 0·8492; iso*butyl*, b. p. 135—140°/atm., d_4^{28} 0·8875, n_D^{28} 1·4316, η^{26} 0·8903; *benzyl*, b. p. 115—120°/27—29 mm., d_4^{25} 1·0296, n_D^{26} 1·5492, η^{25} 2·1711; m-*tolyl*, b. p. 110—112°/25—26 mm.; p-*tolyl*, b. p. 109—110°/25—26 mm.; β-*naphthyl*. Thionpropionates; *propyl*, b. p. 139—144°/atm., d_4^{28} 0·8835, n_D^{28} 1·4396, η^{28} 0·8256; iso*propyl*, b. p. 137—140°/atm., d_4^{22} 0·8714, n_D^{25} 1·4372, η^{22} 0·7318; *butyl*, b. p. 164—167°/atm., d_4^{28} 0·8618, n_D^{28} 1·4303, η^{28} 0·8799; iso*butyl*, b. p. 153—157°/atm., d_4^{28} 0·8678, n_D^{28} 1·4286, η^{28} 0·9001; *benzyl*, b. p. 132—136°/28—30 mm., d_4^{25} 1·0009, n_D^{26} 1·5178, 2·0846; *phenyl*. Thionbenzoates; *methyl*, b. p. 112—115°/26 mm., d_4^{28} 1·0710, n_D^{29} 1·5606, η^{28} 1·6866; *propyl*, b. p. 127—132°/29 mm., d_4^{28} 1·0133, n_D^{29} 1·5289, η^{28} 2·4550; iso*propyl*, 117—122°/27 mm., d_4^{27} 1·0060, n_D^{27} 1·5241, η^{27} 2·1376; *butyl*, b. p. 137—142°/23 mm., d_4^{28} 0·9732, n_D^{28} 1·5293, η^{28} 2·6357; iso*butyl*, b. p. 133—137°/27 mm., d_4^{28} 0·9694, n_D^{27} 1·5049, η^{28} 2·5415; iso*amyl*, b. p. 170—175°/54 mm., d_4^{23} 0·9748, n_D^{25} 1·4974, η^{23} 3·1700; *phenyl*, b. p. 155—160°/40 mm.; *benzyl*, b. p. 165—170°/38—40 mm.; β-*naphthyl*. Phenyl-

thionacetates; *methyl*, b. p. 145—149°/82—84 mm., d_4^{28} 1·0551, n_D^{30} 1·5612, η^{28} 1·9296; *propyl*, b. p. 130—133°/25 mm., d_4^{17} 1·0139, 1·5104, η^{27} 2·7187; iso*propyl*, b. p. 140—145°/50 mm., d_4^{22} 1·0078, n_D^{25} 1·5026, η^{22} 2·4672; *butyl*, b. p. 155—160°/36 mm., d_4^{23} 0·9930, n_D^{28} 1·5138, η^{28} 2·9127; iso*butyl*, b. p. 138—143°/25 mm., d_4^{23} 1·0010, n_D^{28} 1·5065, η^{23} 2·7713; iso*amyl*, b. p. 168—169°/50 mm., d_4^{23} 0·9801, n_D^{23} 1·4902, η^{23} 3·1369; *phenyl*, b. p. 202—206°/65 mm.; *benzyl*, b. p. 180—185°/26 mm., d_4^{28} 1·0866, η^{28} 5·2005. Thion-*p*-toluates; *methyl*, b. p. 170—173°/150 mm., d_4^{28} 1·0478, η^{28} 2·5396; *propyl*, b. p. 130—135°/23 mm., d_4^{25} 0·9858, n_D^{25} 1·5289, η^{30} 2·1789; iso*propyl*, b. p. 138—142°/48—50 mm., d_4^{22} 0·9880, η^{22} 1·9882; *butyl*, b. p. 150—152°/23 mm., d_4^{23} 0·9905, n_D^{23} 1·5315, η^{23} 2·7505; iso*butyl*, b. p. 144—148°/38—40 mm., d_4^{25} 0·9757, 1·5215, η^{25} 2·4254; iso*amyl*, b. p. 155—158°/32 mm., d_4^{23} 0·9856, n_D^{23} 1·5252, η^{22} 2·2020; *benzyl*, b. p. 185—190°/21 mm., d_4^{23} 1·0648, η^{23} 3·8893. Thionoxalates; *dimethyl*, b. p. 50—53°/21 mm.; *diethyl*, b. p. 80—82°/32 mm., d_4^{21} 1·0565, η^{21} 1·1707; *diiso*propyl, b. p. 91—93°/43 mm. The ethyl esters of thionacetic, thionpropionic, thionbenzoic, and thion-*p*-toluic acids react with aniline to form the corresponding thianilides in ethereal solution, and phenylimino-esters in alcoholic solution. Thionic esters, hydrolysed with alcoholic potassium hydroxide, yield the unstable thionic acids; *thionacetic*, *thionpropionic*, *thionphenylacetic*, *thion*-p-*toluic*, *thion*-β-*naphthoic*, and *thionoxalic acids* were prepared. B. W. Anderson.

Carbolthionic acids and esters. III. Carbithionic acids and esters. Y. Sakurada (Mem. Coll. Sci. Kyōtō, 1926, **10**, 79—83; cf. Houben, A., 1912, i, 5).—By passing dry hydrogen sulphide into an ethereal solution of the corresponding thio-imino-esters the following carbithionic esters were prepared: ethyl dithioacetate, b. p. 128—132°/atm., d_4^{28} 0·9807, n_D^{28} 1·5303; ethyl dithiopropionate, b. p. 150—155°/atm., d_4^{17} 0·9711, n_D^{27} 1·5259, η^{27} 2·1535; *ethyl dithiobenzoate*, b. p. 122—125°/70 mm.; *ethyl dithiophenylacetate*, b. p. 140—144°/45 mm., d_4^{28} 1·0462, η^{28} 2·9831; *ethyl dithio*-p-*toluate*, b. p. 160—165°/85 mm., d_4^{27} 1·0085, η^{27} 2·3215; *ethyl dithio*-β-*naphthoate*, b. p. 200—205°/45 mm.; *diethyl tetrathionoxalate*, b. p. 90—93°/43 mm. By hydrolysis of these esters with alcoholic potassium hydroxide, dithioacetic, *dithiopropionic*, dithiobenzoic, dithiophenylacetic, *dithio*-p-*toluic*, and *tetrathionoxalic acids* were isolated. B. W. Anderson.

Constitution of carminic acid. I. Miyagawa (Mem. Coll. Eng. Kyushu Imp. Univ., 1926, **4**, 99—113).—On treatment with ozone in aqueous solution, carminic acid affords an optically active product which on oxidation with barium permanganate yields an optically active *acid*, $C_6H_{12}O_6$, $[\alpha]_D^{28}$ +12·07° (*barium* salt, $[\alpha]_D^{28}$ +4·73°; *potassium* salt, $[\alpha]_D^{22}$ +5·96°). Reduction of this acid with sodium amalgam affords a *sugar*, $C_6H_{12}O_5$, $[\alpha]_D^{28}$ +8·13°, which is not identical with any of the known methylpentoses. The $C_6H_{11}O_5$– side-chain in carmini cacid (cf. Dimroth and Kämmerer, A., 1920, i, 442) accordingly possesses the probable constitution Me·[CH·OH]$_4$·CO–. Octa-acetylcarmmic acid and *tetra-acetylcarminic acid*, decomp. 155—170° (obtained by partial hydrolysis of the octa-acetyl compound with *N*-sodium hydroxide), on treatment with ozone in chloroform solution, afford no definite products. Dextrose and penta-acetylglucose are practically unattacked by ozone in aqueous solution. R. Brightman.

Faught test for acetone. H. T. Schaeffer (Amer. J. Pharm., 1926, **98**, 643—645).—The Faught test for acetone (F. A. Faught, "Essentials of Laboratory Diagnosis") is the most efficient known, dilutions of 1 : 100,000 giving positive results. Further, the test may be used in presence of dextrose and albumin. The costliness of the reagent, however (ethylenediamine hydrate), makes Legal's test the more generally useful. B. W. Anderson.

Mesityl oxide and certain halogen derivatives. J. Doeuvre (Bull. Soc. chim., 1926, [iv], **39**, 1594—1600).—The method of quantitative ozonisation shows that at least 95% of mesityl oxide exists in the form $CMe_2{:}CH{\cdot}COMe$. The system of conjugated double linkings does not appear to affect the value of the parachor (Sugden, A., 1924, ii, 662), since n_D^{22}=1·4425, d_4^{22}=0·860, γ^{22}=27·7 dyn./cm., P=261·7 (calc. 266·2). The products obtained by bubbling a mixture of chlorine and dry air through mesityl oxide in well-cooled carbon tetrachloride include the monochloro-derivative, $CMe_2{:}CCl{\cdot}COMe$, d_4^{17} 1·061, n_D^{17} 1·4703 [*semicarbazone*, m. p. 195° (corr.)], the dichloro-derivative, $CMe_2Cl{\cdot}CHCl{\cdot}COMe$, d_4^{17} 1·170, n_D^{17} 1·4632, and probably a *trichloro*-derivative, $CMe_2Cl{\cdot}CCl_2{\cdot}COMe$, b. p. 104—105°, d_4^{20} 1·313, n_D^{20} 1·4873. The monobromo-derivative, $d_4^{12·5}$ 1·376, $n_D^{12·5}$ 1·4982 [*semicarbazone*, m. p. 186—187° (corr.)], undergoes slow polymerisation when preserved. M. Clark.

Syntheses by means of inorganic magnesyl derivatives. Q. Mingoia (Gazzetta, 1926, **56**, 839—843).—Just as with aldehydes, magnesium bromohydrosulphide (A., 1926, 388) reacts with ketones, giving additive products, SH·CRR′·OMgBr, which are decomposed by water, giving thioketones, $\longrightarrow$ SH:CRR′·OH $\longrightarrow$ CS:RR′. With carbonyl chloride, the reaction gives rise to carbon oxysulphide, and with ethyl oxalate to dithioloxalic acid, $(COSH)_2$ (cf. Auger and Billy, *ibid.*, 1903, i, 310), the *lead* and *ammonium* salts of which were prepared.

The action of magnesium bromohydrosulphide on acetone yields trimeric thioacetone, and that on acetophenone, thioacetophenone. T. H. Pope.

Dioximes. XXXII. G. Ponzio (Gazzetta, 1926, **56**, 701—705).—Methylhydroxyglyoxime can form in acetone complexes of one or two molecules with one molecule of nickelous chloride or sulphate, or cuprous chloride. These differ from the complexes previously described (A., 1925, i, 1041) in that the metal is contained in a complex cation. *Nickel dimethylhydroxyglyoxime chloride*, $[Ni(C_3H_6O_3N_2)_2]Cl_2,H_2O$, emerald-blue, and *sulphate*, $[Ni(C_3H_6O_3N_2)_2]SO_4$, azure, and *cuprous methylhydroxyglyoxime chloride*, $[Cu(C_3H_6O_3N_2)]Cl_2$, greyish-green, are described; all are decomposed by water. Methylhydroxyglyoxime forms a *diacetate*, CMe(:N·OAc)·C(:N·OAc)·OH, m. p. 96—98°, and a *monobenzoate*, CMe(:N·OBz)·C(:N·OH)·OH, m. p. 146—147° (decomp.), which gives a red colour with ferric

chloride; the *dibenzoate*, CMe(:N·OBz)·C(:N·OBz)·OH, m. p. 177—178° (decomp.), when heated in alcohol, gives an *isomeride*, m. p. 151—152° (decomp.), reconverted by benzoyl chloride into the original derivative, and hydrolysed to benzhydroxamic acid. Hydrolysis of methylhydroxyglyoxime itself yields α-oximinopropionic acid, from which it can be prepared. E. W. WIGNALL.

Dioximes. XXXIII. G. PONZIO and I. DE PAOLINI (Gazzetta, 1926, **56**, 705—709).—Hydroxyglyoxime can be prepared more readily than before (A., 1925, i, 1041) by the action of hydroxylamine on ethyl dichloroacetate. The *sodium*, *potassium*, and *ammonium dihydroxyglyoxime nickelates*, $[(C_2H_2O_3N_2)_2Ni]M_2$, red, crystalline substances, are described, and *nickel dihydroxyglyoxime chloride*, $[Ni(C_2H.O_3N_2)_2]Cl_2$, emerald-green, are described.

The *diacetate*, CH(:N·OAc)·C(:N·OAc)·OH, has m. p. 113—114°, and is reconverted into hydroxyglyoxime on hydrolysis; the *tribenzoate*, m. p. 142—143°, is hydrolysed to benzhydroxamic acid. E. W. WIGNALL.

Dioximes. XXXIV. G. PONZIO and R. SISMONDI (Gazzetta, 1926, **56**, 709—713).—Oxaldihydroxamic acid (dihydroxyglyoxime), m. p. 165°, forms complex salts similar to those obtained from other hydroxyglyoximes, and not the compounds described by Hofmann and Ehrhardt (A., 1913, i, 599). The following are described: *sodium bisdihydroxyglyoxime nickelate*, $[(C_2H_2O_4N_2)_2Ni]Na_2$, which forms a *di-* and a *trihydrate*, explosive on heating; the corresponding *potassium* salt, which forms red *di-* and *pentahydrates*; *potassium bisdihydroxyglyoxime cuprate*, coffee-coloured, $[(C_2H_2O_4N_2)_2Cu]K_2$. The dibenzhydroxamic acid, m. p. 161°, described by Schafer, has m. p. 165—167° (decomp.) and is to be regarded as benzoylated on the oxime groups, viz., HO·C(:N·OBz)·C(:N·OBz)·OH, dibenzoximinoethylene glycol, since with sodium hydroxide it gives benzoic acid, hydrazine, and carbon dioxide, which may be regarded as products of a double Beckmann transformation to an unstable dibenzoylhydrazinedicarboxylic acid. E. W. WIGNALL.

Dioximes. XXXIX. G. B. SEMERIA and B. BOCCA (Gazzetta, 1926, **56**, 746—756).—Thermal diagrams obtained by a modified "thaw-melt" method (cf. Rheinboldt, A., 1926, 25) are given for mixtures of glyoxime or its methyl, dimethyl, or methylethyl derivatives, all in the β-forms, which give nickel complexes insoluble in dilute acetic acid, with xanthone, or with antipyrine. Xanthone gives *compounds*: $C_2H_4O_2N_2,2C_{13}H_8O_2$; $MeC_2H_3O_2N_2,C_{13}H_8O_2$; $Me_2C_2H_2O_2N_2,2C_{13}H_8O_2$, and $MeEtC_2H_2O_2N_2,C_{13}H_8O_2$. Antipyrine gives $C_2H_4O_2N_2,C_{11}H_{12}ON_2$; $MeC_2H_3O_2N_2,C_{11}H_{12}ON_2$; $Me_2C_2H_2O_2N_2,C_{11}H_{12}ON_2$; and $MeEtC_2H_2O_2N_2,C_{11}H_{12}ON_2$ and $MeEtC_2H_2O_2N_2,2C_{11}H_{12}ON_2$. E. W. WIGNALL.

Dioximes. XL. [Action of bromine on hydroxamic acids.] I. DE PAOLINI (Gazzetta, 1926, **56**, 757—758).—Bromine converts acethydroxamic acid into acetic acid and nitrous oxide; benzhydroxamic acid into benzoic acid and nitrous oxide; phenylacethydroxamic acid into phenylacetic acid; carbamylhydroxamic acid into oxamic acid; phenylcarbamylhydroxamic acid into *p*-bromo-oxanilic acid. E. W. WIGNALL.

Reactions between sugars and amines. III. H. VON EULER and E. BRUNIUS (Z. physiol. Chem., 1926, **161**, 265—269).—The lowering of f. p. with lævulose–alanine mixtures is greater than would be expected from those of the components. The affinity constant for the reaction is K 0·133. On mixing 0·1*N*-solutions, the immediate reaction utilises about 2% of the lævulose present (cf. A., 1926, 714, 822). P. W. CLUTTERBUCK.

Constitution of the disaccharides. XI. Maltose. W. N. HAWORTH and S. PEAT (J.C.S., 1926, 3094—3101).—Thorough methylation of maltobionic acid yielded *methyl octamethylmaltobionate*, b. p. 170—173°/0·05 mm., 1·4620, which, on hydrolysis, formed crystalline tetramethylglucose and βγεζ-tetramethylgluconic acid. This acid, when heated, forms βγεζ-tetramethyl-γ-gluconolactone. Mixed m.-p. determinations confirmed the identity of the phenylhydrazide of this acid, m. p. 134—136°, with specimens from two other sources. The constitution of maltose thus seems definitely proved, the oxide ring being amylene oxidic. B. W. ANDERSON.

Synthesis of disaccharides. IV. Two β-*d*-glucose tetra-acetates. B. HELFERICH and W. KLEIN (Annalen, 1926, **450**, 219—229).—6-Triphenylmethyl-β-*d*-glucose (A., 1925, i, 790), when treated at 0° with hydrobromic acid in acetic acid, gives a triphenylmethyl bromide and β-d-*glucose*-1 : 2 : 3 : 4-*tetra-acetate*, m. p. 128—129°, $[\alpha]_D^{24}$ +12·1° in chloroform, +21·7° in water before mutarotation. This is reconverted by triphenylmethyl chloride into the initial material (thus showing that the 6-hydroxyl group is free) and acetylated by acetic anhydride to β-*d*-glucose penta-acetate, m. p. 134°.

If excess of β-*d*-glucose tetra-acetate is shaken with acetobromoglucose and silver oxide in chloroform, gentiobiose octa-acetate, m. p. 196°, is readily obtained.

If β-*d*-glucose 1 : 2 : 3 : 4-tetra-acetate is treated in pyridine with toluenesulphonyl chloride, β-d-*glucose* 1 : 2 : 3 : 4-*tetra-acetate* 6-*toluenesulphonate*, m. p. 203—205°, $[\alpha]^{20}$ +23·9° in chloroform, separates.

Study of the mutarotation of β-*d*-glucose 1 : 2 : 3 : 4-tetra-acetate at 41·5° shows a gradual decrease in rotation in aqueous solution in ordinary glass vessels, but not in other solvents, or in Jena glass. The product at equilibrium, in which α has decreased to one tenth of its original value, has m. p. 97—98°, and consists of a mixture of the initial material with an isomeride. This is isolated by crystallisation from pyridine; the product containing 1 mol. of pyridine of crystallisation has m. p. 108—110°, $[\alpha]^{20}$ —22·0° in water. The pyridine-free β-*d*-*glucose* 1 : 2 : 3 : 6(?)-*tetra-acetate* has m. p. 132°, which is strongly depressed by mixing with the 1 : 2 : 3 : 4-isomeride. The new substance does not form a derivative with triphenylmethyl chloride under the conditions employed with the 1 : 2 : 3 : 4-compound (indicating that the 6-hydroxyl group is not free); it is acetylated in pyridine to β-*d*-glucose penta-acetate, identical with that previously described; it reacts with toluenesulphonyl

chloride to give a new β-d-*glucose* 1 : 2 : 3 : 6(?)-*tetra-acetate* 4(?)-*toluenesulphonate*, m. p. 111—112°, $[\alpha]^{20}$ −15·9° in chloroform.

Directions are given for the preparation of the reactive silver oxide employed by the authors.

E. W. WIGNALL.

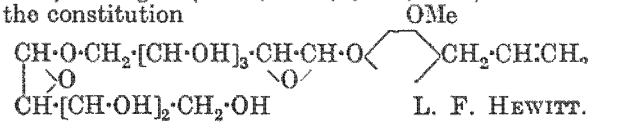
Sugar syntheses. V. Synthesis of trisaccharides. B. HELFERICH and W. SCHÄFER (Annalen, 1926, 450, 229—237).—The preparation of β-*d*-glucose 1 : 2 : 3 : 4-tetra-acetate (see preceding abstract) has made it possible to prepare trisaccharides. Thus this substance condenses with acetobromocellobiose in chloroform in presence of silver oxide to give 6-β-*cellobiosido*-β-d-*glucose hendeca-acetate*, m. p. 245—247°, $[\alpha]^{21}$ −10·2°, −10·4° in chloroform, which when hydrolysed by the method of Zemplén (A., 1926, 822) gives 6-β-*cellobiosido*-β-d-*glucose*, m. p. 247—252°, $[\alpha]_D$ +15·0° to +8·4° in water. A monohydrate, m. p. 200° (decomp.) is described. The sugar has about 42% of the reducing power of dextrose. The *osazone* has m. p. 224°, $[\alpha]^{22}$ −61·5° in pyridine. Treatment of the hendeca-acetate with hydrobromic acid in acetic acid yields 6-β-*hepta-acetylcellobiosido-acetobromoglucose*, m. p. 231°.

In a similar manner, from acetobromolactose, 6-β-*lactosido*-β-d-*glucose*, m. p. 257° (decomp.), $[\alpha]_D$ +34·7° to +22·6° in water, is obtained by way of its *hendeca-acetate*, m. p. 198°, $[\alpha]^{22}$ −2·53° in chloroform. The reducing power towards Fehling's solution is about 37% of that of dextrose. The *osazone* has m. p. 233°, $[\alpha]_D^{22}$ −50·5° in pyridine.

Acetobromogentiobiose yields 6-β-*gentiobiosido*-β-d-*glucose hendeca-acetate*, m. p. 221°, $[\alpha]^{23}$ −8·0° in chloroform. The free sugar has been obtained as a syrup, of reducing power about 40% of that of dextrose.

E. W. WIGNALL.

Constitution of gein (geoside). H. HÉRISSEY and J. CHEYMOL (Compt. rend., 1926, **183**, 1307—1308).—To gein (cf. A., 1925, i, 487, 1383) is ascribed the constitution



L. F. HEWITT.

Synthesis and degradation of polysaccharides. H. PRINGSHEIM (Ber., 1926, 59, [*B*], 3008—3018).—A lecture delivered before the Gesellschaft Deutscher Naturforscher und Ärzte.

H. WREN.

Röntgenographic elucidation of the structure of organic substances, particularly those of high mol. wt. H. MARK (Ber., 1926, 59, [*B*], 2982—3000).—A lecture delivered before the Gesellschaft Deutscher Naturforscher und Ärzte.

H. WREN.

Chemistry of complex organic compounds in the light of Kekulé's theory of structure. H. PRINGSHEIM (Ber., 1926, 59, [*B*], 3019—3043).—A lecture delivered before the Gesellschaft Deutscher Naturforscher und Ärzte.

H. WREN.

Starch. XIX. Fermentative fission of the polyamyloses. H. PRINGSHEIM, J. LEIBOWITZ, and P. MECHLINSKI (Ber., 1926, 59, [*B*], 2738—2746; cf. A., 1926, 1128).—Amylase can be removed almost completely and maltase largely from weakly acid taka-diastase solution by β-aluminium hydroxide; the residual solution hydrolyses the polyamyloses readily, giving dextrose and, possibly, maltose. In weakly alkaline solution, the polyamylases are adsorbed by kaolin, which has no effect on maltase and amylase, but elution of the active polyamylases could not be effected. Variation in the nature of the admixed products of taka-diastase renders repetition of the experiments uncertain with different specimens. Complete fission of the polyamyloses to dextrose appears a complicated change, since it does not follow any simple law. Within each polyamylose series the fermentative behaviour of the members is independent of the degree of polymerisation. Hydrolysis of α-di- and α-tetra-amylose or of β-tri- and β-hexa-amylose occurs qualitatively and quantitatively similarly, so that the enzyme appears directly to attack the associated molecule. Under like conditions, tri- and hexa-amylose are more rapidly attacked than di- and tetra-amylose and are smoothly transformed into dextrose in 100% yield, whereas with the α-polyamyloses a "false equilibrium" is somewhat rapidly established and quantitative production of dextrose can be secured only by the use of large amounts of enzyme. Apparently fission of the α- and β-polyamyloses is due to two different enzymes. The enzymes under observation are specifically adapted to certain chemical structures of the substrates and not to definite degrees of association or polymerisation. The observations also bring new indirect evidence of the structural difference of the α- and β-polyamyloses and of their non-identity with the fundamental components of starch.

H. WREN.

Structure of starch. E. PEISER (Z. physiol. Chem., 1926, 161, 210—217).—Starch, acetylated in the cold, yields a compound, $C_{48}H_{56}O_{42}Ac_{26}$, $[\alpha]^{26}$ +276·3°, which on hydrolysis regenerates the original amylose. If the acetylation is carried out at 55°, a substance, $C_{24}H_{38}O_{22}Ac_{14}$, is obtained. A third acetyl derivative, $C_{24}H_{29}O_{22}Ac_{13}$, is obtained by warming the compound $C_{48}H_{56}O_{42}Ac_{26}$ with phosphorus pentachloride, and this on further acetylation yields the higher acetyl derivative, $C_{24}H_{28}O_{22}Ac_{14}$.

P. W. CLUTTERBUCK.

Relation of lichosan to lichenin. H. PRINGSHEIM and O. ROUTALA (Annalen, 1926, 450, 255—272).—The criticisms of Bergmann and Knehe (A., 1926, 1230) are refuted. In contrast with the grey powder obtained by these authors, pure white lichosan can be dried satisfactorily. The viscosity curve of lichosan in water shows that the particles are smallest at 70°; the mol. wt. determined at this temperature by the Barger–Rast method is 162, that of a glucose anhydride. The viscosity curve resembles that of cellosan, except that with rise of temperature from 70° to 100° the viscosity rises only slightly. At 45°, the mol. wt. is about 486. $[\alpha]_D$ in water 0; in 2*N*-sodium hydroxide +33·5°; in 95% pyridine +93·2°.

Lichosan has been prepared by another method. Lichenin acetylated by acetic anhydride and a trace of sulphuric acid gives lichenin acetate, $C_6H_7O_5Ac_3$, $[\alpha]_D$ −17·7 to 23·1° in chloroform (Hess and Schultze,

A., 1926, 715), which is hydrolysed to lichenin by methyl-alcoholic ammonia, if this contains a little water. Lichenin acetate heated with naphthalene gives pure white *lichosan acetate*, $C_6H_7O_5Ac_3$, $[\alpha]^{20}$ $-21{\cdot}8°$ in chloroform, mol. wt. in phenol 327—445. This hydrolyses under the conditions employed with lichenin to lichosan, identical with that obtained by heating lichenin in glycerol.

The association of molecules in a polysaccharide is considered to be due to molecular valencies. These give with lichosan polymerides of 3—7 mols.; the simple "elementary substance" nevertheless exists, and there is no reason for assuming that chemical changes occur during deassociation.

E. W. WIGNALL.

[**Lignin.**] W. FUCHS and E. HONSIG (Ber., 1926, 59, [*B*], 2850—2856).—A criticism of the work of Schmidt (A., 1925, i, 1370, and previous abstracts). Treatment of wood with chlorine dioxide and sodium sulphite gives products the total weight of which, calculated to ash-free material, does not differ greatly from the weight of the initial substance. In spite of this, decomposition, oxidation, and hydrolysis occur. Elementary analysis of the initial material and the products derived therefrom shows that about one fourth of the initial carbon is oxidised to carbon dioxide, oxalic acid, etc. In the course of the treatment, the original methoxyl content disappears completely. Hence the decomposition takes place mainly at the expense of the lignin. Elementary analysis also indicates that even if lignin persists in individual fractions, its composition must differ widely from that of original lignin. The greater part of the lignin appears to suffer complete decomposition, as would be expected from the behaviour of phenols under similar conditions. Experience with individual lignin preparations indicates the possibility that they may yield polysaccharides in small amount, but not to the extent assumed by Schmidt. The expression "polysaccharides from lignin" is not admissible. H. WREN.

Crystalline nature of the chief constituent of ordinary coal. C. S. FOX (Nature, 1926, 118, 913).—Coal from the Raniganj coalfield contains one main constituent ("vitro-clarain" or "anthraxylon"), which simulates a crystalline structure, together with resinous substances, fusain, and inorganic matter. A. A. ELDRIDGE.

Crystalline nature of the chief constituent of ordinary coal. M. C. STOPES (Nature, 1926, 118, 913).—Polemical (cf. Fox, preceding abstract).

A. A. ELDRIDGE.

Syntheses of tetramethylenediamine and pyrrolidine. W. KEIL (Ber., 1926, 59, [*B*], 2816—2817).—γ-Phthalimido-*n*-butyronitrile is reduced by sodium and alcohol, and the resulting substituted diamine is distilled with concentrated alkali hydroxide, whereby tetramethylenediamine is obtained in more than 60% yield. The corresponding hydrochloride is transformed by dry distillation into pyrrolidine hydrochloride and ammonium chloride. H. WREN.

Additive compounds of halides of bivalent metals with organic bases. III. G. SCAGLIARINI and G. TARTARINI (Atti R. Accad. Lincei, 1926, [vi], 4, 387—389; cf. A., 1926, 1113).—In alcoholic solution, hexamethylenetetramine forms with the halides of bivalent metals the *compounds* $CoCl_2,C_6H_{12}N_4$, ultramarine; $CoBr_2,C_6H_{12}N_4$, blue, and $NiCl_2,C_6H_{12}N_4$, greenish-yellow. T. H. POPE.

Action of Grignard reagent on amino-acids. XII. Determination of free carboxyl groups in peptides. F. BETTZIECHE (Z. physiol. Chem., 1926, 161, 178—190).—Glycylalanine, glycylphenylglycine, benzoylglycylalanine, and benzoylglycylphenylglycine, on esterification and treatment with magnesium phenyl bromide and hydrolysing, respectively, give yields of dibenzyl ketone, 52%; triphenylethanone, 59%; dibenzyl ketone 41%, and triphenylethanone, 50%. The method is adapted to small amounts (40—100 mg.) of the following, the yields with magnesium phenyl and benzyl bromides being tabulated; phenylglycine, glycine, alanine, phenylalanine, leucine, glycylglycine, hippurylglycine, glycylalanine, hippurylalanine, glycylphenylglycine, and hippurylphenylglycine. P. W. CLUTTERBUCK.

Preparation of β-aminoaryl-aliphatic acids. I. W. M. RODIONOV and E. T. MALEWINSKAJA (Ber., 1926, 59, [*B*], 2952—2958).—Piperonal is converted by malonic acid and boiling alcoholic ammonia into a mixture of piperonylacrylic acid, methylenedioxystyrenedicarboxylic acid, and β-*amino*-β-*piperonylpropionic acid hydrochloride*, m. p. 232—234°, the relative proportion of the latter increasing with increase in the quantity of alcoholic ammonia. β-Amino-β-piperonylpropionic acid has m. p. 224—225°. Similarly, piperonal, malonic acid, and alcoholic methylamine afford β-*methylamino*-β-*piperonylpropionic acid hydrochloride* (corresponding *acid*, m. p. 199—200°). The following compounds are analogously prepared: β-*amino*-β-*phenylpropionic acid hydrochloride*, m. p. 218°, and the acid, m. p. 228° (also obtained from benzhydramide); β-*amino*-β-*m-nitrophenylpropionic acid hydrochloride*, m. p. 210—211·5°, and the acid, m. p. 226—227°. H. WREN.

Optically active, internally complex salts. H. LEY and T. TEMME (Ber., 1926, 59, [*B*], 2712—2719; cf. A., 1917, i, 707).—α-Bromopropionic acid is resolved by means of an excess of cinchonine in acetone solution into its optical isomerides, which are converted by an excess of methylamine at 0° into the corresponding α-methylaminopropionic acid; after treatment with lead hydroxide to decompose any methylamide, the latter are transformed into the *copper* salts, $(C_4H_8O_2N)_2Cu,2H_2O$, $[\alpha]_{blue}$ $+35{\cdot}2°$ and $34{\cdot}1°$, respectively. The *l-acid*, m. p. 274° (decomp.), has $[\alpha]_{red}$ $-5{\cdot}1°$, $[\alpha]_{yellow}$ $-6{\cdot}85°$, whereas for the d-*acid* (from the lævorotatory copper salt), $[\alpha]_{yellow}$ $+7{\cdot}92°$ is recorded. The *hydrochloride* and *sodium* salt of the *l*-acid have $[\alpha]_{red}$ $-6{\cdot}25°$ and $[\alpha]_{red}$ $-2{\cdot}4°$, respectively. With increasing concentration of ammonia, the specific rotation of the copper salt of *l*-methylalanine diminishes to zero, and then attains maximum lævorotation, followed by a decline; a similar behaviour is shown by the corresponding salt of *d*-alanine. Attempts to prepare cobaltic salts of the active methylalanines gave resinous products with high optical activity. With potassium chloroplatinite, the *l*-acid yields the *salt*,

$K[PtCl_2,C_4H_8NO_2]$, $[\alpha]_{red}$ −12·7°, $[\alpha]_{yellow}$ −16·76° in water. The normal *nickel* salt is described. The red *cobaltic* salt of l-*alanine* has $[M]_{red}$ +475°, whereas the corresponding violet *salt* has $[M]_{red}$ −1315° in 50% sulphuric acid. H. WREN.

Action of sodium hypobromite on derivatives of carbamide and guanidine. III. V. CORDIER (Monatsh., 1926, 47, 327—339; cf. A., 1914, i, 258).—The volume of nitrogen (if any) evolved under the prolonged action of sodium hypobromite has been determined for a large number of substances, including derivatives of carbamide, thiocarbamide, guanidine, and the cyclic ureides. The results of this and the previous investigations are collected in tabular form. G. M. BENNETT.

Metal alkyls. F. HEIN and F. A. SEGITZ (Z. anorg. Chem., 1926, 158, 153—174; cf. A., 1925, ii, 217).—Tetraethylammonium iodide and tetrapropylammonium iodide dissolve in zinc ethyl and zinc methyl, and tetraethylammonium iodide also dissolves in cadmium ethyl, forming conducting solutions. With increasing dilution, the molecular conductivity increases, and apparently tends to a limit. The loose *compound*, $NPr_4I,ZnEt_2$, can be separated from the corresponding solution. Since, according to Walden, the tetra-alkylammonium iodides can be regarded as standard electrolytes, the view that the alkali alkyls, considered with respect to their solutions in the above metal alkyls, are salts (cf. *loc. cit.*) is confirmed. An approximate calculation indicates that in all the solutions in metal alkyls the solute molecules are highly polymerised. The behaviour of various metals as anodes in the electrolysis of solutions of sodium ethyl in zinc ethyl has been examined. Antimony, aluminium, magnesium, cadmium, bismuth, thallium, gold, and, in certain circumstances, tin, but not copper, platinum, iron, or tantalum, are attacked almost quantitatively by the ethyl radicals. R. CUTHILL.

Action of tungsten hexachloride on magnesium phenyl iodide. (MLLE.) W. BRYDOWNA (Bull. Soc. chim., 1926, [iv], 39, 1771).—The action of tungsten hexachloride on magnesium phenyl iodide in ether affords diphenyl in 50% yield (cf. A., 1924, i, 381). R. BRIGHTMAN.

Isomeric changes in cyclic compounds with catalysts. I. Hydrocarbons. M. N. DOJARENKO (J. Russ. Phys. Chem. Soc., 1926, 58, 1—15).—The isomeric changes to open-chain structures of cyclic compounds, *e.g.*, hydrocarbons and alcohols, were studied at 250—430° in the presence of alumina as catalyst. The products were fractionated and further separated and identified by treatment with bromine. Methylene*cyclo*butane at 400—430° gave a fraction, b. p. 31—39°/735 mm., containing β-methyl-Δ^{β}-butene, β-methyl-Δ^{α}-butene, and isoprene, identified by the physical constants of the bromine derivatives formed. The fractions of higher b. p. gave *p*-cymene and a rubber-like residue. It is probable that isoprene is the main product.

Methyltrimethylene at 340—360° gave a gas, chiefly Δ^{β}-butene and β-methyl-Δ^{α}-propene. The liquid portion was probably composed of substances, C_8H_6 and C_4H_6.

By comparing these and other results, the conclusion is reached that in isomeric changes of cyclic to open-chain compounds, the tendency is to increase the number of methyl groups.

The theoretical significance of the reactions is discussed. The catalyst causes, by the influx of external energy, the loosening of a C—C linking, with the formation of intermediate labile forms, which give various products, depending on the external energy conditions. In all cases, the final product has a smaller energy content than the initial compound, as is shown by the values calculated from Fajans' and Hückel's data for C—C and C—H linkings in rings and chains. M. ZVEGINTZOV.

Isomeric transformations of cyclic compounds under the influence of catalysts. I. Isomerisation of cyclic hydrocarbons with aluminium oxide as catalyst. M. DOJARENKO (Ber., 1926, 59, [*B*], 2933—2948).—A more extended account of work already reported (preceding abstract). H. WREN.

Isomeric changes in cyclic compounds with catalysts. II. Dehydration of the alcohols C_4H_8O. III. Dehydration of the alcohols $C_5H_{10}O$. M. N. DOJARENKO (J. Russ. Phys. Chem. Soc., 1926, 58, 16—26, 27—38; cf. preceding abstract).—II. *cyclo*Propylcarbinol, *cyclo*butanol, and allylcarbinol were investigated by the method described in Part I. *cyclo*Propylcarbinol gave a liquid and a gaseous product: propylene (main product), erythrene and butylene (traces). The liquid contained water (which increased with rise of temperature) and an oil (which decreased) consisting of aldehydes, *cyclo*butanone, and polymerides. Some carbon was also deposited. The proportions of the products depend on the temperature. *cyclo*Butanol at 360—390° gave propylene, erythrene, water, carbon, and traces of *cyclo*butanone, aldehydes, and polymerides. Erythrene gave two stereoisomeric tetrabromides, m. p. 39° and 118°. Allylcarbinol (into which *cyclo*propylcarbinol often isomerises) at 400° gave results analogous to the cyclic compounds. The cyclic alcohols isomerise to an open chain, which is then split, giving propylene as the main product.

III. Methyl*cyclo*propylcarbinol was treated at 240—265° and at 350—365°. The effect of rise of temperature was as before. The products were mainly piperylene and divinylmethane, with a little methyl-*cyclo*butene (identified by its dibromide, b. p. 66—73°/13 mm., d_4^{17} 1·744, 1·576), *i.e.*, there was some 3- to 4-ring isomerism.

Methyl*cyclo*butanol at 370—375° and at 410—420° gave mainly isoprene and β-methyl-Δ^{β}-butene, together with cymene and a rubber-like residue. There was a complete analogy in behaviour and proportions of products obtained with the preceding case.

*cyclo*Butylcarbinol at 415—430° gave mainly *cyclo*pentene, b. p. 43—44°/751 mm., d_4^{19} 0·7776, n^{19} 1·4287. No open-chain compounds or polymerides were formed.

By grouping the alcohols according to homologous series, it is found that the dehydration products are also in series. Water is often eliminated in the 1 : 3 positions ("abnormal"), and may be followed by migration of a hydrogen atom.

The energy relations discussed in the previous papers hold good. All the reactions are shown to be in accordance with the principle that the final product has the smaller energy content. M. ZVEGINTZOV.

Condensations of chloral and bromal with phenolic ethers in presence of anhydrous aluminium chloride. E. E. HARRIS and G. B. FRANKFORTER (J. Amer. Chem. Soc., 1926, 48, 3144—3150).—The following compounds were prepared by condensing chloral, bromal, dibromoacetaldehyde, bromoacetal, and chloral alcoholate with the appropriate aromatic derivatives, in carbon disulphide solution in presence of aluminium chloride at 0° (cf. Frankforter and Kritchevsky, A., 1914, i, 1059): ββββ-trichloro-αα-diphenylethane, m. p. 64°; ββββ-trichloro-αα-ditolylethane, m. p. 89°; ββββ-trichloro-αα-dianisylethane; ββββ-trichloro-αα-diphenetylethane, m. p. 105·5°; ββββ-*trichloro-αα-di*-(6-*methoxy*-m-*tolyl*)*ethane*, m. p. 159°; ββββ-*trichloro-αα-di*-(6-*ethoxy*-m-*tolyl*)*ethane*, m. p. 128°; ββββ-tribromo-αα-diphenylethane, m. p. 76°; ββββ-*tribromo-αα-ditolylethane*, m. p. 104°; ββββ-*tribromo-αα-dianisylethane*, m. p. 115°; ββββ-tribromo-αα-diphenetylethane, m. p. 118°; ββββ-*tribromo-αα-di*-(6-*methoxy*-m-*tolyl*)*ethane*, m. p. 192°; ββββ-*tribromo-αα-di*-(6-*ethoxy*-m-*tolyl*)-*ethane*, m. p. 171°; ββ-*dibromo-αα-dianisylethane*, m. p. 122°; ββ-*dibromo-αα-diphenetylethane*, m. p. 104°; ββ-*dibromo-αα-di*-(6-*methoxy*-m-*tolyl*)*ethane*, m. p. 152°; ββ-*dibromo-αα-di*-(6-*ethoxy*-m-*tolyl*)-*ethane*, m. p. 131°; β-*bromo-αα-dianisylethane*, liquid; and β-*bromo-αα-diphenetylethane*, liquid. The following ethylene derivatives were obtained by treating the above compounds with alcoholic potassium hydroxide: ββ-dichloro-αα-diphenyl-, m. p. 80°; ββ-dichloro-αα-ditolyl-, m. p. 85°; ββ-dichloro-αα-dianisyl-, m. p. 109°; ββ-dichloro-αα-diphenetyl-, m. p. 105°; ββ-*dibromo-αα-diphenyl*-, m. p. 84°; ββ-*dibromo-αα-ditolyl*-, m. p. 118°; ββ-*dibromo-αα-dianisyl*-, m. p. 91°; ββ-*dibromo-αα-diphenetyl*-; β-*bromo-αα-dianisyl*-, m. p. 85°; β-*bromo-αα-diphenetyl*-, m. p. 64°; β-*bromo-αα-di*-(6-*methoxy*-m-*tolyl*)-, m. p. 105°; αα-dianisyl-, m. p. 142°; and *αα-diphenetylethylene*, m. p. 138°. When heated on the steam-bath with sodium ethoxide, the trihalogenodiphenylethanes and the corresponding ditolyl derivatives are converted into diphenylacetic acid and ditolylacetic acid, respectively. The nucleus-substituted trihalogenodiphenylethanes, di- and mono-halogenoethylenes yield, when heated with sodium ethoxide in a sealed tube at 180—200°, the corresponding tolanes; *diethoxytolane*, m. p. 160°, is described. Metallic sodium in boiling benzene converts the trihalogenoethanes into symmetrically substituted stilbenes, and the dihalogenoethylenes into tolanes. When boiled with silver oxide in aqueous suspension, the tribromoethanes are oxidised to substituted benzoic acids, whilst oxidation of the trihalogenoethanes with chromic acid in glacial acetic acid affords substituted benzophenones. F. G. WILLSON.

Arylsulphonyl chlorides. E. GEBAUER-FULNEGG and F. RIESENFELD (Monatsh., 1926, 47, 185—206).—When benzenesulphonyl chloride is treated with sodium iodide in acetone solution (cf. Finkelstein, A., 1910, i, 453), the main products are αα′-diphenyldisulphone and sodium benzenesulphinate, iodine being liberated. A little benzenesulphonyl iodide is also formed. Similar results are obtained in liquid sulphur dioxide solution. When zinc-dust is added to the reaction mixture, benzenesulphinic acid is obtained in 70% yield, with some benzenesulphonic acid. From benzenesulphonyl chloride and pyridine in ether, $C_5H_5N,Ph{\cdot}SO_2Cl$, m. p. 110—112° (Schwartz and Dehn, *ibid.*, 1918, i, 61), is formed, but the compound $(C_5H_5N)_2Ph{\cdot}SO_2Cl$ could not be obtained. In the absence of a solvent, however, owing to the instability of solutions of the additive compound towards moisture, only pyridinium benzenesulphonate, m. p. 132—133°, can be isolated; this is also formed when a solution of benzenesulphonyl chloride in pyridine is electrolysed or treated with sodium iodide. Similarly, when *o*- and *p*-toluenesulphonyl chlorides and *p*-chlorobenzenesulphonyl chloride are heated with pyridine, the corresponding pyridinium salts, m. p. 121—123°, 115—120°, and 137—140°, respectively, are produced, whilst naphthalene-1 : 5-disulphonyl chloride gives *dipyridinium naphthalene*-1 : 5-*disulphonate*, m. p. 245°, at the ordinary temperature. Quinoline and benzenesulphonyl chloride give *quinolinium benzenesulphonate*, m. p. 126—127°. There is no indication of the formation of free arylsulphonyl radicals in any of the above experiments. An equimolecular mixture of benzenesulphonyl chloride and pyridine affords, on treatment with 0·5—2·0 mols. of potassium hydroxide solution, an intense reddish-violet colour. Homologues of pyridine give a pomegranate-red; other cyclic bases give no coloration. Other sulphonyl chlorides may be used, the colour being discharged by light and oxidising agents in the cold, and by acids on heating. This test is the most delicate colour reaction of pyridine known; it is given by 10 c.c. of 0·01% aqueous pyridine or of a 0·002% solution in 5% alcohol. H. E. F. NOTTON.

Space formula of diphenyl. E. E. TURNER and R. J. W. LE FEVRE (Chem. and Ind., 1926, 831—833).—The literature is reviewed, and a new theory is put forward to explain the existence of optical activity among derivatives of diphenyl.

Photochemical reactions in the o-nitrotriphenylmethane series. I. TANASESCU (Bull. Soc. chim., 1926, 39, [iv], 1718—1724).—2 : 4-Dinitrotriphenylmethane on insolation behaves similarly to *o*-nitrotriphenylmethane (A., 1926, 1247), affording in neutral solution the red *o*-quinone derivative and in pyridine the green nitrosocarbinol. Since 2-nitro- and 2 : 4-dinitro-4′ : 4″-diaminotriphenylmethane on insolation in benzene are rapidly isomerised to the corresponding (colourless) nitroso-carbinols, the stability of hexanitrotriphenylmethane under similar conditions is attributed to the electronegative character of the substituent groups, and not to the accumulation of nitro-groups *ortho* to the methine carbon atom. 2 : 4-Dinitrobenzylidene chloride with benzene and aluminium chloride affords 2 : 4-*dinitrotriphenylmethane*, m. p. 93—94°. 2-*Nitro*-4′ : 4″-*diaminotriphenylmethane*, m. p. 64°, and 2 : 4-*dinitro*-4′ : 4″-*diaminotriphenylmethane*, m. p. 132°, are obtained by the condensation of aniline with the nitrobenzalde-

hyde in chloroform solution in the presence of sulphuric acid. *2-Nitroso-4′ : 4″-diaminotriphenylcarbinol*, colourless, has m. p. 151°, and *4-nitro-2-nitroso-4′ : 4″-diaminotriphenylcarbinol*, m. p. 227°.

R. BRIGHTMAN.

Coloured hydrocarbons. I. A. A. VANSCHEIDT (J. Russ. Phys. Chem. Soc., 1926, **58**, 39—54).—A *resume* of the work of Thiele, Graebe, Kauffmann, and Staudinger on the preparation and properties of coloured hydrocarbons of the diphenylene-ethene type, and a discussion of the possibilities of its extension. Substances of the type $\begin{matrix}\text{Ar}\\|\\\text{Ar}\end{matrix}\!\!>\!\text{CH}\cdot\text{CH}\!<\!\!\begin{matrix}\text{Ar}\\|\\\text{A}\end{matrix}$, if symmetrical, can be easily synthesised by the action of metals on halogen derivatives of the fluorenes; if unsymmetrical, by the action of alcoholic potassium hydroxide on a mixture of the appropriate fluorene and halogen derivative in acetone. The resulting hydrogenated derivatives are colourless, crystalline compounds, easily oxidised in pyridine by silver oxide on gentle warming, or by air and alcoholic potassium hydroxide in the cold to the coloured hydrocarbons. Their properties, behaviour, and relation to the colourless hydrogenated derivatives, "hydrobifulvenes," are closely analogous to those of dyes of the indigo series and their leuco-bases.

M. ZVEGINTZOV.

Coloured hydrocarbons. III. Synthesis of naphthalene derivatives of bifluorenyl. A. A. VANSCHEIDT (J. Russ. Phys. Chem. Soc., 1926, **58**, 69—83; cf. preceding abstract).—*Bis-chrysofluorenyl*, $\begin{matrix}\text{C}_6\text{H}_4\\|\\\text{C}_{10}\text{H}_6\end{matrix}\!\!>\!\text{CH}\cdot\text{CH}\!<\!\!\begin{matrix}\text{C}_6\text{H}_4\\|\\\text{C}_{10}\text{H}_6\end{matrix}$, m. p. 221°, and *bisdi-α-naphthofluorenyl*, $\begin{matrix}\text{C}_{10}\text{H}_6\\|\\\text{C}_{10}\text{H}_6\end{matrix}\!\!>\!\text{CH}\cdot\text{CH}\!<\!\!\begin{matrix}\text{C}_{10}\text{H}_6\\|\\\text{C}_{10}\text{H}_6\end{matrix}$, m. p. 353—355° (obtained by boiling an acetone solution of the bromide with copper powder), are described. Both symmetrical and unsymmetrical hydrocarbons are synthesised by the action of alcoholic potassium hydroxide on a mixture of the fluorene and its halide in acetone. *Bisdi-α-naphthofluorenyl*, m. p. 353°, *fluorenyldi-α-naphthofluorenyl*, m. p. 270°, and *chrysofluorenyldi-α-naphthofluorenyl*, m. p. 267°, are thus prepared. All three on oxidation with lead oxide give vividly-coloured substances. Chrysofluorene and fluorenyl chloride are not condensed by alcoholic potassium hydroxide in acetone. When the fluorenes are treated with alcoholic potassium hydroxide, colours are developed, probably due to the formation of alkali metal complexes with the active methylene group, which then react with the halogen derivatives to give the hydrocarbons.

M. ZVEGINTZOV.

Alkylanthracenes and "transannular tautomerism." II. E. DE B. BARNETT, J. W. COOK, and M. A. MATTHEWS (Ber., 1926, **59**, [*B*], 2863—2877; cf. A., 1926, 1030).—1 : 5-Dichloroanthrone is converted by magnesium methyl iodide into 1 : 5-*dichloro-9-hydroxy-9-methyl-9* : 10-*dihydroanthracene*, m. p. 115—116°, which is readily transformed by mineral acid in the presence of glacial acetic acid into 1 : 5-*dichloro-9-methylanthracene*, m. p. 115°. 1 : 5-*Dichloro-9-hydroxy-9-ethyl-9* : 10-*dihydroanthracene*, m. p. 120°, and 1 : 5-*dichloro-9-ethylanthracene*, m. p. 108°, are similarly prepared. The action of magnesium *n*- or *iso*-propyl, *n*-butyl, or *iso*amyl bromide on 1 : 5-dichloroanthrone gives either unchanged initial material or 1 : 5-dichloroanthracene; bromination of a viscous oil obtained by the aid of magnesium *iso*propyl bromide affords a *compound*, $\text{C}_{17}\text{H}_{13}\text{Cl}_2\text{Br}_3$, m. p. 184°. 1 : 5-Dichloro-9-methylanthracene is converted by bromine (1 mol.) into 1 : 5-*dichloro-9-bromomethylanthracene*, m. p. 180—184° (or, possibly, a mixture of this substance with 1 : 5-dichloro-10-bromo-9-methylene-9 : 10-dihydroanthracene), which is also obtained by the action of hydrogen bromide on a solution of 1 : 5-dichloro-9-hydroxymethylanthracene in boiling benzene. 1 : 5-*Dichloro-9-chloromethylanthracene*, m. p. 149°, is obtained by chlorination of 1 : 5-dichloro-9-methylanthracene suspended in cold carbon tetrachloride or from 1 : 5-dichloro-9-hydroxymethylanthracene and hydrogen chloride; in the latter action, a *compound*, m. p. about 290° (decomp.), probably di-1 : 5-dichloro-9-anthranyl methyl ether, is also produced. 1 : 5-*Dichloro-9-acetoxymethylanthracene*, m. p. 149°, from the bromo-compound, sodium acetate, and acetic acid, is hydrolysed by alcoholic potassium hydroxide to 1 : 5-*dichloro-9-hydroxymethylanthracene*, m. p. 138—139° (*phenylurethane*, m. p. 179°), which is reconverted into the original acetate by acetic anhydride and pyridine and oxidised to 1 : 5 : 1′ : 5′-tetrachlorodianthrone. Direct hydrolysis of 1 : 5-dichloro-9-bromomethylanthracene in boiling aqueous acetone in presence of calcium carbonate yields a *hydroxy*-compound, m. p. 133—134° (*phenylurethane*, m. p. 193°), which when treated with acetic anhydride gives the above acetate, m. p. 149° (after repeated crystallisation of the crude product), and is oxidised to 1 : 5 : 1′ : 5′-tetrachlorodianthrone. The following derivatives of 1 : 5-dichloroanthracene are described: 9-*methoxymethyl*-, m. p. 154°; 9-*ethoxymethyl*-, m. p. 105—106°; 9-*anilinomethyl*-, m. p. 190°; 9-*dimethylaminophenylmethyl*-, m. p. 195°. Treatment of 1 : 5-dichloro-9-bromomethylanthracene with pyridine or of 1 : 5-dichloro-9-methylanthracene with pyridine and bromine affords 1 : 5-*dichloro-9-anthranylmethylpyridinium bromide*, m. p. 250° (decomp.) after darkening (corresponding *picrate*, m. p. 212°). Nitrogen peroxide converts 1 : 5-dichloro-9-methylanthracene into 1 : 5-*dichloro-10-nitro-9-methylanthracene*, m. p. 174°. 1 : 5-Dichloro-9-bromomethylanthracene is transformed by magnesium methyl iodide, magnesium phenyl bromide, or by copper powder in boiling xylene into a *substance*, $\text{C}_{30}\text{H}_{18}\text{Cl}_4$, m. p. 287° (decomp.) [a *by-product*, m. p. 205° (decomp.), is also obtained when the Grignard reagents are used].

1 : 5-Dichloro-9-methylanthracene is converted by an excess of bromine into 1 : 5-*dichloro-9* : 10-*dibromo-9-bromomethyl-9* : 10-*dihydroanthracene*, m. p. 130—132° (decomp.), which is decomposed when heated into 1 : 5-dichloro-9-bromomethylanthracene and 1 : 5-*dichloro-10-bromo-9-bromomethylene-9* : 10-*dihydroanthracene*, m. p. 192° (decomp.); the latter compound is also obtained as by-product of the above bromination, but is most conveniently isolated by slowly distilling a solution of 1 : 5-dichloro-9-methylanthracene in benzene containing an excess of bromine. Hydrolysis

of the tribromo-derivative in aqueous acetone in the presence of calcium carbonate affords two *compounds*, $C_{15}H_{10}OCl_2$ and $C_{15}H_{11}O_2Cl_2Br$, m. p. 191—192° and 179—181°, respectively. 1 : 5-*Dichloro*-9-*bromo*-10-*ethoxy*-9-*ethoxymethyl*-9 : 10-*dihydroanthracene*, m. p. 120—121°, and 1 : 5-*dichloro*-9-*bromo*-10-*anilino*-9-*anilinomethyl*-9 : 10-*dihydroanthracene*, m. p. 160—162°, are described. The tribromo-compound is converted by pyridine into the pyridinium bromide described above. 1 : 5-*Dichloro*-10-*anilino*-9-*bromomethylene*-9 : 10-*dihydroanthracene* has m. p. 140—141°. 1 : 5-Dichloro-10-bromo-9-bromomethylene-9 : 10-dihydroanthracene is converted by copper powder in boiling xylene into the *substance*, $C_{30}H_{16}Cl_4Br_2$, m. p. 309° (decomp.).

1 : 5-Dichloro-9-ethylanthracene is converted by bromine (1 mol.) into 1 : 5-*dichloro*-9-α-*bromoethyl*-*anthracene*, m. p. 135—136° (decomp.), and by the halogen (2 mols.) into 1 : 5-*dichloro*-9 : 10-*dibromo*-9-α-*bromoethyl*-9 : 10-*dihydroanthracene*, m. p. 126—127° (decomp.), which is converted into the monobromo-derivative in boiling toluene. 1 : 5-*Dichloro*-9-α-*acetoxyethylanthracene*, m. p. 156—157°, is described.

H. WREN.

Structure of the benzene nucleus. V. *meso*-Derivatives of anthracene. C. K. INGOLD and P. G. MARSHALL (J.C.S., 1926, 3080—3089).—The reactivity of the *meso*-carbon atoms of anthracene may be due to disturbance of valency round the central ring, or to a dissociable *p*-linking. In the latter case, 9 : 10-diarylanthracenes might show properties similar to those of hexa-arylethanes. This is found to be the case; the colourless compounds form coloured solutions, and colorimetric determinations of the degree of dissociation yield results consistent with a reversible unimolecular reaction. Further, *p*-substituents influence dissociation, and in ionising solvents dissociation is partly ionic. The following have been prepared: 9 : 10-*dianilino*-9 : 10-*diphenyl*-9 : 10-*dihydroanthracene*, m. p. 232—234°; 9 : 10-*diphenyl*-9 : 10-*dihydroanthracene*, m. p. 222—225° (*disodio*- and *dipotassio*-derivatives); 9 : 10-*dihydroxy*-9 : 10-*di*-p-*tolyl*-9 : 10-*dihydroanthracene*, softens at 270°, m. p. 275°; 9 : 10-*di*-p-*tolylanthracene*, m. p. 278—279° (*dipotassio*- and *disodio*-derivatives); 9 : 10-*dihydroxy*-9 : 10-*di*-p-*chlorophenyl*-9 : 10-*dihydroanthracene*, m. p. 267° (decomp.); 9 : 10-*di*-p-*chlorophenylanthracene*, m. p. 306—307·5°; 9 : 10-*di*-p-*chlorophenyl*-9 : 10-*dihydroanthracene* (isomerides, m. p. about 206° and about 165°); 9 : 10-*dihydroxy*-9 : 10-*di*-p-*bromophenyl*-9 : 10-*dihydroanthracene*, m. p. 273—274°; 9 : 10-*di*-p-*bromophenylanthracene*, shrinks at 315°, m. p. 326—327°; 9 : 10-*dihydroxy*-9 : 10-*di*-p-*anisyl*-9 : 10-*dihydroanthracene*, m. p. 258—262°; 9 : 10-*di*-p-*anisylanthracene*, m. p. 282°; 2-*chloro*-9 : 10-*dihydroxy*-9 : 10-*diphenyl*-9 : 10-*dihydroanthracene*, m. p. 220—221°; 2-*chloro*-9 : 10-*diphenylanthracene*, m. p. 193°; 2-*bromo*-9 : 10-*dihydroxy*-9 : 10-*diphenyl*-9 : 10-*dihydroanthracene*, m. p. 206—209°; 2-*bromo*-9 : 10-*diphenylanthracene*, m. p. 185—187°; 9-*hydroxy*-9-*triphenylmethylanthrone*, m. p. 183—190°; 9 : 10-*dichloro*-9 : 10-*di*-p-*bromophenyl*-9 : 10-*dihydroanthracene*, m. p. 218°; and a *substance*, $C_{26}H_{15}Cl_2$, m. p. 294—295°, of the 9 : 10-diarylanthracene type.

B. W. ANDERSON.

Molecular organic compounds. I. Molecular organic compounds of *m*-dinitrobenzene, 2 : 4-dinitrotoluene, and 2 : 4-dinitrophenol. C. A. BUEHLER and A. G. HEAP (J. Amer. Chem. Soc., 1926, **48**, 3168—3172).—The following new molecular compounds have been prepared: *benzidine*–2 : 4-*dinitrotoluene* (1 : 1), black, m. p. 127·6—128°; *benzidine*–2 : 4-*dinitrophenol* (1 : 1),brown, m. p. 143·5—143·8°, or yellow ($1H_2O$), m. p. 134° (decomp.); *naphthalene*–2 : 4-*dinitrophenol* (1 : 1), yellow, m. p. 94·7—95·0° (cf. Hepp, A., 1883, 315); and *aniline*–2 : 4-*dinitrophenol* (1 : 1), yellow, m. p. 76·7—77·3° (cf. Kremann, *ibid.*, 1906, i, 834). The following compounds, previously known to exist in solution, have been isolated: *m*-dinitrobenzene–α-naphthylamine (1 : 1), red, m. p. 65·1—65·7°, and –β-naphthylamine, red, m. p. 53·9—55·7° (cf. Kremann, *loc. cit.*); *m*-dinitrobenzene–naphthalene (1 : 1), greenish-yellow, m. p. 50·7—51·6° (cf. Kremann, A., 1905, ii, 77; Hepp, *loc. cit.*); *m*-dinitrobenzene–benzidine (1 : 1), black, m. p. 127·6—128°; and *m*-dinitrobenzene–aniline (1 : 1), red, m. p. 38·3—39·3° (cf. Kremann, *loc. cit.*); 2 : 4-dinitrotoluene–α-naphthylamine (1 : 1), orange-red, m. p. 62·9—63·7°; 2 : 4-dinitrotoluene–naphthalene (1 : 1), colourless, m. p. 60·1—60·9° (cf. Kremann, *loc. cit.*); 2 : 4-dinitrophenol–α-naphthylamine (1 : 1), red, m. p. 107·3—107·7°, and –β-naphthylamine (1 : 1), reddish-orange, m. p. 77·6—77·9°; 2 : 4-dinitrophenol–naphthalene (1 : 1), m. p. 94·7—95 0° (cf. Hepp, *loc. cit*).; 2 : 4-dinitrophenol–aniline (1 : 1), yellow, m. p. 76·7—77·3° (cf. Kremann, A., 1906, i, 834); 2 : 4-dinitrophenol–*o*-phenylenediamine (1 : 1), yellow, m. p. 93·6—94·0°, and –*m*-phenylenediamine (1 : 1), orange-yellow, m. p. 107·9—108·2° (cf. Kremann, *ibid.*, 1921, i, 601).

F. G. WILLSON.

Interaction of thiocarbonyl chloride and chloro-substituted anilines and the inhibitory action of *ortho*-substituents. G. M. DYSON, H. J. GEORGE, and R. F. HUNTER (J.C.S., 1926, 3041—3044).—The reaction between thiocarbonyl chloride and chloro-substituted anilines is found to be inhibited when one chlorine atom is *ortho* to the amino-group, and does not take place if there are two. The following new thiocarbimides are described: 2 : 3-*dichlorophenylthiocarbimide*, b. p. 256—258°/760; 3 : 4 : 5-*trichlorophenylthiocarbimide*, b. p. 280° (decomp.); 3 : 4 : 6-*trichlorophenylthiocarbimide*, b. p. 280°. Treatment of the thiocarbimides with warm alcoholic ammonia yields the thiocarbamides, 2 : 3-*dichlorophenylthiocarbamide*, m. p. 148°; 3 : 4 : 6-*trichlorophenylthiocarbamide*, m. p. 162°: treatment with a chloroaniline yields a substituted diphenylthiocarbamide; *s-di*-2 : 3-*dichlorophenylthiocarbamide*, m. p. 140°; *s-di*-3 : 4 : 5-*trichlorophenylthiocarbamide*, m. p. 140°.

Improved methods of preparation of 2 : 6- and 3 : 5-dichloroanilines, 3 : 4 : 5- and 3 : 4 : 6-trichloroanilines, and 2 : 3 : 5 : 6-tetrachloroaniline are given.

H. BURTON.

Decomposition of substituted carbamyl chlorides by hydroxy-compounds. III. Influence of substituent groups. T. W. PRICE (J.C.S., 1926, 3230—3233).—The rate of decom-

position by ethyl alcohol at 100° has been studied of the following substituted carbamyl chlorides, prepared by the action of carbonyl chloride on the requisite secondary amine; phenylmethyl-, phenylethyl-, *phenyl*-n-*propyl*-, m. p. 45·5°; *phenyl*iso*propyl*-, m. p. 90—90·5°; *phenyl*-n-*butyl*-, b. p. 165—166°/20 mm.; *phenyl*iso*butyl*-, b. p. 149—151°/19 mm.; *phenyl*iso*amyl*-, b. p. 153—153·5°/10 mm.; phenylbenzyl-, diphenyl-, and o-*tolylethyl-carbamyl chloride*, m. p. 36·5—37°. The mean velocity coefficients of the reaction are, for the phenylalkyl compounds: ethyl, 0·0631; *n*-butyl, 0·0545; *n*-propyl, 0·0527; methyl, 0·0427; *iso*propyl, 0·215; *iso*amyl, 0·0414; *iso*butyl, 0·0295. The replacement of the methyl group in phenylmethylcarbamyl chloride by phenyl or benzyl decreases the reactivity. H. Burton.

Diphenyl series. IV. Halogenation of 4-aminodiphenyl. J. Kenyon and P. H. Robinson (J.C.S., 1926, 3050—3054).—4-Acetamidodiphenyl on bromination in acetic acid solution yields 3-*bromo*-4-*acetamidodiphenyl* (50%), m. p. 161°, together with 4′-bromo-4-acetamidodiphenyl (30%) (cf. Scarborough and Waters, A., 1926, 512). Hydrolysis of the former compound gives 3-*bromo*-4-*aminodiphenyl*, m. p. 66°, which on bromination furnishes 3 : 5-dibromo-4-aminodiphenyl [*acetyl* derivative, m. p. 212° (Scarborough and Waters, *loc. cit.*, give m. p. 162°); *diacetyl* derivative, m. p. 184°]. 4-Dimethylaminodiphenyl on bromination yields (3 ?)-*bromo*-4-*dimethylaminodiphenyl*, m. p. 82°, whilst 4′-nitro-4-aminodiphenyl furnishes (3 : 5 ?)-*dibromo*-4′-*nitro*-4-*aminodiphenyl*, m. p. 184° (*diacetyl* derivative, m. p. 228°). Nitration of 3 : 5-dibromo-4-acetamidodiphenyl gives a *dinitro*-derivative, m. p. 269—270° (*diacetyl* compound, m. p. 140°). Treatment of 4-aminodiphenyl with *N*-bromoacetanilide, followed by hydrolysis, gives 3-bromo-4-aminodiphenyl. Chlorination of 4′-chloro-4-acetamidodiphenyl with sodium hypochlorite gives 4′ : N-*dichloro*-4-*acetamidodiphenyl*, m. p. 128°, which is decomposed by warm acetic acid to 3 : 4′-*dichloro*-4-*acetamidodiphenyl*, m. p. 184°, a small quantity of which was obtained by the action of hot acetic acid on the unstable 3 : *N*-dichloro-4-acetamidodiphenyl. Chlorination of 3 : 4′-dichloro-4-acetamidodiphenyl gives 3 : 5 : 4′-trichloro-4-acetamidodiphenyl. H. Burton.

Reactions of nitroxyl with aromatic nitro-derivatives and with azoxy-compounds. D. Bigiavi (Atti R. Accad. Lincei, 1926, [vi], 4, 457—459).—Arylnitrosohydroxylamines (cf. Angeli, A., 1900, i, 221) may be obtained by the action on nitro-derivatives of nitroxyl, prepared, together with nitrous acid, when the sodium salt of nitrohydroxylamine, N(ONa):NO·Na, is gently heated in solution. In this reaction the sodium salt of the nitroxyl is first oxidised to sodium nitrite by the nitro-compound, which is transformed into the nitroso-compound, this reacting immediately with the nitroxyl to form the nitrosoarylhydroxylamine. The reaction has been used to prepare m-*nitrophenylnitrosohydroxylamine*, $NO_2 \cdot C_6H_4 \cdot NO{:}N \cdot OH$, m. p. 75—76° (decomp.), from *m*-dinitrobenzene; p-*nitrophenylnitrosohydroxylamine*, m. p. 73—75° (decomp.); and p-*phenylenebisnitroso-hydroxylamine*, $C_6H_4(\cdot NO{:}N \cdot OH)_2$, blackening, without melting at 90°; the last compound is probably polymerised.

Azoxy-compounds react similarly to the nitro-derivatives with nitroxyl, azoxybenzene yielding azobenzene and a sodium salt apparently of the form NPh:NPh.NONa. *pp′*-Dinitroazoxybenzene and *p*-nitroazoxybenzene give, together with other products, respectively *pp′*-dinitroazobenzene and *p*-nitroazobenzene. T. H. Pope.

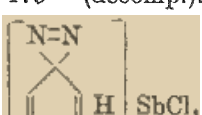
o-Chloro- and o-bromo-benzeneazonaphthylhydrazinesulphonic acids. J. Tröger and H. Bertram (J. pr. Chem., 1926, [ii], 114, 269—286).—*o*-Chlorobenzenediazonium chloride couples with α-naphthylamine at 35—40° in presence of sodium acetate, forming yellow 4-o-*chlorobenzeneazo*-α-*naphthylamine*, m. p. 128—129° (*hydrochloride*; *picrate*, decomp. 201°; *perchlorate*; *acetyl* derivative; *benzoyl* derivative, m. p. 193°), which may be diazotised in strong hydrochloric acid solution at 45°, giving 4-o-*chlorobenzeneazonaphthalene*-1-*diazonium chloride*, decomp. 112°. 4-o-*Chlorobenzeneazo*-α-*naphthaleneazo*-m-*phenylenediamine*, decomp. 180°, and 4-o-*chlorobenzeneazo*-α-*naphthaleneazoresorcinol* are described. Brown *sodium* 4-o-*chlorobenzeneazonaphthalene*-α-*diazoniumsulphonate* is reduced by the calculated quantity of stannous chloride to reddish-violet, amorphous 4-o-*chlorobenzeneazo*-α-*naphthylhydrazinesulphonic acid* (*potassium* salt; p-*toluidine* salt, decomp. 161°). Other reducing agents such as ammonium sulphide (cf. A., 1926, 1032) decompose the compound altogether. The hydrazinesulphonic acid readily condenses with aldehydes in presence of hydrogen chloride. In this way, the 4-o-*chlorobenzeneazo*-α-*naphthylhydrazones* of *p*-anisaldehyde, m. p. 170°; cinnamaldehyde, m. p. 182°; salicylaldehyde, m. p. 186°; *p*-hydroxybenzaldehyde, m. p. 134°, and *m*-methoxybenzaldehyde, m. p. 142°, are prepared. 4-*o*-Bromobenzeneazo-α-naphthylamine [*hydrochloride*; *sulphate*; *perchlorate*, m. p. 201° (decomp.); *picrate*, m. p. 198° (decomp.); *acetyl* derivative, m. p. 229°; *benzoyl* derivative, m. p. 196°] is successively converted into 4-*o*-bromobenzeneazonaphthalene-α-diazonium chloride (*loc. cit.*), from which 4-o-*bromobenzeneazo*-α-*naphthaleneazo*-β-*naphthol*, m. p. 217—218°, and 4-o-*bromobenzeneazo*-α-*naphthaleneazoresorcinol*, decomp. 181°, are prepared; *potassium* 4-o-*bromobenzeneazonaphthalene*-α-*diazoniumsulphonate*, 4-o-*bromobenzeneazo*-α-*naphthylhydrazinesulphonic acid* (*potassium* and p-*toluidine*, m. p. 152°, salts), and the 4-o-*bromobenzeneazo*-α-*naphthylhydrazones* of *p*-anisaldehyde, m. p. 164°, *p*-tolualdehyde, m. p. 185°, and cinnamaldehyde, m. p. 176°, are described. The above hydrazinesulphonic acids are more unstable than any previously described. Attempts to prepare the bromo-acid by the method of Tröger and Schafer (*loc. cit.*) from 4-*o*-bromobenzeneazonaphthalene-1-diazonium chloride and sulphur dioxide were unsuccessful, the products being the corresponding diazosulphonic acid and a *sulphone*, $(BrC_6H_4 \cdot N_2 \cdot C_{10}H_6)_2SO_2$. H. E. F. Notton.

Constitution of the azo-dyes. J. S. P. Blumberger (Chem. Weekblad, 1927, 24, 2—12, 42—50).—A critical survey of our present knowledge of the

constitution of the hydroxyazo-dyes, indicating that present conceptions of valency render many differences of opinion meaningless (cf. this vol., 55). S. I. Levy.

***as-p*-Nitrophenylethylhydrazine.** G. Barattini (Gazzetta, 1926, **56**, 821—825; cf. A., 1924, i, 578).—This compound forms a yellow *benzoyl* derivative, m. p. 147°; an *acetyl* derivative, m. p. 144°; a *hydrochloride*, m. p. 212°, and a *picrate*, m. p. 125°. The hydrazones formed with aldehydes and ketones give no coloration with alcoholic potassium hydroxide, the migration of the secondary hydrazinic hydrogen atom to the nitro-group and consequent formation of a quinononitronic complex salt, $NO_2K{:}C_6H_4{:}N{\cdot}N{:}CHR$, which occurs with *p*-nitrophenylhydrazones, being impossible in this case. The formaldehyde compound is obtained in a 1 : 5000 solution of the aldehyde. The as-p-*nitrophenylethylhydrazones* prepared were: formaldehyde, yellow, m. p. 100°; acetaldehyde, pale yellow, m. p. 94°; *o*-nitrobenzaldehyde, orange, m. p. 157°; *m*-nitrobenzaldehyde, pale yellow, m. p. 262°; *p*-dimethylaminobenzaldehyde, bright red, m. p. 187°; cinnamaldehyde, pale yellow, m. p. 160°; salicylaldehyde, pale yellow, m. p. 175°; anisaldehyde, yellow, m. p. 162°; vanillin, orange-yellow, m. p. 153°; piperonal, pink, m. p. 152°; furfuraldehyde, orange, m. p. 150°. T. H. Pope.

Action of antimony trichloride on diazotised diamines. [Determination of antimony in organic compounds.] W. H. Gray (J.C.S., 1926, 3174—3182).—Diazotised acetyl-*m*-phenylenediamine and acetyl-*p*-phenylenediamine, when treated with antimony trichloride, form the additive compounds *di*-(m-*acetamidobenzenediazonium chloride*)*antimony trichloride*, m. p. 94°, and *di*-(p-*acetamidobenzenediazonium chloride*)*antimony trichloride*, m p. 147°. The additive compound from the *m*-diamine is decomposed when warmed with dilute acid. Decomposition with cold water followed by treatment with chromic acid gives m-*acetamidobenzenediazonium chromate* (explodes violently on warming or on treatment with ammonia). The additive compound from the *p*-diamine gives p-*acetamidobenzenediazonium chloride*, m. p. 131°, when decomposed by water, whilst boiling dilute hydrochloric acid converts it into *p-diazoiminobenzene hydrochloride-antimony trichloride*, (I), m. p. 179° (decomp.). This substance is decomposed by water, giving p-*diazoiminobenzene hydrochloride*, explodes at 155° (*picrate*, explodes at 160°; *chromate*, explodes at 160°). Acetic anhydride in bright sunlight converts *p*-diazoiminobenzene hydrochloride into *p*-acetamidobenzenediazonium chloride, whilst acetic anhydride and sulphuric acid convert it into a neutral *compound*, $C_{10}H_{13}O_5N_3S$, which when treated with chromic acid or picric acid yields p-*acetamidobenzenediazonium chromate*, m. p. 136° (decomp.), or p-*acetamidobenzenediazonium picrate*, m. p. 146·5° (decomp.).



(I.)

The method for the determination of antimony in organic compounds (see A., 1922, i, 404) has been modified by using oxalic acid to remove manganese oxides and carbamide to remove nitrous acid. To determine chlorine in presence of antimony, 0·2 g. of substance is mixed with potassium permanganate (1 g.), a little water, and concentrated sulphuric acid. The liberated chlorine is absorbed in potassium iodide solution. A small correction has to be applied. H. Burton.

Nuclear condensation of phenols and phenolic ethers with nitriles to ketimines and ketones of phenols and phenolic ethers. J. Houben [with G. Blaese] (Ber., 1926, **59**, [*B*], 2878—2891).—In the action of hydrogen chloride and nitriles on phenols the change may affect the hydroxyl group or the *para*-hydrogen atom. These changes are opposed to one another in such a manner that reaction with the hydroxyl hinders the entry of the radical into the nucleus, and nuclear substitution hampers the reactivity of the hydroxyl group. Gattermann's synthesis of hydroxyaldehydes and its extension to higher nitriles appears to depend directly on nuclear substitution. Although phenolic ethers react much more smoothly than phenols in Gattermann's synthesis, this does not necessarily appear to be the case when hydrocyanic acid is replaced by other nitriles and the use of zinc or aluminium chloride is omitted.

Phenol is converted by acetonitrile and hydrogen chloride into *acetiminophenyl ether hydrochloride*, $OPh{\cdot}CMe{:}NH,HCl$, m. p. 160° (decomp.) after change at 145°. *Chloroacetiminophenyl ether hydrochloride*, decomp. 110° after softening at 95—100°, the corresponding *dichloro*-compound, decomp. 80—90°, and the *trichloro*-compound are described. *Benziminophenyl ether hydrochloride*, m. p. 180° (decomp.), *phenylacetiminophenyl ether hydrochloride*, m. p. 155° (decomp.), *acetimino-β-naphthyl ether hydrochloride*, decomp. 200°, and *chloroacetimino-β-naphthyl ether hydrochloride* are analogously prepared (*β-naphthyl chloroacetate*, m. p. 97°, is described incidentally). The arylimino-ether hydrochlorides are exceedingly unstable, so that the free ethers have not been isolated. In acid solution, the hydrochlorides are converted into ammonium chloride and aryl ester or its hydrolytic products, whilst in alkaline solution phenol and nitrile or acylamide are produced. Resorcinol, acetonitrile, and hydrogen chloride in the absence of other condensing agent afford *resacetophenoneimine hydrochloride*, m. p. 228° (decomp.), which is easily converted into the free *imine*, decomp. 239° after blackening at 100°, converted by hydroxylamine hydrochloride into resacetophenoneoxime, m. p. 369°. *Diresacetophenoneimine sulphate* is described. α-Naphthol is converted by acetonitrile and hydrogen chloride into a mixture of *acetimino-α-naphthyl ether hydrochloride*, decomp. above 200°, and 4-*hydroxynaphthyl methyl ketimine hydrochloride*, m. p. 251° (decomp.), converted by boiling water into 4-hydroxynaphthyl methyl ketone, m. p. 198°. Attempts to effect the reciprocal conversion of imino-ether into ketimine were unsuccessful. 4-*Hydroxynaphthyl chloromethyl ketone*, m. p. 185°, and 4-*hydroxynaphthyl chloromethyl ketimine hydrochloride* are described. α-Naphthyl methyl ether is not attacked by chloroacetonitrile. H. Wren.

Nitration by means of a mixture of nitrosulphuric and fuming nitric acids. I. J. Rinkes (Rec. trav. chim., 1926, **45**, 845—848).—Nitration of

o-nitrophenol with a mixture of nitrosulphuric and nitric acids under the conditions used by Varma and Kulkarni (A., 1925, i, 238) yields a mixture of 2 : 4- and 2 : 6-dinitrophenols (separated by the difference in solubility of their barium salts), and not 2 : 5-dinitrophenol, as stated by these authors. Further nitration yields only picric acid, and not 2 : 4 : 5-trinitrophenol, whilst nitration of hydroxytoluic acid yields mainly 6-nitro-3-hydroxy-*p*-toluic acid, identical with that obtained by Borsche and Berkhout (*ibid.*, 1904, i, 415; the compound is wrongly called in the abstract 6-nitro-3-hydroxycresotic acid), together with a small quantity of 4-nitro-*m*-cresol, m. p. 56°, which is also formed when the nitration conditions of the last-mentioned authors are employed. J. W. BAKER.

Influence of substitution in the nucleus on the stability and reactivity of aromatic compounds. K. VON AUWERS and P. BULLMANN (Ber., 1926, 59, [*B*], 2719—2737).—Further examples are cited in favour of the hypothesis that tenacity of organic residues cannot be considered as the sole measure of affinity demand (cf. A., 1924, i, 1055). 2 : 5-Dibromo-4-hydroxy-3 : 6-dimethylbenzyl bromide is converted by potassium hydrogen sulphide into the corresponding benzyl sulphide, m. p. 245—246°; isolation of the thiol appears impossible, although the corresponding alcohol is a stable substance and the thiol of the 4-ethoxy-compound can be prepared. 2 : 5-Dibromo-4-hydroxy-3 : 6-dimethylbenzyl acetate yields the ether of the alcohol under the influence of hydrogen fluoride.

The stability of the condensation products of 2 : 5-dibromo-4-hydroxy-3 : 6-dimethylbenzyl bromide and aromatic amines towards boiling 5% aqueous sodium hydroxide has been examined, reaction proceeding mainly according to the equation $2OH\cdot C_6Me_2Br_2\cdot CH_2\cdot NHR+H_2O=(OH\cdot C_6Me_2Br_2)_2CH_2+CH_2O+2R\cdot NH_2$, but frequently giving also 2 : 5-dibromo-4-hydroxy-3 : 6-dimethylbenzyl alcohol. The presence of a methyl group in the *ortho* or *para* position of the amine nucleus decreases the stability of the compound, whereas the contrary effect is exercised by the group in the *meta* position. The methoxy-group resembles the methyl group. A formulation of the distribution of valency in the derivatives of the three toluidines is put forward with reserve.

2 : 5-Dibromo-4-hydroxy-3 : 6-dimethylbenzyl bromide reacts readily with aromatic amines, giving mainly nuclear benzyl derivatives; simultaneously, di-2 : 5-dibromo-4-hydroxy-3 : 6-dimethylphenylmethane and the polymerised 2 : 5-dibromo-3 : 6-dimethyl-4-methylenebenzoquinone, $O{:}C_6Br_2Me_2{:}CH_2$, are frequently obtained. Explanation of this reaction, which has been investigated with many amines, is difficult, since the mechanism of the change is unknown. All ring-methylated dialkylanilines condense readily with the benzyl bromide. The nature of the radical attached to the nitrogen atom appears unimportant. Methoxy-, hydroxy-, and amino-groups in the amine do not hinder normal condensation, whereas this appears to be generally hindered by the presence of chloro-, bromo-, aldehydic, or carboxymethyl substituents, except in certain cases. With substituted pyrazoles, condensation occurs, but not with indazole. The position of the substituents has the same effect on the condensation of amines with the benzyl bromide as on the coupling with diazonium compounds or the formation of nitroso-derivatives, whereas the nature of the substituent has a different effect in the various processes.

The following condensation *products* are obtained from 2 : 5-dibromo-4-hydroxy-3 : 6-dimethylbenzyl bromide: with *o*-anisidine, m. p. 161—162°, *p*-anisidine, m. p. 141—142°, 6-chloro-*o*-toluidine, m. p. 191·5—192·5°, and from the tertiary amines, methylethylaniline (as *hydrobromide*, m. p. 140°), diallylaniline (as *picrate*, m. p. 182°), dimethyl-*o*-toluidine (as *hydrochloride*), dimethyl-*m*-toluidine, m. p. 144°, dimethyl-*p*-toluidine, m. p. 149—151·5°, dimethyl-*o*-anisidine, m. p. 120—121°, dimethyl-*as*-*m*-xylidine, dimethyl-*p*-xylidine, m. p. 147°, dimethyl-*as*-*o*-xylidine, m. p. 144—145°, dimethyl-*s*-*m*-xylidine (as *hydrochloride*, m. p. 207—209°), dimethyl-α-naphthylamine, m. p. 173°, diethyl-α-naphthylamine (as *hydrochloride*, m. p. 225°), *m*-bromodimethylaniline, m. p. 136—137°, *m*-hydroxydimethylaniline, m. p. 154·5—155°, and *m*-aminodimethylaniline. 3-Methylpyrazole yields two 2 : 5-dibromo-4-hydroxy-3 : 6-dimethylbenzyl *derivatives*, m. p. 183° and 206°, respectively. The corresponding 3 : 5-*dimethyl*- (m. p. 248—249°), 5 : 3-*phenylmethyl*- (m. p. 181—183°), and 3 : 5-*diphenyl-pyrazole* (m. p. 165—167°) compounds are described. p-*Nitrobenzeneazo*-N-*dimethyl*-m-*toluidine*, m. p. 179·5—180·5°, p-*nitrobenzeneazo*-N-*dimethyl*-o-*anisidine*, m. p. 132—133°, *benzeneazo*-m-*bromo*-N-*dimethylaniline*, m. p. 92—93°, and m-*bromo*-p-*nitrosodimethylaniline hydrochloride*, m. p. 163° (decomp.), have been prepared. H. WREN.

Amidines of the holocaine type. II. Ester-substituted amidines. A. J. HILL and M. V. COX (J. Amer. Chem. Soc., 1926, 48, 3214—3219; cf. A., 1926, 516).—Substituted amidines of the types $CR(:N\cdot C_6H_3\cdot OEt)(NH\cdot C_6H_4\cdot CO_2Et)$ and $CR(:N\cdot C_6H_4\cdot CO_2Et)(NH\cdot C_6H_4\cdot CO_2Et)$ are obtained in good yields by treating an appropriate acylamino-derivative with phosphorus pentachloride in benzene in the cold, and treating the resulting chloride with an amine. The product is best isolated by evaporating off the benzene, dissolving the residue in just sufficient alcohol, and precipitating the amidine with excess of concentrated ammonia. An analogous method gave 70—95% yields of holocaine and its ethyl, propyl, and *iso*butyl homologues. Substituted *amidines* were prepared from ethyl *p*-aminobenzoate and the following acylamines: acetyl-*p*-phenetidine (m. p. 142°; *hydrochloride*, m. p. 182—183°); propionyl-*p*-phenetidine (m. p. 146°; *hydrochloride*, m. p. 147—148°); butyryl-*p*-phenetidine (m. p. 97°); *iso*valeryl-*p*-phenetidine (m. p. 106°); *n*-valeryl-*p*-phenetidine (m. p. 91°), and benzoyl-*p*-phenetidine (m. p. 117; *hydrochloride*, m. p. 220°); from ethyl aminosalicylate and acetyl-*p*-phenetidine (m. p. 103°; *hydrochloride*, m. p. 152°); and from ethyl *p*-aminobenzoate and ethyl *p*-acetamidobenzoate (m. p. 156°; *hydrochloride*, m. p. 214—215°) and ethyl *p*-propionamidobenzoate (m. p. 135°; *hydrochloride*, m. p. 184—185°). *Ethyl* p-*propionamido*-

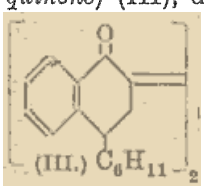
benzoate, m. p. 111°, *ethyl* p-*butyramidobenzoate*, m. p. 87°, and n-*valeryl*-p-*phenetidine*, m. p. 92°, are described. F. G. Willson.

Derivatives of thymol. R. Delaby (Bull. Soc. chim., 1926, [iv], 39, 1612—1618).—Reaction of methylene bromide with the sodium derivative of thymol in alcoholic solution gives a 43% yield of odourless, crystalline dithymoxymethane, m. p. 52° (Arnhold, A., 1887, 911, gives m. p. 36°). A lower yield is obtained using methylene sulphate in alcoholic solution, and a by-product is formed, thymoxyethoxymethane. *αγ-Dithymoxypropane*, obtained in 53% yield by reaction of trimethylene bromide with the sodium derivative of thymol in alcoholic solution, has b. p. 249·5°/21 mm., d^{17} 0·9944; n^{18} 1·5326.

M. Clark.

Homologous naphthols, their oxidation and hydrogenation products. B. Alberti (Annalen, 1926, 450, 304—318).—α-Naphthol and *cyclo*hexanol condense under the influence of zinc chloride to give a resinous product containing 4-cyclo*hexyl*-α-*naphthol* (I), m. p. 142—143°, b. p. 228°/14·5 mm., 11% of theoretical, and 2-cyclo*hexyl*-α-*naphthol* (II), m. p. 99—100°, b. p. 218°/14 mm., 15% of theoretical. Concentrated sulphuric acid containing nitrous acid dissolves both to a deep green solution, which becomes colourless on dilution in the case of (I), but red in that of (II). The *sodium* salt of (I) crystallises from dilute alkali; that of (I) is more soluble.

Oxidation of (I) with ferric chloride, ferricyanide, or chromic acid yields "*bis*-4-cyclo*hexylnaphthaleneindigo*" (4 : 4′-*dicyclohexyl*-2 : 2′-*dinaphthyl*-1 : 1′-*quinone*) (III), dark violet crystals with red reflex, m. p. 192°. Similar oxidation, or keeping in the air for several months, gives from (II) "*bis*-2-cyclo*hexylnaphthalenelignone*" (3 : 3′-*dicyclohexyl*-1 : 1′-*dinaphthyl*-4 : 4′-*quinone*), (IV), ruby-red crystals with golden-green reflex, m. p. 199°. Both these substances are reduced only very slowly by hyposulphite; (IV) is reduced by zinc and acetic acid to the corresponding "*dihydrolignone*," m. p. 216—218° (not sharply), which is also obtained during the above-mentioned oxidation by air.



Catalytic hydrogenation of a solution of (I) in hexahydrotoluene at 210° and 27 atm. for 40 min. gives 4-cyclo*hexyldecahydro*-α-*naphthol*, m. p. 166—167°, with other products. If the total hydrogenation product is dissolved in decahydronaphthalene and heated with zinc chloride, water is eliminated (the clouding due to the separation of which may be used as a test for the secondary hydroxyl group) and 1-cyclo*hexyl*-Δ^4-*octahydronaphthalene*, b. p. 162—163°/12 mm., d_4^{20} 0·9546, 1·51754, is obtained. Hydrogenation of this at 160° and 25 atm. gives α-cyclo*hexyldecahydronaphthalene*, b. p. 161—162·5°/12 mm., d_4^{20} 0·9438, n_D^{20} 1·49951.

Similar treatment of (II) at 180° and 25 atm. for 30 min. yields a product from which 2-cyclo*hexyldecahydro*-α-*naphthol*, m. p. 156—157°, is obtained; and at 215°, 26 atm., and 25 min., employing a regenerated catalyst, a second form, m. p. 120—121°. Treatment of this with zinc chloride and rehydrogenation gives β-cyclo*hexyldecahydronaphthalene*, b. p. 160·5—162°/12 mm., d_4^{20} 0·9315, n_D^{20} 1·49951.

β-Naphthol condensed with *cyclo*hexanol gives 1-cyclo*hexyl*-β-*naphthol* (V), m. p. 107—108°, and 6-cyclo*hexyl*-β-*naphthol* (VI), m. p. 161—162°. The former colours nitrous sulphuric acid green, which changes to brown, and the latter deep red, changing to dark brown. Aerial oxidation of (V) yields a yellow *substance*, $C_{16}H_{18}O_3$, sintering at 153°, m. p. 162—163°, which liberates iodine from potassium iodide, is rapidly coloured an intense yellow by insolation, and readily resinifies. In the hydrogenation of (V) as before, intermediate products could not be isolated; the product of the series of operations, β-*cyclo*hexyldecahydronaphthalene, had b. p. 160·5—162°/12 mm., d_4^{20} 0·9448, n_D^{20} 1·50559. From (VI) by hydrogenation, 6-cyclo*hexyldecahydro*-β-*naphthol*, m. p. 114—115°, is obtained, from which the β-*cyclo*hexyldecahydronaphthalene has b. p. 160·5—162·5°/12 mm., d_4^{20} 0·9282, n_D^{20} 1·49835.

ar-Tetrahydro-β-naphthol on condensation with *cyclo*hexanol gives ar-*tetrahydro*-3-cyclo*hexyl*-β-*naphthol* (VII), m. p. 103°, b. p. 209°/7·5 mm., the distillate being a resin which crystallises very slowly. Sodium nitrite added to a sulphuric acid solution gives a brown colour, which at once becomes lighter; if a little water is added, the liquid turns an intense sky-blue, and a blue amorphous substance is deposited, soluble in acetic or sulphuric acid to give a red colour and a strong fluorescence. Catalytic hydrogenation of (VII) gives a resin, b. p. 182—184·5°/7·5 mm., which acetylates to a mixture, m. p. 117—118°, of stereoisomeric 3-cyclo*hexyldecahydro*-β-*naphthyl acetates*, from which 3-cyclo*hexyldecahydro*-β-*naphthol* is isolated in two forms: A, plates, m. p. 99—100°; B, tables, m. p. 116—117°, somewhat less soluble than A in light petroleum. Dehydration by zinc chloride gives 3-cyclo*hexyl*-Δ$^{\alpha}$-*octahydronaphthalene*: from A, b. p. 163—164°/13 mm., d_4^{20} 0·9422, 1·51029; from B, b. p. 161—164°/12 mm., d_4^{20} 0·9454, n_D^{20} 1·49960.

E. W. Wignall.

Diphenyl series. III. Derivatives of 4-hydroxydiphenyl. F. Bell and J. Kenyon (J.C.S., 1926, 3044—3050).—4-Hydroxydiphenyl reacts with nitrous acid, yielding 3-nitro-4-hydroxydiphenyl; with diazotised aniline, forming 2-*hydroxy*-5-*phenylazobenzene*, m. p. 129°, which on reduction with sodium hyposulphite gives 3-amino-4-hydroxydiphenyl; with chloroform and aqueous sodium hydroxide, furnishing 4-*hydroxy*-3(?)-*aldehydodiphenyl*, m. p. 102° (*phenylhydrazone*, m. p. 210°). These results are claimed to indicate that there is no permanent linking between the 4- and 4′-positions in diphenyl (see Turner, A., 1923, i, 1085).

4-Methoxydiphenyl on nitration with fuming nitric acid in acetic anhydride solution yields mainly 3-*nitro*-4-*methoxydiphenyl*, m. p. 91—92°, together with 4′-*nitro*-4-*methoxydiphenyl*, m. p. 111°. The identity of these nitro-compounds was established by methylation of 3-nitro-4-hydroxydiphenyl and 4′-*nitro*-4-*hydroxydiphenyl*, m. p. 203°. The latter compound was obtained from diazotised 4′-nitro-4-aminodiphenyl. Further nitration of these isomeric nitro-methoxydiphenyls yields 3 : 4′-*dinitro*-4-*methoxydiphenyl*, m. p. 171°. 3 : ɔ-*Dinitro*-4-*methoxydiphenyl*

has m. p. 137—138°. Nitrous acid converts 4′-nitro-4-hydroxydiphenyl into 3 : 4′-*dinitro*-4-*hydroxydiphenyl*, m. p. 172° (p-*toluenesulphonate*, m. p. 147—148°), whilst bromine converts it into (3 : 5 ?)-*dibromo*-4′-*nitro*-4-*hydroxydiphenyl*, m. p. 232—234°. 4-p-*Toluenesulphonyloxydiphenyl*, m. p. 177°, on nitration gives 4′-*nitro*-4-p-*toluenesulphonyloxydiphenyl*, m. p. 156—158°.

Attempts to resolve diphenic acid and methyl hydrogen diphenate have been unsuccessful, indicating that free rotation of the two nuclei in diphenyl is possible in lightly-substituted diphenyl derivatives. The hypothesis is put forward that when free rotation is inhibited, the two nuclei adopt a configuration in which they have a common axis, but are not co-planar. H. BURTON.

Aromatic derivatives of the hypothetical orthophosphoric acid $P(OH)_5$. L. ANSCHÜTZ and W. BROCKER (Ber., 1926, 59, [*B*], 2848—2849; cf. Zetzsche and Aeschlimann, A., 1926, 1225).—The following substances are obtained by the action of phosphorus pentachloride on pyrocatechol in an indifferent solvent; *phosphorus pyrocatechyl trichloride*, $C_6H_4<\begin{matrix}O\\O\end{matrix}>PCl_3$, b. p. 132°/11 mm., m. p. 61—62°, which is converted by methyl alcohol into *methyl* o-*phenylene phosphate*, b. p. 148°/11 mm. (corresponding *ethyl* ester, b. p. 157°/12 mm.); *phosphorus dipyrocatechyl monochloride*, unimolecular *form*, m. p. 166—168°, b. p. 194°/11 mm., bimolecular *variety*, m. p. (indef.) 180—210° (decomp.); o-*phenylene orthophosphate*, $P_2(O_2C_6H_4)_5$, m. p. 200—240° (decomp.). *Pentaphenyl orthophosphate*, $P(OPh)_5$, m. p. 46—52°, is obtained by the action of phenol on phosphorus triphenoxydichloride. H. WREN.

Condensation of resorcinol with ethylene dicyanide [succinonitrile]. J. MURAI (Sci. Rep. Tohoku, 1926, **15**, 675—678).—See A., 1926, 951.

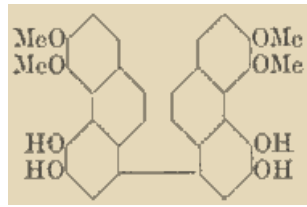
Alleged nitration of *S*-methylthioguaiacol. Criticism. A. POLLARD and R. ROBINSON (J.C.S., 3090—3093).—Nitric acid acts on *S*-methylthioguaiacol, giving 2-methoxyphenyl methyl sulphoxide, and then o-*nitro*-2-*methoxyphenyl methyl sulphoxide*, m. p. 144—145°. These results are contrary to the statement of Holmes, Ingold, and Ingold (A., 1926, 947). Hydrolysis of 5-nitro-2-methoxyphenyl methyl sulphoxide or the corresponding sulphone, m. p. 149—150°, with boiling aqueous sodium hydroxide gives 5-*nitro*-2-*hydroxyphenylmethylsulphone*, m. p. 167°, which on further nitration yields 3 : o-*dinitro*-2-*hydroxyphenylmethylsulphone*, m. p. 166°

H. BURTON.

Action of nitric acid on *S*-methylthioguaiacol. Correction. C. K. INGOLD and E. H. INGOLD (J.C.S., 1926, 3093—3094).—The compound previously described (A., 1926, 947) as 6-nitro-2-methoxyphenylmethylsulphone, m. p. 144—145°, is shown to be 5-nitro-2-methoxyphenyl methyl sulphoxide (cf. preceding abstract). The action of nitric acid on *S*-methylthioguaiacol may be to convert it first into the sulphoxide, or nitration may occur through the thionium nitrate with subsequent oxidation.

H. BURTON.

Sinomenol and disinomenol. K. GOTO (Proc. Imp. Acad. Tokyo, 1926, 2, 414—416; cf. A., 1926, 1160).—Mol. wt. determinations of the low-melting (*A*) and high-melting (*B*) series of dibenzoyl-, diacetyl-, and dimethyl-sinomenols (*diacetylsinomenol*-B has m. p. 285°, and *dimethylsinomenol*-A has m. p. 122°) show that the members of series *B* have approximately the same empirical formulæ as, but twice the mol. wt. of those of series *A*. The colour reactions of each series in sulphuric acid are characteristic, and compounds of series *B* are sparingly soluble in methyl alcohol. The author regards sinomenol-*B* as disinomenol (annexed formula), which is produced from sinomenol (m. p. 279°) by atmospheric oxidation during the action of 66% potassium hydroxide on sinomenine. The amount of disinomenol formed is almost trebled by doubling the duration of alkaline fusion. Dibenzoylsinomenol-*B* cannot be converted into the *A*-form. J. M. GULLAND.



Side-chain oxidations by means of nitro-compounds. L. T. SMITH and R. E. LYONS (J. Amer. Chem. Soc., 1926, 48, 3165—3167).—When benzyl alcohol (10 g.) is heated with nitrobenzene (12 g.) and sodium hydroxide (10 g.) for 4 hrs. at 138—140° in an autoclave, benzoic acid is obtained in 86·8% yield, together with an equivalent amount of azobenzene. *o*-Nitrotoluene reacts to a rather less extent under the same conditions. Reduction of the proportion of alkali present, or addition of water, reduces the extent of reaction. *m*-Dinitrobenzene reacts with benzyl alcohol in alkaline solution, with evolution of ammonia and formation of a charred mass, whilst picric acid and benzyl alcohol react explosively when mixed with sodium hydroxide. Toluene, benzyl chloride, and benzyl bromide are not oxidised by nitrobenzene or *o*-nitrotoluene under the above conditions. F. G. WILLSON.

Removal of the amino-group from aromatic amino-alcohols. M. TIFFENEAU and J. LÉVY (Compt. rend., 1926, **183**, 969—971).—When β-amino-α-phenyl-*n*-butyl, β-amino-α-phenyl-γ-methyl-*n*-butyl, β-amino-α-phenyl-*n*-amyl, and β-amino-α-phenyl-*n*-hexyl alcohols are treated with nitrous acid, phenyl *n*-propyl ketone, phenyl β-methyl-*n*-propyl ketone, phenyl *n*-butyl ketone, and phenyl *n*-amyl ketone, respectively, are formed. Intermediate formation of unsaturated compounds is probable, but no transposition of the phenyl group occurs.

L. F. HEWITT.

Coloured salts of the di- and tri-phenylmethane series. III. Basic coloured salts of diphenylmethane derivatives in which the central carbon atom is united to hydrogen or an aliphatic residue. W. MADELUNG and F. VOLKER (J. pr. Chem., 1927, [ii], **115**, 24—44).—The formation and reactions of coloured salts obtained from *pp*′-tetramethyldiaminobenzhydrol, the corresponding diphenylalkylcarbinols, and the ethylene derivatives obtained from them, have been studied with the object of elucidating their constitutions, and their relation-

ships are discussed from the point of view of the authors' colour theory (Madelung, A., 1925, i, 1459; this vol., 54). *pp'*-Tetramethyldiaminobenzhydrol forms a blue crystalline *perchlorate*, $C_{17}H_{21}O_4N_2Cl$, and a *double zinc chloride*, $C_{17}H_{21}N_2Cl_3Zn$. The action of magnesium alkyl halides on *pp'*-tetramethyldiaminobenzophenone yields, not the carbinol, but the corresponding ethylene derivative in all cases except with *tert.*-butyl chloride, which yields pp'-*tetramethyldiaminodiphenyl-tert.-butylcarbinol*, m. p. 147°. Benzyl chloride yields as-pp'-*tetramethyldiaminodiphenylstyrene*, m. p. 129°, as the chief product, together with pp'-*tetramethyldiaminodiphenylbenzylcarbinol*, m. p. 173°. Dilution with water of the solutions of the carbinol in acids precipitates the styrene derivative. The same coloured solutions are obtained when a solution of either a *pp'*-tetramethyldiaminodiphenylalkylcarbinol or its corresponding ethylene derivative in acetic acid or alcohol is treated with less than one equivalent of a mineral acid. Addition of water to these solutions first decolorises them and ultimately precipitates the ethylene base. The addition of 0·33 mol. of a 0·5% alcoholic solution of perchloric acid to a hot, saturated solution of *as-pp'*-tetramethyldiaminodiphenylethylene yields a blue *perchlorate* of composition 3B,1A (B=base, A=acid). On the other hand, the coloured solutions obtained by the action of oxidising agents, or sodium nitrite, on solutions of diphenylethylene bases (cf. Lemoult, A., 1909, i, 836) retain their colour on dilution with water, and on addition of alkali the corresponding carbinol is precipitated. Thus *αα'-pp'*-tetramethyldiaminodiphenylpropylene, treated in acetic acid solution with sodium nitrite, yields a coloured solution from which the green carbonium *perchlorate* is precipitated on treatment with perchloric acid. This is a true ethylene derivative of the constitution $[CR_2{\cdot}CH{:}CH_2]ClO'_4$ (R= $C_6H_4{\cdot}NMe_2$), from which is obtained the corresponding colourless *carbinol* $CR_2(CH{:}CH_2){\cdot}OH$, m. p. 160°. Similar treatment of *pp'*-tetramethyldiaminodiphenylstyrene yields pp'-*tetramethyldiaminodiphenylhydroxybenzyl perchlorate*, $[CR_2{\cdot}CHPh{\cdot}OH]ClO'_4$, from which is obtained the corresponding *αα'*-pp'-*tetramethyldiaminodiphenyl β-phenyl glycol*, m. p. 141°. Benzhydrol in concentrated sulphuric or perchloric acid solution exhibits halochromism, and dilution with water yields the unchanged carbinol, whilst diphenylmethylcarbinol yields a yellow solution from which the diphenylethylene is precipitated on dilution, the latter compound itself behaving in a similar manner. J. W. Baker.

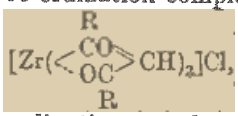
Catalytic hydrogenation of aromatic acids and their salts. V. N. Ipatiev and G. A. Rasuvaev (J. Russ. Phys. Chem. Soc., 1926, **58**, 122—128).—The hydrogenation of lithium, calcium, barium, zinc, ferrous, and nickel benzoates, as also of the sodium salts of salicylic, *p*-hydroxybenzoic, and mandelic acids, was carried out by Ipatiev's method (A., 1908, ii, 342) in the solid state, nickel sesquioxide being used as catalyst. The alkali and alkaline-earth salts hydrogenated smoothly and rapidly, giving a 60—70% yield of hexahydrobenzoic acid, but the ferrous, nickel, and zinc salts decomposed with the formation of an orange sublimate. The residual gases contained more than 90% of hydrogen. Salicylic and *p*-hydroxybenzoic acids gave 80% yields of *cyclo*hexanol, through loss of the carboxyl group. The residual gas contained much methane. Mandelic acid gave, with decomposition, a 40% yield of phenylacetic acid, with traces of *cyclo*hexylacetic acid, *i.e.*, in this case it is the hydroxyl group which is removed.
M. Zvegintzov.

Stereochemistry of hydronaphthalenes. I. Decahydro-β-naphthamides. F. W. Kay and N. Stuart (J.C.S., 1926, 3038—3041).—Decahydro-β-naphthoic acid should exist in four racemic forms, two being derivatives of the *cis*-modification, and two of the *trans*-modification, assuming Mohr's theory of the isomerism of the decahydronaphthalenes to be correct. Reduction of *ar*-tetrahydro-β-naphthoic acid with sodium and amyl alcohol at 150° gave a decahydro-acid, which after conversion through the chloride into the amide was examined for isomeric constituents. An amide, m. p. 195—196° (cf. Borsche and Lange, A., 1924, i, 32), was obtained, together with a small quantity of another amide, m. p. 171—174°. When sodium and ethyl alcohol were used for the reduction, two amides, m. p. 169—171° and m. p. 139—140°, were obtained.
H. Burton.

α-Selenobenzoic acid. Q. Mingoia (Gazzetta, 1926, **56**, 835—839).—Passage of a current of dry hydrogen selenide through an ethereal solution of magnesium ethyl bromide (cf. A., 1926, 388) results in the formation of ethane and magnesium bromohydroselenide. The latter is readily decomposed by water, giving hydrogen selenide and magnesium hydroxybromide, and may be isolated in the form of the additive product; it yields with *pyridine*, $MgBr{\cdot}SeH,2C_5H_5N$ (cf. Oddo, *ibid.*, 1904, i, 920; 1907, i, 549, 668). The action of benzoyl chloride on magnesium bromohydroselenide gives *α-selenobenzoic acid*, $Ph{\cdot}COSeH$, which is moderately stable and obtainable from methyl alcohol in lustrous, red crystals, m. p. 133°. Some of the esters of this acid were described by Taboury (*ibid.*, 1906, i, 834). Evaporation of the acid in presence of aqueous ammonia results in decomposition, selenium, ammonium benzoate, and ammonium hydroselenide being formed. T. H. Pope.

Addition and substitution reactions with zirconium chloride. G. Jantsch (J. pr. Chem., 1927, [ii], **115**, 7—23).—Additive and substitution products of zirconium chloride with various aldehydes, ketones, esters, and phenols, analogous to those obtained from thorium chloride (Jantsch and Urbach, A., 1919, i, 566), have been prepared, the rigid exclusion of moisture being necessary. Additive compounds (1 mol. of zirconium chloride and 2 mols. of the secondary component) could be isolated only at low temperatures, since the elimination of hydrogen chloride to form substitution products occurs with much greater ease than in the case of the thorium compounds. As in the earlier investigation, substitution occurs in stages which depend mainly on the temperature. The action of acetophenone and benzophenone on zirconium chloride in ethereal suspension at −5° yields the *additive compounds* of

the type $ZrCl_4,2Ph{\cdot}COR$. Benzoic acid in boiling benzene solution yields the *tetrabenzoate*, $Zr(CO_2Ph)_4$, in addition to the compounds obtained by Rosenheim and Hertzmann (A., 1907, ii, 271), whose observations are confirmed. Phenol at −10° yields an *additive compound* which is too unstable to be isolated, and in boiling ether yields the *chlorophenoxide*, $ZrCl(OPh)_3$. In boiling benzene, complete substitution of the chlorine occurs to yield the *tetraphenoxide*, $Zr(OPh)_4$. Acetylacetone in light petroleum at −10° yields an unstable *additive compound*, whilst in ether at the ordinary temperature, the *diacetylacetone chloride*, $ZrCl_2(C_5H_7O_2)_2$, is obtained, and in boiling benzene the trisacetylacetone chloride obtained by Morgan and Bowen (*ibid.*, 1924, i, 1079). In anhydrous media the tetra-acetylacetone compound (Biltz and Clinch, *ibid.*, 1904, i, 705) could not be obtained. Ethyl lactate and methyl mandelate yield unstable *additive compounds* at −10°, whilst in ether the *dichlorides* of the type $ZrCl_2[CHR(CO_2Me)O]_2$ (R=Me and Ph, respectively) are obtained. Salicylaldehyde yields an additive compound, and in boiling ether the dichloride obtained by Rosenheim and Hertzmann (*loc. cit.*). Higher substitution products could not be obtained. Similar compounds were obtained from methyl salicylate, and in addition the *trismethyl salicylate chloride*, $ZrCl[C_6H_4(CO_2Me)O]_3$, m. p. 222—225°, was obtained in boiling benzene. In boiling xylene, hydrolysis occurs, yielding the *compound* $Zr(\cdot O{\cdot}C_6H_4{\cdot}CO_2)_2$. Pæonol in ether at −10° yields an *additive compound*, in boiling ether the disubstitution *compound* $ZrCl_2R_2$, m. p. 185° (decomp.), and in boiling benzene the trisubstituted *compound* $ZrClR_3$, where $R=C_6H_3(OMe)(COMe){\cdot}O{\cdot}$. Since with all compounds in which the hydroxyl group is in the β- or γ-position to the carbonyl group it was found impossible to form tetrasubstitution products, it is assumed that the trisubstituted compounds are co-ordination complexes of the type



in which the metal has a co-ordination number of 6. With benzoin only an additive compound could be obtained.

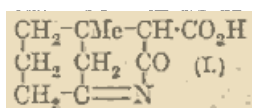
J. W. BAKER.

Chlorides and amides of hexahydrodiphenyl-*o*-carboxylic acid. J. RANEDO and A. LÉON (Anal. Fís. Quím., 1926, 24, 552—559; cf. A., 1925, i, 665).—Hexahydrodiphenyl-*o*-carboxylic acid, obtained by reduction of diphenyl-*o*-carboxylic acid with sodium and amyl alcohol, has m. p. 103—105°, whilst the isomeride obtained by catalytic hydrogenation has m. p. 102—103°. The former compound yields a crystalline acid *chloride*, m. p. 85—86°, and a crystalline *amide*, m. p. 137°. The other isomeride yields a *chloride*, b. p. 184—186°/38 mm., and a crystalline *amide*, m. p. 101—103°. G. W. ROBINSON.

Reactivities of some tertiary bromides. W. H. CAROTHERS (J. Amer. Chem. Soc., 1926, 48, 3192—3197).—*Methyl diphenylbromoacetate* (I), m. p. 38·5—38·8° (decomp. when kept), is obtained by the action of phosphorus tribromide (43·3 g.) and bromine (25·6 g.) on methyl benzilate (38·5 g.). When boiled with potassium thiocyanate in acetone, it affords *methyl diphenylthiocyanoacetate*, m. p. 82·5—83·5°. Bromination of dimethyl phenylmalonate in chloroform yields *dimethyl phenylbromomalonate* (II), b. p. 170—174°/8 mm., m. p. 45·5—46·5°. Similar bromination of tricarbomethoxymethane yields *bromotricarbomethoxymethane* (III), m. p. 50·5—51°, b. p. 116—117°/9 mm. The relative reactivities of (I), (II), (III), and triphenylmethyl bromide (IV) towards silver nitrate in acetonitrile and silver nitrate in absolute methyl alcohol are in the order (IV)>(I)>(II)>(III), whilst the relative reactivities towards potassium thiocyanate in absolute acetone are in the order (IV)>(III)>(I)>(II). F. G. WILLSON.

Manufacture of intermediates [nitro- and amino-4-hydroxy-3-carboxydiphenyl sulphide] and [azo] dyes. BRITISH DYESTUFFS CORP., LTD., K. H. SAUNDERS, and M. MENDOZA.—See B., 1927, 8.

Formation and stability of associated alicyclic systems. III. Change from "*meta* to "*para*"-bridged rings. E. H. FARMER and J. Ross (J.C.S., 1926, 3233—3240; cf. A., 1904, i, 509; 1926, 66, 834).—1-Methyl-Δ^1-*cyclo*hexen-3-one condenses with ethyl sodiocyanoacetate, giving *ethyl* 1-*methyl*cyclo*hexan*-3-*one*-1-*cyanoacetate*, b. p. 197°/2 mm. (*semicarbazone*, m. p. 166°), together with 1-*methyl*cyclo*hexenylidene*-3-*cyanoacetic acid*, m. p. 183° (*methyl* ester, m. p. 60°). *Methyl* 1-*methyl*cyclo*hexan*-3-*one*-1-*cyanoacetate*, b. p. 185°/2 mm. (*semicarbazone*, m. p. 183°), and the ethyl ester, on hydrolysis with aqueous sodium carbonate, yield 1-*methyl*cyclo*hexan*-3-*one*-1-*cyanoacetic acid*, m. p. 106°. This acid is converted by hot hydrochloric acid into *propane*-$^{1:3}$II$^{2\ 4}$-6-*keto*-4-*methyl*-3 : 4 : 5 : 6-*tetrahydropyridine*-5-*carboxylic acid* (I), m. p. 181° (*bromo*-derivative, m. p. 186°).



On complete fission with aqueous potassium hydroxide, (I) yields β-methylpimelic-β-acetic acid, whilst partial fission produces 1-*methyl*cyclo*hexan*-3-*one*-1-*malonamic acid*, m. p. 151°, and β-methylpimelic acid δ-acetamide. The latter compound, on treatment with hot dilute hydrochloric acid, passes into δ-*methylglutarimide*-β-*butyric acid*, m. p. 139°, identical with the substance obtained by passing dry ammonia through the molten anhydride of β-methylpimelic-β-acetic acid, followed by treatment with hot dilute hydrochloric acid. H. BURTON.

Acidity and isomerism of thioglycollic acid derivatives. O. BEHAGHEL (J. pr. Chem., 1926, [ii], 114, 287—312).—In general, introduction of oxygen or sulphur into carboxylic acids greatly increases their strength (cf. A., 1889, 818; 1894, i, 325; 1902, ii, 643; 1909, i, 286; 1925, i, 397). Replacement of carbonyl or hydroxylic oxygen by sulphur increases the acidity, but in the case of ethereal oxygen, the opposite effect is observed. Thus, derivatives of phenoxyacetic acid are 2·4—3·6 times as strong as the corresponding phenylthiolacetic acids. The following new values are recorded for the dissociation coefficients [K (acetic

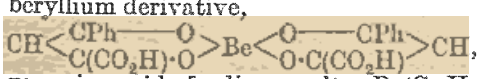
acid)=0·18] of some derivatives of phenoxyacetic acid: *o*-methyl-, 6·819; *m*-methyl-, 6·632, *p*-methyl-, 7·026; *o*-methoxy-, 5·845; o-*chloro*-, m. p. 145—146°, 10·24; *p*-chloro-, 9·617; and of phenylthiolacetic acid, 2·971: *o*-methyl-, 2·819; m-*methyl*-, m. p. 103—104°, 2·728; *p*-methyl-, 2·464; o-*methoxy*-, m. p. 114—115°, 1·822; *o*-chloro-, 3·04; *p*-chloro-, 2·41; *o*-nitro-, 5·546; *p*-nitro-, 6·927; o-*methylthiol*-, m. p. 120°, 1·81; p-*methylthiol*-, m. p. 106—107°, 1·767; *p*-amino-, 0·1403; p-*ethyldithiocarbonato*-, m. p. 101—102°; p-*thiol*-, m. p. 108·5—109·5°; also *p*-phenylenedioxydiacetic acid, 37·64; bis-p:p′-*thiophenylthiolacetic acid*, $(\cdot S\cdot C_6H_4\cdot S\cdot CH_2\cdot CO_2H)_2$, m. p. 166·5°; and p-*phenylenedithioldiacetic acid*, 4·507. The last occurs in two modifications, (*a*) colourless, m. p. 210—214°, (*b*) yellow, m. p. 214°, after sintering at 208—209°. Microscopical examination of *o*-methylthiolphenylthiolacetic acid shows that this also is polymorphic. H. E. F. Notton.

Synthesis of 6-chloro-3-hydroxybenzoic acid. V. I. Minaev (J. Russ. Phys. Chem. Soc., 1926, **58**, 115—118).—The method consists in nitrating *o*-chlorobenzoic acid, reducing, diazotising, and decomposing the diazo-compound by heat in aqueous solution. The author discusses the various conditions of diazotisation and decomposition, so as to avoid resinification. If sulphuric acid is used, the diazo-solution, prepared at 5°, must be added very slowly to much water at 80°, when a 60% yield of pure product, m. p. 173°, is obtained. Using hydrochloric acid, the water should be at 60°, then cautiously heated to 90°. The yield is 70%.

M. Zvegintzov.

Carbylamines. XV. Reactions with aliphatic carbylamines. M. Passerini (Gazzetta, 1926, **56**, 826—829; cf. A., 1926, 952).—The reactions of the aromatic carbylamines already described may be extended to the aliphatic carbylamines. *Benzoylmandelylpropylamide* [*α-benzoyloxyphenylacetpropylamide*], Ph·CO·O·CHPh·CO·NHPr, prepared by the interaction of propylcarbylamine, benzaldehyde, and benzoic acid in ethereal solution, m. p. 117—119°, on hydrolysis yields benzoic acid and *mandelylpropylamide*, OH·CHPh·CO·NHPr, m. p. 64—65°. *Trichlorolactylpropylamide*, $CCl_3\cdot CH(OH)\cdot CO\cdot NHPr$, obtained from chloral hydrate and propylcarbylamine, has m. p. 116—118° (decomp. and gas), and yields trichlorolactic acid and propylamine on hydrolysis.

T. H. Pope.

Optical activity dependent on co-ordinated beryllium, copper, and zinc. W. H. Mills and R. A. Gotts (J.C.S., 1926, 3121—3131).—The beryllium derivative,  , of benzoylpyruvic acid [*sodium* salt, $Be(C_{10}H_6O_4Na)_2,H_2O$] forms a crystalline brucine salt showing mutarotation in chloroform or alcoholic solution (cf. A., 1925, i, 46). Anhydrous *brucine* d-*berylliobenzoylpyruvate* [hydrated salt, $Be(C_{10}H_7O_4,C_{23}H_{26}O_4N_2)_2,8H_2O$] has m. p. 212—215° (decomp.). It gives $[\alpha]^{20}_{5461}$ +25·06° ⟶ +5° in chloroform and +39·9° ⟶ +13·1° in alcohol. *Brucine* l-*berylliobenzoylpyruvate* gives $[\alpha]^{20}_{5461}$ −11·8° ⟶ +5° in chloroform. The mutarotation was proved to be due to the disappearance of an unstable optical activity associated with the co-ordinated beryllium, since the greater part of the brucine could be removed (by precipitation as hydrochloride from absolute-alcoholic solution) without a corresponding diminution of the optical activity of the solution. *Dimethylammonium berylliobenzoylpyruvate*, thus obtained, has m. p. 95—96°. The strychnine salt of the copper derivative of benzoylpyruvic acid and the brucine salt of the zinc derivative show analogous mutarotation in chloroform solution, and variation takes place, as in the case of the beryllium compounds, in accordance with the unimolecular law. It is concluded that co-ordinated copper and zinc, as well as beryllium, can give rise to optical activity, and that, in the cases considered, the four oxygen atoms are disposed tetrahedrally about the metallic atom, although the valencies of copper and zinc are differently directed in compounds in which their co-ordination number is six.

Strychnine cupribenzoylpyruvate, $+4H_2O$, has m. p. 97—98° (decomp.). *Brucine zincibenzoylpyruvate* decomposes at 185°. M. Clark.

Reactions with fulminic acid. I. Nitriles from naphthols and 2-methylindole. M. Passerini and B. Grulis (Gazzetta, 1926, **56**, 829—835).—Although fulminic acid is analogous in structure to the carbylamines, neither the acid nor its mercury salt reacts with α- or β-naphthol, but the additive compounds formed by mercury fulminate with potassium cyanide, potassium iodide, and ammonium thiocyanate readily react, giving good yields of the nitriles of α-naphthol-2-carboxylic and β-naphthol-1-carboxylic acids with α- and β-naphthols, respectively. Similarly, the additive product of mercury fulminate with potassium iodide or cyanide reacts with 2-methylindole, giving the *nitrile* of 2-methylindole-3-carboxylic acid, m. p. 207—210° (browning). T. H. Pope.

Action of hydrochloric acid on desmotroposantonin. P. Bertolo (Gazzetta, 1926, **56**, 852—855).—Although dihydroartemisic acid appears to be formed as an intermediate compound in the conversion of desmotroposantonin into artemisic acid by the action of iodine (A., 1925, i, 546), it has not been found possible to isolate it by moderating the reaction. *Dihydroartemisic acid*. $C_{15}H_{18}O_3$, m. p. 97—98°, may, however, be obtained by heating either desmotroposantonin or santonin in acetic acid solution with concentrated hydrochloric acid in presence of zinc chloride. If the solution in acetic acid is replaced by a suspension in absolute alcohol, *ethyl dihydroartemisate*, m. p. 74—75°, is obtained.

T. H. Pope.

Product of the scission of artemisic acid (1:4-dimethyl-7-ethyl-β-naphthol). P. Bertolo (Gazzetta, 1926, **56**, 856—859).—The compound obtained when artemisic acid is fused with potassium hydroxide and considered to be identical with 1:4-dimethyl-β-naphthol, which is formed on fusion of santonous acid with potassium hydroxide or on reduction of artemisin with stannous chloride (A., 1902, i, 814), is now shown to be 1:4-*dimethyl*-7-*ethyl*-β-*naphthol*, m. p. 126° (*methyl ether*, m. p. 72°).

The difference in behaviour of santonous acid and artemisic acid is explained by the fact that in the former the propionic acid radical is united to a carbon atom of the hydrogenated naphthalene nucleus, so that fusion with potassium hydroxide yields 1 : 4-dimethylnaphthol, propionic acid, and hydrogen; in artemisic acid, however, the carbon atom with which the propionic acid radical is connected is not hydrogenated, so that, on fusion with potassium hydroxide, this radical undergoes partial decomposition into carbon dioxide, which is eliminated, and the ethyl group, which remains. T. H. POPE.

Preparation of *d*-santonous acid from desmotroposantonin. P. BERTOLO (Gazzetta, 1926, **56**, 859—861).—The action of hydriodic acid and red phosphorus on hyposantonin yields dihydrosantinic acid (cf. Gucci and Grassi-Cristaldi, A., 1892, 869), but similar treatment of desmotroposantonin gives, not dihydroartemisic acid, but an almost theoretical yield of an acid which agrees in all its characters with *d*-santonous acid and is regarded by the author as true desmotroposantonous acid. T. H. POPE.

***cyclo*Propenedicarboxylic acids.** F. FEIST and C. A. CHEN (Ber., 1926, **59**, [*B*], 2707—2709).—Ethyl 3-phenyl*cyclo*propane-1 : 2-dicarboxylate reacts very incompletely with bromine at 180° in presence of phosphorus pentachloride, iron, and iodine (cf. Haerdi and Thorpe, A., 1925, i, 923). The free acid with water and bromine at 50° gives 1-bromo-3-phenyl*cyclo*propane-1 : 2-dicarboxylic acid, m. p. 226°, which is reduced by sodium amalgam to 3-phenyl-*cyclo*propane-1 : 2-dicarboxylic acid and transformed by molten potassium hydroxide into 1-*hydroxy*-3-*phenyl*cyclo*propane*-1 : 2-*dicarboxylic acid*, m. p. about 65° (*methyl* ester, b. p. 210—215°/3 mm.). H. WREN.

***cis*-o-Carboxy*cyclo*hexaneacetic acid.** G. A. R. KON and M. QUDRAT-I-KHUDA (J.C.S., 1926, 3071—3073).—*cyclo*Hexenyl methyl ketone condenses with ethyl sodiomalonate, giving *ethyl* 1 : 3-*diketodecahydronaphthalene*-4-*carboxylate*, m. p. 114°, which on hydrolysis with alcoholic alkali passes into 1 : 3-*diketodecahydronaphthalene*, m. p. 142°. Sodium hypobromite converts the diketone into *cis*-*o*-carboxy*cyclo*hexaneacetic acid, m. p. 146—147° (anhydride, m. p. 57°), whilst alkaline potassium permanganate oxidises it to *trans*-*cyclo*hexane-1 : 2-dicarboxylic acid, m. p. 222°. H. BURTON.

Derivatives of succinic and glutaric acids with cyclic, quaternary carbon atom. W. HUCKEL and F. WIEBKE (Ber., 1926, **59**, [*B*], 2838—2844).—*trans*-1-Ketodecahydronaphthalene is converted by ethyl cyanoacetate and alcoholic ammonia into trans-*decahydronaphthalene*-1 : 1-*dicyanoacetimide*, m. p. 261—263° (decomp.), which is hydrolysed by concentrated hydrochloric acid at 150—160° to trans-*decahydronaphthalene*-1 : 1-*diacetic acid*, m. p. 169°, converted by acetic anhydride into the corresponding *anhydride*, m. p. 94°. *trans*-1-Ketodecahydronaphthalene is converted by anhydrous hydrocyanic acid into the corresponding *cyanohydrin*, m. p. 82°. With methyl bromoacetate and zinc, *trans*-1-ketodecahydronaphthalene affords the two theoretically possible *methyl* 1-*hydroxydecahydronaphthalene*-1-*acetates*, m. p. 106° and 45°, respectively (corresponding *acids*, m. p. 144° and 150°). The hydroxy-ester, m. p. 106°, is converted by loss of water and subsequent hydrolysis into an *acid*, $C_{12}H_{18}O_2$, m. p. 155°. Subsequent efforts to prepare the hydroxy-esters were accompanied by loss of water during distillation, and the product when hydrolysed gave an oily *acid*, b. p. 198—210°/33 mm. [*methyl* ester, $C_{13}H_{20}O_2$, $d_4^{14\cdot2}$ 1·0371, $n_D^{13\cdot0}$ 1·50019; *amide*, m. p. 119°; *dibromide*, m. p. 172—173° (decomp.); *methyl* ester of dibromo-acid, m. p. 53°]. *cis*-2-Ketodecahydronaphthalene gives successively cis-*decahydronaphthalene*-2 : 2-*dicyanoacetimide*, m. p. 238—239°, cis-*decahydronaphthalene*-2 : 2-*diacetic acid*, m. p. 167°, and the corresponding *anhydride*, m. p. 91°. cis-2-*Ketodecahydronaphthalene cyanohydrin*, m. p. 81°, is converted by ethyl sodiocyanoacetate and subsequent hydrolysis into cis-*decahydronaphthalene*-2-*acetic*-2-*carboxylic acid*, m. p. 168—170° (decomp.) (*anhydride*, m. p. 97°). trans-2-*Ketodecahydronaphthalene cyanohydrin*, m. p. 108°, trans-2-*carboxydecahydronaphthalene*-2-*acetic acid*, m. p. 149—150°, and its *anhydride*, m. p. 91°, are described. 2-*Carboxy*-1-*methyl*cyclo*hexane*-2-*acetic acid* has m. p. 166° (decomp.) after softening at 135°. H. WREN.

Orientation of the bromine atom in bromodimethoxybenzoic acid. G. P. RICE (J. Amer. Chem. Soc., 1926, **48**, 3125—3130).—Bromination of γ-2 : 4-dimethoxybenzoylpropionic acid, and subsequent elimination of hydrogen bromide, yields ɔ-*bromo*-2 : 4-*dimethoxybenzoylacrylic acid* (cf. A., 1926, 270), the orientation of the bromine atom in which was determined by the following transformations. On oxidation with permanganate, the acid affords 5-*bromo*-2 : 4-*dimethoxybenzoic acid*, m. p. 193°, of which the *methyl* ester, m. p. 117°, yields, when treated with activated magnesium and carbon dioxide, methyl 5-bromo-2-hydroxy-4-methoxybenzoate (cf. Spath, A., 1914, i, 650). Elimination of carbon dioxide from the 5-bromo-2 : 4-dimethoxybenzoic acid could not be effected. Bromination of β-resorcylic acid in glacial acetic acid (cf. Hemmelmayr, A., 1912, i, 977) affords 5-*bromo*-2 : 4-*dihydroxybenzoic acid* ($+1H_2O$), m. p. 204° (anhydrous), together with a *dibromo*-derivative which yields a soluble dibromoresorcinol when boiled with water. The former yields, on treatment with methyl sulphate and alkali, the above 5-bromo-2 : 4-dimethoxybenzoic acid, m. p. 193°, and the methyl 5-bromo-2-hydroxy-4-methoxybenzoate, m. p. 143°, together with 5-*bromo*-2-*hydroxy*-4-*methoxybenzoic acid*, m. p. 247° (decomp.), which, when boiled with water, yields 4-*bromoresorcinol* 3-*methyl ether*. By elimination of carbon dioxide, 5-bromo-2 : 4-dihydroxybenzoic acid is converted into 4-*bromoresorcinol*, m. p. 103° (cf. Zehenter, A., 1882, 193; 1887, 924), of which the *dimethyl ether*, b. p. 135°/18 mm., and the 1-*methyl ether*, b. p. 152°/25 mm., are described. The dimethyl ether yields the dimethyl ether of β-resorcylic acid, m. p. 108°, when treated with magnesium and carbon dioxide. 3-Bromo-2 : 4-dihydroxybenzoic acid (cf. Hemmelmayr, *ibid.*, 1914, i, 283) yields 2-*bromoresorcinol*, m. p. 102·5°, when boiled with water. The action of methyl sulphate and alkali on 2 : 6-dibromoresorcinol

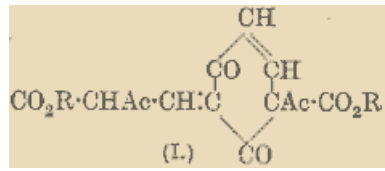
affords the *dimethyl ether*, b. p. 155°/15 mm., and, presumably, 2 : 6-*dibromoresorcinol* 3-*methyl ether*, b. p. 160°/24 mm. Treatment of 3-bromo-2 : 4-dihydroxy-5-nitrobenzoic acid with warm, concentrated nitric acid affords 2-bromo-4 : 6-dinitroresorcinol, m. p. 189—191° (cf. Dahmer, *ibid.*, 1904, i, 871), whilst 5-bromo-β-resorcylic acid yields similarly 2 : 4 : 6-trinitroresorcinol. F. G. Willson.

Action of arsenic acid on gallic acid. L. F. Iljin (J. pr. Chem., 1927, [ii], **115**, 1—7; cf. A., 1919, i, 908).—The reaction between arsenic and gallic acids in methyl-alcoholic solution (*d* 0·796) yields, by a method of isolation similar to that previously employed, *methyl trigalloylarsenate*, $(C_8H_7O_5)_3AsO$, obtained both as an amorphous powder and in a crystalline form (the former being converted into the latter by slow crystallisation from methyl alcohol–ether solution), and methyl gallate, m. p. 195—196°, which is also obtained by the action of hydrogen sulphide on a solution of the arsenic compound in dilute sulphuric acid. The trigalloylarsenate is converted by methyl sulphate into a *dimethyl ether*, $(C_7H_2O_5Me_3)_3AsO$, which with hydrogen sulphide yields methyl 5-hydroxy-3 : 4-dimethoxybenzoate, m. p. 83—84° (cf. Herzig and Pollak, A., 1903, i, 89). Hydrolysis of methyl trigalloylarsenate with alcoholic potassium hydroxide in an atmosphere of hydrogen yields the corresponding free *acid*. J. W. Baker.

Opianic acid. W. M. Rodionov and A. M. Fedorowa (Ber., 1926, **59**, [*B*], 2949—2952; cf. A., 1924, i, 1196).—Opianic acid is readily converted by thionyl chloride into *opianyl chloride*, m. p. 93—94°, from which methyl opianate is obtained by the action of methyl alcohol and pyridine. The ester or the corresponding ethyl ester is transformed by potassium hydroxide in the requisite alcohol into methyl or ethyl ψ-opianate, $(OMe)_2C_6H_2<^{CH(OAlk)}_{CO}>O$. Phenol and potassium hydroxide do not react with methyl opianate, whereas opianic acid is transformed by phenol at 120° into a *substance*, m. p. 145—146°.

H. Wren.

Xanthophanic acids. I. F. Feist, D. Delfs, and B. Langenkamp (Ber., 1926, **59**, [*B*], 2958—2972; cf. Liebermann and others, A., 1906, i, 556; 1907, i, 889; 1908, i, 548; 1909, i, 403, 405).—The constitution assigned by Liebermann (*loc. cit.*) to xanthophanic acid obtained by Claisen by the action of solid ethyl sodioacetoacetate on ethyl ethoxymethyleneacetoacetate is unsatisfactory, since it assumes the presence of the resacetophenone nucleus. The reactants, however, do not yield ethyl resacetophenonecarboxylate, but ethyl methenyldiacetoacetate, which, by internal ring closure, affords ethyl hydrogen *m*-hydroxyavitinate. Further, xanthophanic acid cannot be synthesised from the diethyl ether of ethyl resacetophenonecarboxylate and ethyl ethoxymethyleneacetoacetate. A guide to the constitution of the substance is found in its production in good yield from ethyl methenyldiacetoacetate and ethyl ethoxymethyleneacetoacetate with elimination of alcohol. It is shown by variation of the alkoxy-groups of the esters that the alkoxy-group of alkoxymethyleneacetoacetic esters and that of one of the two ·CO_2Alk groups of the diester are removed during the action, whereas the remaining ·CO_2Alk groups remain intact. Further, the hydrogen atoms of the acetyl group of ethoxymethyleneacetoacetic esters are not involved. On the basis of these observations, the constitution (I) (R=Et) or one of its three other desmotropic forms is ascribed to xanthophanic acid.

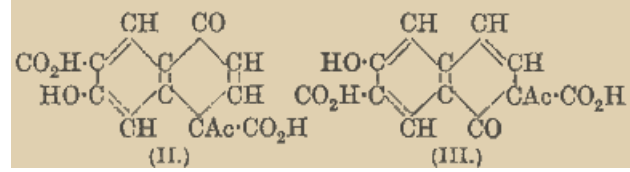


(I.)

The following substances are incidentally described: *methyl αγ-diacetylglutaconate*, m. p. 85°, from methyl sodioacetoacetate and methyl ethoxymethyleneacetoacetate; *γ-methyl α-ethyl αγ-diacetylglutaconate*, m. p. 87°, from ethyl sodioacetoacetate and methyl ethoxymethyleneacetoacetate; *α-methyl γ-ethyl αγ-diacetylglutaconate*, m. p. 73°, from methyl sodioacetoacetate and ethyl ethoxymethyleneacetoacetate; *ethyl ethoxymethylenebenzoylacetate*, b. p. 203°/13 mm.; ethyl 2 : 4-diketo-1-acetyl-3-β-carbethoxy-β-acetylethylidene-Δ⁵-*cyclo*hexene-1-carboxylate (Claisen's diethylxanthophanic acid), m. p. 144°, from ethyl diacetylglutaconate and ethyl ethoxymethyleneacetoacetate in presence of sodium ethoxide, and the corresponding dimethyl ester, m. p. 179°; *ethyl* 2 : 4-*diketo*-1-*acetyl*-3-β-*carbomethoxy*-β-*acetylethylidene*-Δ⁵-cyclo*hexene*-1-*carboxylate*, m. p. 167°; *methyl* 2 : 4-*diketo*-1-*acetyl*-3-β-*carbethoxy*-β-*acetylethylidene*-Δ⁵-cyclo*hexene*-1-*carboxylate*, m. p. 151°; *ethyl* 2 : 4-*diketo*-1-*benzoyl*-3-β-*carbethoxy*-β-*acetylethylidene*-Δ⁵-cyclo*hexene*-1-*carboxylate* (*diethylerythrophanic acid*), m. p. 157°, from ethyl diacetylglutaconate and ethyl ethoxymethylenebenzoylacetate; the *copper* salt, $(C_{18}H_{19}O_8)_2Cu$, and *benzoyl* derivative, m. p. 146°, of "diethylxanthophanic acid."

The "transformation product," $C_{17}H_{18}O_8$, m. p. 161—162°, obtained by the action of magnesium methoxide on xanthophanic acid (cf. Liebermann, *loc. cit.*), is converted by phenylhydrazine into the *phenylhydrazone* of *methyl resacetophenonecarboxylate*, which appears to exist in two forms, m. p. 242—243° and m. p. 248—249°.

Xanthophanic acid is converted by concentrated sulphuric acid into a substance, $C_{14}H_{10}O_7$, m. p. 187° (cf. Liebermann, *loc. cit.*), and an isomeric *compound* (*barium* salt). The product, which is acidic and does not contain an ethoxy-group, appears to have the constitution (II) or (III).



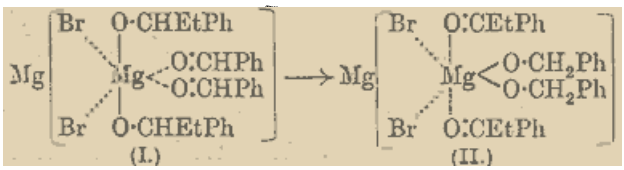
(II.) (III.)

Liebermann's "hydrazone," from diethylxanthophanic acid or ethylglaucophanic acid, m. p. 194—195°, has the composition $C_{12}H_{12}O_4N_2$, and is therefore obtained from the diethyl compound by loss of an acetoacetic residue. It contains an ethoxy-group and is hydrolysed to an *acid*, $C_{10}H_8O_4N_2$, m. p. 331—333°. It is converted by silver oxide and ethyl iodide into a neutral *compound*, $C_{14}H_{16}O_4N_2$, m. p. 75—76°. The

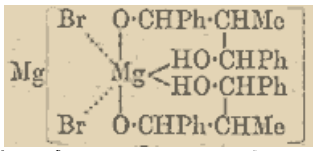
hydrazone and nitric acid afford a *product*, m. p. 214°, whereas the ethylated hydrazone yields a *mononitro*-derivative, $C_{11}H_{15}O_4N_2(NO_2)$, m. p. 98—99°.

Diethylxanthophanic acid is reduced by zinc and dilute sulphuric acid to a *dihydro*-derivative, $C_{18}H_{22}O_8$, m. p. 60—70°, decomp. 120°, which affords a *monobenzoyl* compound and is converted by phenylhydrazine into a *substance*, $C_{18}H_{20}O_4N_2$, decomp. 140° after softening at 110°. H. WREN.

Condensation of benzaldehyde with organomagnesium compounds. A. P. TERENTJEV (Z. anorg. Chem., 1927, **159**, 226—230).—An attempt to explain the formation of the various products resulting from the reaction between benzaldehyde and magnesium ethyl bromide (Marshall, A., 1915, i, 409; Hess and Rheinboldt, *ibid.*, 1921, i, 777; Meisenheimer, *ibid.*, 1925, i, 527). The scheme suggested by Meisenheimer (*ibid.*, 1926, 68) explains the appearance of propiophenone and benzyl alcohol, but fails to account for the formation of αγ-dihydroxy-αγ-diphenyl-β-methylpropane. The present explanation is based on the author's co-ordination formula (*ibid.*, 1130) and the assumption that the individual hydrogen atoms of the co-ordinatively bound components are extremely mobile and can wander from one component to another. Meisenheimer's scheme now becomes:



By the wandering of a hydrogen atom from each of the two ethyl groups, formula (I) becomes:



which explains the appearance of αγ-dihydroxy-αγ-diphenyl-β-methylpropane. The essential difference between this reaction scheme and that of Meisenheimer is that in the present instance two molecules of benzaldehyde are bound co-ordinatively, and by the wandering of an atom of hydrogen can condense to form benzyl benzoate. In support, it is found that by using an excess of benzaldehyde, benzyl benzoate can be isolated from the products of the reaction. As a result of interaction between benzyl benzoate and the magnesium bromoalkoxide of phenylethylcarbinol, phenylethylcarbinyl benzoate is a possible reaction product. The evidence for the existence of this ester is indirect (detection of benzoic acid after hydrolysis of a small fraction boiling above 330°) and inconclusive. J. S. CARTER.

***p*-Dimethylaminobenzylidenepentaerythritol.** A. FAIRBOURNE and J. W. WOODLEY (J.C.S., 1926, 3240—3241).—*p*-Dimethylaminobenzaldehyde condenses with pentaerythritol in presence of warm 50% sulphuric acid, giving *p-dimethylaminobenzylidenepentaerythritol*, m. p. 140° (decomp.) (*methiodide*, decomp. 175°). Condensation of this benzylidene derivative with another mol. of the aldehyde yields bis-*p*-dimethylaminobenzylidenepentaerythritol (*methiodide*, decomp. 220°). Attempts to condense the mono-*p*-dimethylaminobenzylidene derivative with different aldehydes caused elimination of the *p*-dimethylaminobenzylidene radical and the formation of spirans identical with those from 2 mols. of the aldehyde. *p-Dimethylaminobenzaldehyde methiodide* decomposes at 160°. H. BURTON.

5-Methoxy-α-naphthaldehyde. J. B. SHOESMITH and H. RUBLI (J.C.S., 1926, 3241—3243).—5-Hydroxy-α-naphthoic acid, prepared by fusing 1-cyanonaphthalene-5-sulphonic acid with sodium hydroxide, is converted into 5-methoxy-α-naphthoic acid by methyl sulphate. Treatment of the potassium salt of this acid with thionyl chloride yields *5-methoxy-α-naphthoyl chloride*, b. p. 194°/11 mm., m. p. 80—81°. Reduction of this compound with hydrogen in presence of palladium produced *5-methoxy-α-naphthaldehyde*, m. p. 66° (*p-nitrophenylhydrazone*, m. p. 246°; *semicarbazone*, m. p. 246°; *oxime*, m. p. 104°). H. BURTON.

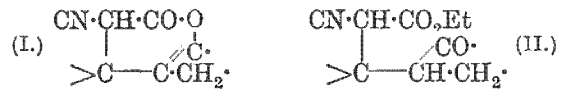
Acyl migration during the partial hydrolysis of acylated polyphenolic aldehydes. E. PASSU and L. VON VARGHA (Ber., 1926, **59**, [*B*], 2818—2824; cf. A., 1923, i, 338).—3 : 4-*Diacetoxybenzaldehyde*, m. p. 54° [*phenylhydrazone*, m. p. 135°; *semicarbazone*, m. p. 200—202° (decomp.)], is prepared in 95% yield by the action of acetic anhydride on 3 : 4-dihydroxybenzaldehyde in aqueous alkaline solution. It is converted by partial hydrolysis into *4-hydroxy-3-acetoxybenzaldehyde*, m. p. 109—110° (*p-nitrophenylhydrazone*, m. p. 195°), which is obtained in better yield by the partial acetylation of 3 : 4-dihydroxybenzaldehyde. The constitution of the substance is established by its conversion by diazomethane into 3-acetoxy-4-methoxybenzaldehyde, m. p. 88°, which is hydrolysed to *iso*vanillin, m. p. 115—116°. *4-Benzoxy-3-acetoxybenzaldehyde*, m. p. 109° (*phenylhydrazone*, m. p. 158°), prepared by the action of benzoyl chloride and aqueous potassium hydroxide on 4-hydroxy-3-acetoxybenzaldehyde dissolved in acetone, is hydrolysed in acid or aqueous solution with migration of the benzoyl group to *4-hydroxy-3-benzoxybenzaldehyde*, m. p. 136—137° (*phenylhydrazone*, m. p. 192°), which, when acetylated, affords *4-acetoxy-3-benzoxybenzaldehyde*, m. p. 68° (*phenylhydrazone*, m. p. 166°). 4-Hydroxy-3-benzoxybenzaldehyde is converted by diazomethane into 4-methoxy-3-benzoxybenzaldehyde, m. p. 75°, from which *iso*vanillin is obtained by hydrolysis. H. WREN.

Alkyl*cyclo*-pentanones and -hexanones. Action of benzaldehyde and other aromatic aldehydes on cyclanones. Differentiation of the αα- and αα′-dimethylcyclanones. A. HALLER and R. CORNUBERT (Bull. Soc. chim., 1926, [iv], **39**, 1621—1643).—A review of previous work (cf. A., 1914, i, 291; 1920, i, 390, 441; 1924, i, 1203; 1925, i, 1070, 1071). M. CLARK.

Alkyl*cyclo*-pentanones and -hexanones. II. Alkylation of 1-methyl*cyclo*pentan-2-one. A. HALLER and R. CORNUBERT (Bull. Soc. chim., 1926, [iv], **39**, 1724—1732; cf. preceding abstract).—Re-examination of the products obtained on methylating

1-methyl*cyclo*pentan-2-one with methyl iodide and sodamide indicates that the dimethylation product consists of at least 95% of 1 : 1-dimethyl*cyclo*pentanone and only 5% of the 1 : 3-dimethyl isomeride. The trimethylation product reacts with benzaldehyde in presence of hydrochloric acid and appears to contain di- and tetra-methyl*cyclo*pentanones. 1 : 1 : 3-Trimethyl*cyclo*hexanone, like 1 : 1 : 3-trimethyl*cyclo*pentanone, does not react under these conditions. 1 : 1 : 3 : 3-Tetramethyl*cyclo*pentanone, b. p. 155—156°/770 mm., d_4^{20} 0·8653, n_D^{20} 1·4288, probably contains traces of the trimethyl derivative. It is concluded that *gem*-methylation takes place more readily than symmetrical methylation. Ethylation under similar conditions affords about 80% of condensation products and a fraction which is apparently a mixture of mono- and di-ethyl-1-methyl-*cyclo*pentan-2-ones. R. BRIGHTMAN.

Three-carbon system. X. Mobility of some cyclic ketones. G. A. R. KON and J. H. NUTLAND (J.C.S., 1926, 3101—3111; cf. *ibid.*, 1923, **123**, 1361). —2-Δ^1-*cyclo*Hexenyl*cyclo*hexanone gives two semicarbazones, one form m. p. 200—201°, and a small amount of another form, m. p. 172° (cf. A., 1907, i, 220; 1923, i, 142). The ketone regenerated from the semicarbazone of m. p. 200—201° by oxalic acid had b. p. 145°/17 mm., $d_4^{15\cdot1}$ 1·00404, $n_D^{15\cdot1}$ 1·50692, $[R_L]_D$ 52·81, and gave, on oxidation with ozone, adipic acid, indicating the stable βγ-form. Methylation by "molecular" sodium and methyl iodide yielded 2-*methyl*-2-Δ^1-cyclo*hexenyl*cyclo*hexanone*, b. p. 150°/18 mm., $d_4^{19\cdot4}$ 0·98804, $n_D^{19\cdot4}$ 1·50320, $[R_L]_D$ 57·51 (*semicarbazone*, m. p. 204°). Oxidation of the methylated ketone gave adipic acid and δ-acetylvaleric acid (identified as semicarbazone, m. p. 145—146°). The original ketone, when condensed with ethyl sodiocyanoacetate, gave a small amount of a *cyano-lactone*, m. p. 112°, of type (I), formed by the loss of alcohol from the expected cyano-ester (II) [cf. Vorländer, A., 1906, i, 362).



Concentrated sulphuric acid converts the lactone into an *imide*, m. p. 166°.

2-*cyclo*Pentylidene*cyclo*pentanone (semicarbazones, m. p. 223° and 207°) on oxidation gives *cyclo*pentanone and glutaric acid, showing the αβ-formula. Ethylation converts it into 2-*ethyl*-2-Δ^1-cyclo*pentenyl*cyclo*pentanone*, b. p. 140°/22 mm., $d_4^{22\cdot4}$ 0·983385, $n_D^{22\cdot4}$ 1·49756, $[R_L]_D$ 53·07 (*semicarbazone*, m. p. 202°). Oxidation of the ethylated ketone gave glutaric acid and 2-ethyl*cyclo*pentanone formed by decomposition of an acid, probably 2-ω-carboxybutyryl-2-ethyl-*cyclo*pentenone, with boiling water. The ethyl sodiocyanoacetate condensation gave a *cyano*-ester [type (II)], b. p. 164—165°/20 mm., which on hydrolysis furnished an *acid* [type (III)], m. p. 135° (*semicarbazone*, m. p. 2-*iso*Propylidene*cyclo*pentanone (semicarbazone, m. p. 217—218°; oxidation products, acetone and glutaric acid) on ethylation gave 2-*ethyl*-2-iso*propenyl*cyclo*pentanone*, b. p. 97—98°/20 mm., $d_4^{19\cdot7}$ 0·94132, $n_D^{19\cdot7}$ 1·47892, $[R_L]_D$ 45·84 (*semicarbazone*, m. p. 199°; oxidation gave formic acid and probably δ-acetylheptoic acid, identified as the *semicarbazone*, m. p. 141—142°). Ethyl sodiocyanoacetate yielded a *cyano*-ester, b. p. 135°/20 mm., which on hydrolysis gave an *acid*, m. p. 133°. Camphorphorone on ethylation gave 5-*methyl*-2-*ethyl*-2-iso*propenyl*cyclo*pentanone*, b. p. 95—96°/16 mm., $d_4^{18\cdot5}$ 0·91131, $n_D^{18\cdot7}$ 1·46533, $[R_L]_D$ 50·46 (*semicarbazone*, m. p. 184°; oxidation products, formic acid, and δ-acetyl-α-methylheptoic acid, identified as *semicarbazone*, m. p. 147—148°). An *acid*, m. p. 135°, was obtained from the cyanoacetate condensation. Both pulegone and *iso*pulegone, on methylation give 2 : 5-*dimethyl*-2-iso*propenyl*cyclo*hexanone* (2-*methyl*iso*pulegone*), b. p. 108°/19 mm., $d_4^{18\cdot8}$ 0·92081, 1·47163, $[R_L]_D$ 50·51, $[\alpha]_D$ (in alcohol) −122·1° (*semicarbazone*, m. p. 203—204°), whilst condensation with ethyl sodiocyanoacetate gives a cyanolactone. This on hydrolysis yields an imide, m. p. 129°. 5-*Methyl*-2-*ethyl*-2-iso*propenyl*cyclo*hexanone* has b. p. 110°/15 mm., $d_4^{19\cdot1}$ 0·90362, $n_D^{19\cdot1}$ 1·46433, $[R_L]_D$ 55·05, $[\alpha]_D$ (in alcohol) −174·0° (*semicarbazone*, m. p. 207—208°).

*iso*Pulegone is lævorotatory when prepared from pulegone hydrobromide, whereas the natural ketone is dextrorotatory. The results show that the cyclic ketones examined react both as αβ- and βγ-unsaturated ketones. H. BURTON.

Condensations of *p*-dimethylaminobenzaldehyde with special reference to *p*-dimethylaminobenzylideneacetone and its reduction products. H. THOMS and H. SEEBE (Z. angew. Chem., 1926, 39, 1464—1465).—The observation of Meyer and Beer (A., 1913, i, 617) that *p*-dimethylaminobenzaldehyde undergoes the Perkin condensation only in presence of potassium acetate, not the sodium salt, is confirmed. From this and other evidence on condensations with aldehydes and ketones to give *p*-dimethylaminocinnamaldehyde and *p*-dimethylaminostyryl methyl ketone, it is concluded that the introduction of the *p*-dimethylamino-group reduces the reactivity of benzaldehyde, particularly in the case of the cinnamic acid synthesis, and causes a corresponding tendency to form by-products. *p*-Dimethylaminostyryl methyl ketone gives only normal oximes, semicarbazones, and phenylhydrazones, the double linking in the side-chain giving no reaction, as in the case of many αβ-unsaturated ketones. Reduction of this compound with sodium and amyl alcohol gives α-p-*dimethylaminophenylbutan-γ-ol*, whilst reduction with sodium amalgam in weak acetic acid solution under pressure gives a trace of that alcohol, 80% of β-p-*dimethylaminophenylethyl methyl ketone*, and 10—20% of δε-*di*-p-*dimethylaminophenyloctane*-βη-*dione*. Besides these was found a trace of a yellow *product*, m. p. 190°, not further investigated. E. HOLMES.

Semipinacolic transformations; comparative stability of secondary and tertiary hydroxyl groups. M. TIFFENEAU and J. LEVY (Compt. rend., 1926, **183**, 1112—1114).—Since αγ-diphenyl-β-benzylpropane-αβ-diol and γ-phenyl-α-anisyl-β-benzylpropane-αβ-diol when treated with sulphuric acid of any concentration, and the latter when simply

heated, yield only the corresponding ketone, in accordance with the scheme $CHAr(OH)\cdot CR_2\cdot OH \longrightarrow CHAr\cdot CR_2O^- \longrightarrow CHArR\cdot CO\cdot R$ (I), and no aldehyde, in accordance with the scheme $CHAr(OH)\cdot CR_2\cdot OH \longrightarrow CHArO\cdot CR_2 \longrightarrow CArR_2\cdot CHO$ (II) (cf. Orekhov, A., 1919, i, 271); and since α-phenyl-β-methylbutane-αβ-diol yields the ketone with concentrated sulphuric acid, the aldehyde with 8% sulphuric acid, and a mixture with acids of intermediate concentrations, the semipinacolic mechanism (I) for the formation of the ketones is probably correct, since the conversions of trisubstituted aldehydes into ketones (Orékhoff and Tiffeneau, *ibid.*, 1926, 171) occurs only on treatment with concentrated sulphuric acid. The following compounds are obtained: *benzyl* β-*phenyl*-α-*anisylethyl ketone* (*oxime*, m. p. 90—91°; *semicarbazone*, m. p. 138—139°); β-*phenyl*-αβ-*dimethylpropaldehyde*, b. p. 228—230° (*semicarbazone*, m. p. 158—159°). J. W. Baker.

Dehydration of *cyclo*hexylhydrobenzoin and the isomerisation of aldehydes to ketones. S. Danilov (J. Russ. Phys. Chem. Soc., 1926, **58**, 129—147).—Another account of work described elsewhere (A., 1926, 519—520). Benzhydryl *cyclo*hexyl ketone (αα-diphenyl-β-*cyclo*hexylethan-β-one, *loc. cit.*) forms an *oxime*, m. p. 164°, and a *semicarbazone*, m. p. 213°. M. Zvegintzov.

α-Phenyl ββ-di-*p*-tolylethylene glycol and di-*p*-tolylacetophenone. S. Danilov (J. Russ. Phys. Chem. Soc., 1926, **58**, 148—155; cf. A., 1926, 519, 726).—α-*Phenyl* ββ-*di*-p-*tolylethylene glycol*, m. p. 157°, prepared from methyl mandelate and magnesium *p*-tolyl bromide, on dehydration with dilute sulphuric or oxalic acid, gives only traces of the expected phenyldi-*p*-tolylacetaldehyde, but almost exclusively the ketone, *di*-p-*tolylacetophenone*, m. p. 57·5°, decomp. to benzoic acid and di-*p*-tolylmethane by alcoholic potassium hydroxide, giving an *oxime*, m. p. 188°, and a *semicarbazone*, m. p. 186°, which seems to exist in two isomeric forms. This behaviour is in accordance with the author's theory that the acid nature of groups, as shown by the conductivities of the acids they form, determines the mechanism of glycol dehydration. Groups which give acids having approximately the same conductivity do not tend to migrate, when present together, even if they belong to the aromatic series, which, in general, favour structural changes. M. Zvegintzov.

ω-Chloro-*o*-hydroxyacetophenone. K. von Auwers and M. Leo (Ber., 1926, **59**, [*B*], 2899).—ω-Chloro-*o*-hydroxyacetophenone has m. p. 73—74°, in agreement with the observations of Fries and Pfaffendorff (A., 1910, i, 149). The product, m. p. 101°, described as such by Tutin (J.C.S., 1910, **97**, 2503) is coumaranone. H. Wren.

Syntheses of chalkones. H. Simonis and C. Lear (Ber., 1926, **59**, [*B*], 2908—2913).—Phenolic ethers, particularly those containing a substituent in the *para*-position to the alkoxy-group, are converted by suitable acid chlorides in the presence of aluminium chloride (1 mol.) into alkylated chalkones; the use of a further mol. of aluminium chloride causes removal of the alkyl group, with production of the chalkone. Thus *p*-tolyl methyl ether, cinnamoyl chloride, and aluminium chloride afford 4-*methoxy*-m-*tolyl styryl ketone*, m. p. 55—56°, and 4-hydroxy-*m*-tolyl styryl ketone, m. p. 111° (cf. Auwers and Doll, A., 1920, i, 871). Quinol diethyl ether gives 2-*hydroxy*-5-*ethoxyphenyl styryl ketone*, m. p. 83°, converted by sodium hydroxide into 6-ethoxyflavanone. *p*-Tolyl methyl ether, phenylpropiolyl chloride, and aluminium chloride in molecular proportions give 4-*methoxy*-m-*tolyl* β-*phenylethinyl ketone*, m. p. 62°, whereas with a double proportion of aluminium chloride, 4-*methoxy*-m-*tolyl* β-*chlorostyryl ketone*, m. p. 95·5°, is obtained; the latter compound is converted by dilute sodium hydroxide into 6-methylflavone. H. Wren.

Applicability of the Friedel–Crafts reaction to the production of flavones. H. Simonis and S. Danischewski (Ber., 1926, **59**, [*B*], 2914—2919; cf. preceding abstract).—Quinol dimethyl ether, aluminium chloride, and cinnamoyl chloride yield 2 : 5-*dimethoxyphenyl styryl ketone*, m. p. 43°, which is converted by aluminium chloride in presence of benzene into 2-*hydroxy*-5-*methoxyphenyl styryl ketone*, m. p. 49°, transformed by alkali hydroxide into 6-methoxyflavanone. 2 : ο-*Dimethoxyphenyl* β-*phenylethinyl ketone*, m. p. 57°, is converted by aluminium chloride into 2-*hydroxy*-5-*methoxyphenyl* β-*chlorostyryl ketone*, m. p. 90°, or, if hydrogen chloride is also used, into an isomeric *ketone*, m. p. 80°; both ketones are transformed by sodium hydroxide into 6-*methoxyflavone*, m. p. 154°. Resorcinol dimethyl ether and cinnamoyl chloride afford 2 : 6-*dimethoxyphenyl styryl ketone*, m. p. 80°, and thence 2-*hydroxy*-6-*methoxyphenyl styryl ketone*, m. p. 105°, which could not be converted into the corresponding flavanone. 2-*Hydroxy*-6-*methoxyphenyl* β-*chlorostyryl ketone*, m. p. 95°, and 5-*methoxyflavone*, m. p. 133°, are described. 2-*Methoxy*-5 : 6-*dimethylphenyl styryl ketone*, m. p. 78°, is demethylated to 2-*hydroxy*-ο : 6-*dimethylphenyl styryl ketone*, m. p. 116°, which is with difficulty transformable into 5 : 6-*dimethylflavanone*, m. p. 89°. 2-*Hydroxy*-3 : 5-*dimethylphenyl styryl ketone*, m. p. 78°, readily yields 6 : 8-*dimethylflavanone*, m. p. 108°. H. Wren.

Formation of chloranil from aromatic compounds. L. Denis (Bull. Soc. chim. Belg., 1926, **35**, 375—379).—In continuation of work by Michiels and Hingot (Bull. Acad. roy. med. Belg., 1925, 213). the author finds that chloranil is also produced by the action of hydrochloric acid and potassium chlorate on *p*-hydroxybenzoic, 2 : 5-dihydroxybenzoic, and picrolonic acids. The introduction of a nitro-group into benzoic acid or benzaldehyde inhibits the reaction, negative results being obtained with the three nitrobenzoic acids and nitrobenzaldehydes, 2 : 4 : 6-trinitro- and 2 : 4-dinitro-benzoic acids. Similarly, nitro-*p*-cresol and the nitro-*o*- and -*p*-toluidines all give a negative test. None of the nitrotoluenes or nitroxylenes examined affords chloranil in this way, and negative results are similarly obtained with trinitrobenzene, tetrabromo-*p*- and -*m*-xylene, neutral-red, 2-nitroresorcinol, 2 : 4 : 6-trinitroresorcinol, *p*- and *m*-nitrocinnamic acids, 2 : 4-dihydroxybenzoic acid, and 2 : 4-dinitro-α-naphthol. On the other hand, a positive chloranil reaction is obtained with

the three nitroanilines and nitrophenols, with 2 : 4-dinitroaniline, *o*- and *p*-nitroacetanilides, *o*- and *p*-nitroanisole, with alizarin-yellow-GG, and with nitron. Of the three dihydroxybenzenes, only quinol gives a positive reaction. R. BRIGHTMAN.

Alkylation of hydroxynaphthaquinone. II. Carbon alkylation. L. F. FIESER (J. Amer. Chem. Soc., 1926, 48, 3201—3214; cf. this vol., 59).—Whilst alkylation of hydroxynaphthaquinone (through the silver salt) by means of saturated alkyl halides leads to one or both of the isomeric *O*-ethers, similar reaction with allyl, benzyl, and diphenylmethyl halides yields, in addition, *C*-alkyl derivatives, whilst triphenylmethyl and cinnamyl halides yield the *C*-alkyl derivative exclusively. Treatment of the silver salt of hydroxynaphthaquinone with allyl bromide in boiling benzene affords mainly 4-*allyloxy*-β-*naphthaquinone*, m. p. 125°, with 2-*allyloxy*-α-*naphthaquinone*, m. p. 98·5°, and 3-*hydroxy*-2-*allyl*-α-*naphthaquinone* (I), yellow, m. p. 116°, which is also produced, exothermically, when either of the isomeric *O*-ethers is heated above the m. p. A normal acetyl derivative of (I) could not be obtained. When treated with acetic anhydride and sodium acetate, (I) yields a *compound*, $C_{17}H_{14}O_5$, the reaction being apparently analogous to that recorded for lapachol by Paterno and Minnuni (A., 1890, 607) and Hooker (J.C.S., 1892, **61**, 611). Reduction of (I) with zinc dust and acetic acid in presence of acetic anhydride affords the corresponding *quinol triacetate*, m. p. 155·5°, whilst heating with hydrochloric and acetic acids yields 3-*hydroxy*-2-β-*chloropropyl*-α-*naphthaquinone*, yellow, m. p. 147° (*acetyl* derivative, m. p. 102°) (cf. Hooker, *loc. cit.*), together with 1-*methyl*-4 : 5-*benzocoumaran*-3 : 6-*quinone*, yellow, m. p. 166—167°, which is also formed to a slight extent when the above chloro-derivative is boiled in glacial acetic acid. Treatment of (I) with cold, concentrated sulphuric acid affords 1-*methyl*-5 : 6-*benzocoumaran*-3 : 4-*quinone*, red, m. p. 133·5°, which is also obtained from the above chloro-derivative by the action of sulphuric acid at 80°, and is converted into the chloro-derivative by treatment with hydrochloric acid at 55°, whilst the action of cold alkali affords 3-*hydroxy*-2-β-*hydroxypropyl*-α-*naphthaquinone*, yellow, m. p. 108—110° (*acetyl* derivative, m. p. 127°). Benzyl chloride and the silver salt of hydroxynaphthaquinone yield analogously 4-*benzyloxy*-β-*naphthaquinone*, orange-yellow, m. p. 182·5°, 2-*benzyloxy*-α-*naphthaquinone*, yellow, m. p. 145°, and 3-*hydroxy*-2-*benzyl*-α-*naphthaquinone*, golden-yellow, m. p. 175—176°. Diphenylmethyl bromide yields similarly 2-*diphenylmethoxy*-α-*naphthaquinone*, yellow, m. p. 150—151°, and 3-*hydroxy*-2-*diphenylmethyl*-α-*naphthaquinone*, yellow, m. p. 186·5° (*acetyl* derivative, m. p. 170·5°; *quinol triacetate*, m. p. 215°), the latter being also obtained by boiling hydroxynaphthaquinone with benzhydrol in glacial acetic acid in presence of sulphuric acid (cf. Mohlau and Klopfer, A., 1899, i, 912). 3-*Hydroxy*-2-*triphenylmethyl*-α-*naphthaquinone*, yellow, m. p. 211° (decomp.) (*sodium* salt, red), is obtained as above. Treatment of the silver salt of hydroxynaphthaquinone with cinnamyl chloride and sodium carbonate in cold benzene affords 3-*hydroxy*-2-*cinnamyl*-α-*naphthaquinone*, yellow, m. p. 170°, which, when treated with cold, concentrated sulphuric acid, yields what is probably 2-*phenyl*-7 : 8-*benzochroman*-5 : 6-*quinone*, red, m. p. 167°. F. G. WILLSON.

Derivatives of naphthaquinones [1-imino-4-arylimino-2-hydroxy-α-naphthaquinones]. SOC. ANON. DES MAT. COL. ET PROD. CHIM. DE ST.-DENIS, R. LANTZ, and A. WAHL.—See B., 1927, 39.

Preparation of 1 : 4-dichloroanthraquinone from phthalic anhydride and *p*-dichlorobenzene. M. PHILLIPS (J. Amer. Chem. Soc., 1926, 48, 3198—3199).—Phthalic anhydride (1 mol.) is heated with *p*-dichlorobenzene (0·5 mol.) and aluminium chloride (1·5 mol.) at 110—120° for about 4 hrs. The product, o-2′ : 5′-*dichlorobenzoylbenzoic acid*, m. p. 169°, is isolated and heated with excess of sulphuric acid at 150° for 4 hrs., when an 83% yield of 1 : 4-dichloroanthraquinone, m. p. 187·5°, is obtained (cf. Ullmann and Billig, A., 1911, i, 490). F. G. WILLSON.

Fritzsch's reagent [β-dinitroanthraquinone]. E. BORNSTEIN, H. SCHLIEWIENSKY, and S. V. SZCZESNY-HEYL (Ber., 1926, 59, [*B*], 2812—2815).—β-Dinitroanthraquinone, m. p. 290—291° (decomp.), prepared by the action of nitric acid on anthracene, gives additive *compounds* containing the components in equimolecular ratio with the following substances: anthracene, m. p. 263—264°; 1-methylanthracene, m. p. 259°; 2-methylanthracene, m. p. 219°; 1 : 6(or 1 : 7)-dimethylanthracene, m. p. 224—225°; 1 : 3 : 6 : 8-tetramethylanthraquinone, m. p. 260—261° (decomp.); dibromo-2-methylanthracene, m. p. 241° (decomp.); phenanthrene, m. p. 218—219°; acenaphthene, m. p. 227—230°; carbazole, m. p. 260—261°; stilbene, m. p. 248°; chrysene, m. p. 302—303°; retene, m. p. 225—226°; diphenylamine, m. p. 243—244° (decomp.); di-*p*-tolylamine, m. p. 212—213°; di-β-naphthylamine, m. p. 176—177°; xenylamine (diphenylylamine), m. p. 241°; benzidine, m. p. 240—241°; *o*-tolidine, m. p. 202°. It does not form additive compounds with diphenyl, di-*p*-tolyl, fluorene, di- or tri-phenylmethane, naphthalene, tetra- or deca-hydronaphthalene, acetophenone, benzophenone, coumarin, isatin, azobenzene, azoxybenzene, diphenyl sulphide, sulphoxide, or sulphone, diphenol sulphide, carbanilide, thiocarbanilide, pyridine, quinoline, indole, acridine, the three phenylenediamines, and naphthidine. H. WREN.

Genetic relationship of aliphatic to cyclic perfumes; geraniol. H. THOMS (Oesterr. Chem.-Ztg., 1926, 29, 228—229).—When geraniol is heated with 20% sulphuric acid at 200—210° for 6 hrs., or when it is stirred with three times its weight of 65% sulphuric acid at −15° and the product heated to 60°, it yields a *hydrocarbon*, b. p. 183—195°/16 mm., 147—152°/3 mm., d^{20} 0·9116, n_D^{19} 1·50338, which corresponds in its physical properties with a sesquiterpene. On catalytic reduction with palladium, it yields a *tetrahydro*-derivative, $C_{15}H_{28}$, b. p. 175—180°/16 mm., d^{20} 0·8758, n_D 1·47547. The unsaturated hydrocarbon yields an unstable *tetrabromide*, which spontaneously loses hydrogen bromide. J. W. BAKER.

Dehydrogenation of menthol. G. CUSMANO (Atti R. Accad. Lincei, 1926, [vi], 4, 385—387).—

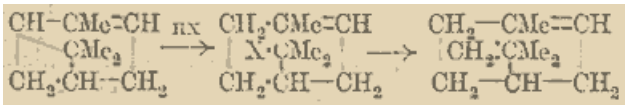
When a solution of sodium in fused menthol is heated at about 300°, hydrogen is evolved in large proportion, the sodium menthoxide losing two atoms of hydrogen to give a sodiomenthone, which afterwards gives up four hydrogen atoms to form sodium thymoxide, possibly by way of a menthenone derivative.

T. H. POPE.

Terpene and sesquiterpene of Mitsubazeri. N. HIRANO (Sci. Rep. Tohoku, 1926, 15, 661—670).—See A., 1926, 408.

Liquid hydrochlorides of pinene. M. DELEPINE and C. CACHAT (Bull. Soc. chim., 1926, [iv], 39, 1745—1755).—Repeated fractional distillation has established the presence of limonene and limonene hydrochloride in the "liquid hydrochloride" obtained in the treatment of Aleppo turpentine (α +41·8°) with hydrogen chloride in the cold or in alcoholic solution, in addition to the products previously observed (cf. A., 1907, i, 630; 1910, i, 400; 1921, i, 795; 1924, i, 1084, 1088; 1926, 1042). R. BRIGHTMAN.

Hydration of nopinene. II. G. AUSTERWEIL and (MLLE.) O. PETROVICI (Bull. Soc. chim., 1926, [iv], 39, 1732—1744; cf. A., 1926, 619).—The reaction between nopinene and organic acids affording bornyl esters is bimolecular, involving addition at the double linking and at the ruptured bridge linkings; it is always accompanied by a unimolecular reaction, affording *l*-α-pinene by addition of 1 mol. of acid at the double linking. The latter reaction is the first stage in the formation of monocyclic terpenes, the latter being produced from pinene according to the scheme:



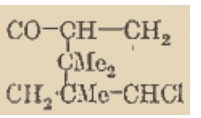
Dilution of the organic acid with a neutral solvent such as toluene almost completely suppresses the formation of monocyclic terpenes, and the reaction product consists of *l*-pinene and bornyl esters. These facts support the view that the hemicyclic double linking in nopinene is more reactive than the bridge linking. Under conditions in which nopinene affords bornyl ethers and *l*-pinene, pinene alone affords neither bornyl ethers nor monocyclic terpenes.

R. BRIGHTMAN.

Nitrogenous derivatives of terpene alcohols [bornyl and menthyl pyridinecarboxylates]. R. WOLFFENSTEIN.—See B., 1927, 28.

Essence of camphor. VI. Dehydration of cyclic terpene alcohols by Japanese acid earth. K. ONO (Bull. Chem. Soc. Japan, 1926, 1, 248—252).—The following products were isolated on dehydrating certain cyclic terpene alcohols with Japanese fuller's earth: dipentene and α-terpineol from terpin hydrate; dipentene from liquid terpineol; *l*-menthene from *l*-menthol; crystalline *d*-camphene and a liquid *d*-camphene from *d*-borneol. S. J. GREGG.

Chromic acid oxidation of bornyl chloride to *p*-ketobornyl chloride. J. BREDT and P. PINTEN (J. pr. Chem., 1927, [ii], **115**, 45—55).—Oxidation of bornyl chloride in acetic acid solution with potassium dichromate and sulphuric acid at 60—70° yields *p*-ketobornyl chloride (annexed formula), m. p. 158° (*semicarbazone*, m. p. 259°), in 10—30% yield, according to the conditions, the effect of varying these being investigated in some detail. The constitution of the product is proved by its reduction with sodium and boiling alcohol to *epi*borneol (*acetate*, b. p. 114°/19 mm., d_4^{14} 0·988, $[\alpha]^{15}$ +15·63°), which is oxidised by chromic and acetic acids to *epi*camphor (*semicarbazone*, m. p. 236—237°; oxime, m. p. 103°). The optical activity of the products obtained varied with the specimens of pinene used for the original preparation of the bornyl chloride. J. W. BAKER.



Co-ordinated mercaptides. A. M. DRUMMOND and D. T. GIBSON (J.C.S., 1926, 3073—3077).—The metallic derivatives of mercaptans containing the CO group are not of the simple type RSM′, but are co-ordinated ring compounds, showing non-ionisable character, solubility in anhydrous organic solvents, anomalous colour, and, in certain cases, stability towards heat.

Thiolcamphor [*cadmibromide*, $C_{10}H_{15}OBrSCd$; *stannochloride*, $(C_{10}H_{15}OSH)_3,Sn_2Cl_4$, m. p. 187°], yields, on treatment with alcoholic silver nitrate, *silver thiolcamphor argentinitrate*, $C_{10}H_{15}O{\cdot}SAg,AgNO_3,H_2O$, charring at 200—210°, $[\alpha]_{5461}^{v}$ +21° in chloroform. This substance reacts with a solution of thiolcamphor in dry benzene, giving a *compound*, $(C_{10}H_{15}O{\cdot}SAg)_2,AgNO_3,H_2O$, decomp. above 230°, $[\alpha]_{5461}$ +64° in chloroform. The following are also described: *nickel thiolcamphor*, $(C_{10}H_{15}O{\cdot}S)_2Ni,C_{10}H_{15}O{\cdot}SH$; *methyl* β-*thiolpropionate*, b. p. 54—55°/14 mm., n^{19} 1·4628, giving *methyl silver* β-*thiolpropionate argentinitrate*, $C_4H_7O_2{\cdot}AgS,AgNO_3{\cdot}H_2O$, and *methyl nickel* β-*thiolpropionate*, $(C_4H_7O_2S)_2Ni$. The five-membered ring compound, *ethyl nickel thiolacetate*, $\left(CH_2<\begin{matrix}C(OEt):O\\ S\end{matrix}\!\!>\right)$ Ni, shows greater stability than the six-membered ring compounds, melting without decomposition at 101°. *Nickel* β-*thiolpropionate*, $(C_3H_5O_2S)_2Ni$, resembles the previous compounds in colour only and is insoluble in organic solvents.

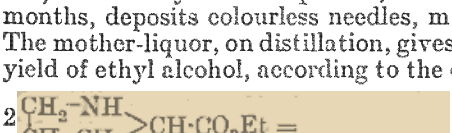
An improved method for the preparation of thiolcamphor is described. M. CLARK.

Ring opening and closing in coumarandione derivatives. K. VON AUWERS and W. HERBENER (J. pr. Chem., 1926, [ii], **114**, 313—336; cf. A., 1908, i, 477; 1911, i, 168).—4 : 6-Dimethylcoumaran-3-one and benzenediazonium chloride in acetic acid solution yield orange-red 4 : 6-*dimethylcoumaran*-2 : 3-*dione*-2-*phenylhydrazone*, m. p. 155—156°. This does not further react with phenylhydrazine. Benzoylation in hot pyridine converts it into the as-*benzoylphenylhydrazone*, m. p. 182—183°, the constitution of which is proved by its quantitative reduction to benzanilide. 4 : 6-Dimethylcoumarandione and phenylhydrazine acetate give the 3-*phenylhydrazone*, m. p. 151—152°, which is hydrolysed by cold 2% alcoholic sodium hydroxide to 2-*hydroxy* : 6-*dimethylphenylglyoxylic acid phenylhydrazone*, m. p. 117°, the reverse change being brought about by heating or desiccation. The

3-benzoylphenylhydrazone, 3-acetylphenylhydrazone, and 3-anil of 4 : 6-dimethylcoumarandione could not be prepared; even in anhydrous solvents the corresponding *derivatives* of 2-hydroxy-4 : 6-dimethylphenylglyoxylic acid, m. p. 96—98°, 141—142°, and 123—124°, respectively, are obtained. The *benzoylphenylhydrazone*, m. p. 147°, and *anil*, m. p. 110—111°, of methyl 2-methoxy-4 : 6-dimethylphenylglyoxylate are unexpectedly resistant towards hydrolysis. 4 : 6-*Dimethylcoumarandione*-3-*methylphenylhydrazone*, m. p. 142°, is immediately soluble in aqueous sodium hydroxide; the free acid rapidly undergoes lactonisation. The corresponding *benzylphenylhydrazone*, m. p. 148—150°, was obtained as a mixture of lactone and free acid. 2-*Hydroxy*-4 : 6-*dimethylphenylglyoxanilide anil*, m. p. 194—195°; 2-*hydroxyphenylglyoxylic acid benzoylphenylhydrazone*, m. p. 60—70°, and *anil-anilide*, m. p. 177—178°, and *ethyl* 2-*hydroxyphenylglyoxylate*-p-*nitrophenylhydrazone*, m. p. 129—130°, are described. The factors affecting the stability of the lactone rings in the above compounds and the corresponding ones from coumarandione and its 5-methyl derivative (*ibid.*, 1911, i, 585; 1912, i, 204) are fully discussed.

[In part with W. Gaertner].—In order to prove that *o*-hydroxyphenylglyoxylic acids have not the constitution of 2 : 2-dihydroxycoumaran-3-ones, some pairs of mixed ether-esters have been prepared. 2-*Methoxy*-5-*methylphenylglyoxylic acid*, m. p. 114—115°, affords a liquid *ethyl* ester, b. p. 168—170°/11 mm.; 2-*ethoxy*-5-*methylphenylglyoxylic acid*, m. p. 142—143°, yields a *methyl* ester, m. p. 53°. If the cyclic formula is correct, these should have been identical. This formula also fails to explain the rapid lactonisation of 2-hydroxy-4 : 6-dimethylglyoxylic acid in presence of water (A., 1921, i, 578). 2-*Methoxy*-4 : 6-*dimethylphenylglyoxylic acid*, m. p. 126—127° (*methyl* ester, m. p. 48°; *ethyl* ester, b. p. 180°/15 mm.), gives a *benzoylphenylhydrazone*, m. p. 143—144°, which is converted through the *silver* salt into a *methyl* ester, m. p. 147°, identical with that obtained above from dimethylcoumarandione. 2-*Ethoxy*-4 : 6-*dimethylphenylglyoxylic acid*, m. p. 141—142° (*methyl* ester, m. p. 85—86°), decomposes on distillation in a vacuum into 3 : 5-dimethylphenetole and 2-*ethoxy*-4 : 6-*dimethylbenzoic acid*, m. p. 125—126°. H. E. F. Notton.

Derivatives of pyrrole. Pyrrolidine. N. J. Putochin (J. Russ. Phys. Chem. Soc., 1926, 58, 119—121).—The ethyl ester of proline, on keeping for 2—3 months, deposits colourless needles, m. p. 183—184°. The mother-liquor, on distillation, gives a quantitative yield of ethyl alcohol, according to the equation :



The acid amide, m. p. 92—93°, and *α-pyrrylmethylamine*, b. p. 96°/6 mm., 1·5533, d_4^{18} 1·064, were also prepared. M. Zvegintzov.

Hydrogenated phenylquinolines and determination of the constitution of "decahydroatophan." A. Skita and C. Wulff [with C. Fehr, W. Winterhalder, and A. Meetz] (Ber., 1926. 59, [*B*], 2683—2691; cf. A., 1916, i, 835).—2-Phenylquinoline-4-carboxylic acid (atophan) is converted by hydrogen at 1—1½ atm. pressure in glacial acetic acid in the presence of colloidal platinum into 2-*phenyl*-1 : 2 : 3 : 4-*tetrahydroquinoline*-4-*carboxylic acid*, m. p. 163—165° (*hydrochloride*, m. p. 235°; *nitroso*-compound, m. p. 110°; *acetyl* derivative, m. p. 193—194°; *ethyl* ester, b. p. 170—180°/0·25 mm.). The acid is converted by distillation with soda-lime into 2-phenyl-1 : 2 : 3 : 4-tetrahydroquinoline, b. p. 341—343° (*benzoyl* derivative, m. p. 101°), obtained also by hydrogenation of 2-phenylquinoline under 2 atm. in presence of colloidal platinum.

The action of hexahydrobenzaldehyde and pyruvic acid on aniline in boiling alcoholic solution yields 2-cyclo*hexylquinoline*-4-*carboxylic acid*, m. p. 137° (*methyl* ester, m. p. 54—55°), and a *substance*, m. p. 230°; the acid, which is also obtained from pyruvic acid and *hexahydrobenzylideneaniline*, b. p. 179°/70 mm., is decarboxylated to 2-cyclo*hexylquinoline*, b. p. 180—183°/20 mm.

Catalytic hydrogenation of atophan under 3 atm. affords 2-*cyclo*hexyl-1 : 2 : 3 : 4-tetrahydroquinoline-4-carboxylic acid (decahydroatophan, *loc. cit.*); the *nitroso*-derivative, m. p. 89°, *acetyl* compound, m. p. above 300°, *amide*, m. p. 156°, *methyl* ester, m. p. 71°, and *ethyl* ester, b. p. 165—173°/0·5 mm., are described. Decarboxylation of the acid affords 2-cyclo*hexyl*-1 : 2 : 3 : 4-*tetrahydroquinoline*, b. p. 314—315° (non-crystalline *nitroso*-derivative; *benzoyl* compound, m. p. 134°; *picrate*, m. p. 204°), also prepared by hydrogenation of 2-phenylquinoline in presence of colloidal platinum at 60° and 3 atm. or, with greater difficulty, from 2-*cyclo*hexylquinoline in presence of spongy platinum.

Hydrogenation of atophan usually ceases at the decahydro-stage, but if fresh platinum is then added, 2-cyclo*hexyldecahydroquinoline*-4-*carboxylic acid* (perhydroatophan), m. p. above 300°, is obtained; the *nitroso*-derivative, decomp. 69°, *ethyl* ester, m. p. 62—63°, and its *hydrochloride*, m. p. 269°, are described. Decarboxylation of the acid gives 2-cyclo*hexyldecahydroquinoline*, b. p. 165°/13 mm. (hygroscopic *hydrochloride*; *nitroso*-derivative, m. p. 179°), also obtained by hydrogenation of 2-phenylquinoline in presence of colloidal platinum at 3 atm. and 60°.

Benzaldehyde and cyclo*hexylamine* yield *benzylidene*cyclo*hexylamine*, b. p. 136°/16 mm. (cyclo*hexylamine benzoate*, m. p. 169°, is incidentally described). With pyruvic acid, benzylidene*cyclo*hexylamine yields a *compound*, $C_{16}H_{19}O_2N$, m. p. 144°, which is readily hydrolysed to benzaldehyde and *cyclo*hexylamine.

H. Wren.

Homologues of indole in coal tar. O. Kruber (Ber., 1926, 59, [*B*], 2752—2760).—The presence of 2-, 3-, 5-, and 7-methylindole in coal tar is established. The residues obtained from the technical isolation of indole are fractionally distilled under reduced pressure. The individual fractions are converted successively into their sodium derivatives and carboxylic acids. The latter compounds are purified by crystallisation and subsequently decarboxylated to the parent indoles. The following new compounds are described : 7-*methylindole*-3-*carboxylic acid*, m. p.

228° (decomp.); 7-*methylindole*, b. p. 266°, m. p. 85° (*picrate*, m. p. 176°); 1-*benzoyl*-7-*methylindole*, m. p. 84°, obtained in very poor yield from benzoyl chloride and the sodium derivative of 7-methylindole and oxidised by permanganate to 2-*benzamido*-m-*toluic acid*, m. p. 178°. The constitution of 7-methylindole is established as follows: 7-methylindole-3-carboxylic acid is reduced by sodium and alcohol to 7-*methyl*-2 : 3-*dihydroindole*-3-*carboxylic acid*, m. p. 237°, from which 7-*methyl*-2 : 3-*dihydroindole*, b. p. 120—122°/10 mm., d_4^{20} 1·044, is prepared (*picrate*, m. p. 186°; *hydrochloride*, m. p. 199—200°; *benzenesulphonyl* derivative, m. p. 131°; *benzoyl* derivative, m. p. 106°). The acid is readily transformed by benzoyl chloride in presence of sodium hydrogen carbonate into 1-*benzoyl*-7-*methyl*-2 : 3-*dihydroindole*-3-*carboxylic acid*, m. p. 163—164°, oxidised by permanganate to 2-*benzamidoisophthalic acid*, m. p. 217—218° (also *dihydrate*), whence 2-amino*iso*phthalic acid, m. p. above 340° (*methyl* ester, m. p. 103—104°); the latter acid is identical with that prepared by reduction of 2-nitro*iso*phthalic acid, obtained by oxidation of 2-nitro-*m*-xylene. 7-Methylindole is obtained synthetically by converting the *o*-tolylhydrazone of ethyl pyruvate by means of zinc chloride into ethyl 7-methylindole-2-carboxylate and hydrolysis of the latter to 7-methylindole-2-carboxylic acid, m. p. 170°, followed by decarboxylation. 3-Methylindole is isolated through the sparingly soluble sodium salt of the corresponding carboxylic acid. 5-Methylindole, b. p. 267°, m. p. 65°, is obtained by decarboxylation of 5-*methylindole*-3-*carboxylic acid*, m. p. 202° (decomp.), and synthesised from the *p*-tolylhydrazone of ethyl pyruvate. 2-Methylindole-3-carboxylic acid has m. p. 190°. H. WREN.

3-Methoxy-2-phenylindole and 3-benzamido-2-phenylindole. R. ROBINSON and S. THORNLEY (J.C.S., 1926, 3144—3145).—3-*Methoxy*-2-*phenyl*-*indole*, m. p. 106°, and 3-*benzamido*-2-*phenylindole*, m. p. 206°, are readily obtained through the phenylhydrazones of ω-methoxyacetophenone and ω-benzamidoacetophenone, respectively, showing that Fischer's method can be extended to the synthesis of indole derivatives in which an oxygen or a nitrogen atom is directly attached to the pyrrole nucleus. *ω-Benzamidoacetophenonephenylhydrazone* has m. p. 153°. M. CLARK.

Reactions of aldehydes with magnesium [magnesyl] indole. Q. MINGOIA (Gazzetta, 1926, **56**, 772—781).—Aromatic aldehydes react with the magnesium compounds of indole and its derivatives to give substituted phenyldi-indolylmethanes. Magnesium indole yields with vanillin *di*-3-*indolyl*-p-*hydroxy*-m-*methoxyphenylmethane*, $(C_6H_4{:}C_2H_2N)_2CH{\cdot}C_6H_3(OH){\cdot}OMe$, m. p. 141—142°; with piperonal *di*-3-*indolylmethylenedioxyphenylmethane*, m. p. 89—91° (*diacetyl* derivative, m. p. 99—100°; *dibenzoyl* derivative, m. p. 70°); and with *m*-nitrobenzaldehyde *di*-3-*indolyl*-m-*nitrophenylmethane*, m. p. above 260°. The magnesium compound of 2-methylindole reacts with benzaldehyde to give *di*-2-*methylindolylphenylmethane*, m. p. 250—251°; with vanillin to give *di*-2-*methylindolyl*-p-*hydroxy*-m-*methoxyphenylmethane*, m. p. 220° (*triacetyl* derivative, m. p. 170°); with piperonal to give *di*-2-*methylindolylmethylenedioxyphenylmethane*, m. p. 211—213° (*diacetyl* derivative, m. p. 112°; *dibenzoyl* derivative, m. p. 135—140°), and with *m*-nitrobenzaldehyde to yield di-2-methylindolyl-*m*-nitrophenylmethane (m. p. 271°; cf. Fischer, A., 1888, 284). The magnesium compound of 3-methylindole reacts with piperonal to give a poor yield of *di*-3-*methylindolylmethylenedioxyphenylmethane*, m. p. 94°, and with *m*-nitrobenzaldehyde to give a little of a *substance*, m. p. 160° (decomp.), which is probably the corresponding di-indolylphenylmethane. G. M. BENNETT.

Syntheses by means of magnesium [magnesyl] pyrrole. II. Reactions with inorganic anhydrides and chloroanhydrides and formation and constitution of some sulphur derivatives of indole. B. ODDO and Q. MINGOIA (Gazzetta, 1926, **56**, 782—797).—Sulphuryl chloride reacts with magnesium pyrrole in ether to give dark brown, amorphous, insoluble products, whilst with magnesium indole the product is *di*-3-*indolylsulphone*, m. p. 151—152°, not reduced by zinc and acetic acid to a sulphide. *Di*-2-*methyl*-3-*indolylsulphone* (decomp.) results from the corresponding reaction using 2-methylindole. Magnesium indole reacts with sulphur dioxide to give di-indolylsulphoxide, m. p. 157° (Madelung and Tencer, A., 1915, i, 719), reduced by zinc and acetic acid to the corresponding sulphide, m. p. 232°, which is also formed as a by-product in the above reaction. Benzenediazonium chloride converts this sulphide into a *bisbenzeneazo*-derivative, m. p. 158°. The corresponding product from 2-methylindole is di-2-methyl-3-indolyl sulphide, m. p. 225—226°. Magnesium pyrrole reacts with carbon disulphide with production of *pyrrole*-2-*dithiocarbonic acid*, a reddish-brown oil (brick-red *lead* and greenish-yellow *mercury* salts described), which is readily oxidised in neutral solution to its *disulphide*, $[C_4H_4N{\cdot}CS{\cdot}S{\cdot}]_2$, m. p. 133°. In the same way, by the action of carbon disulphide on magnesium indole, *indole*-3-*dithiocarbonic acid* (*ammonium* and orange-red *lead* salts described) is obtained, which is readily oxidised to the *disulphide*, m. p. 155° (*bisbenzeneazo*-derivative, m. p. 107°), and is converted by fusion with potassium hydroxide into indole-3-carboxylic acid, m. p. 218°. From the magnesium compound of 2-methylindole there is obtained 2-*methylindole*-3-*dithiocarbonic acid* (*ammonium*, orange-yellow *lead*, and brick-red *mercury* salts described) and its *disulphide*, m. p. 183°. G. M. BENNETT.

[Condensation products of 2-aminopyridine with aliphatic-aromatic ketones.] L. SCHMID and B. BANGLER (Ber., 1926, **59**, [*B*], 2805).—A reply to Tschitschibabin (A., 1926, 1153).

Reducing nitro-compounds [3-nitropyridine]. I. G. FARBENIND. A.-G.—See B., 1927, 8.

Production of 5-nitro-2-hydrazinopyridine [5-nitro-2-pyridylhydrazine]. DEUTSCHE GOLD- & SILBER-SCHEIDEANSTALT.—See B., 1927, 29.

6-Methoxyquinoline. E. MASCHMANN (Ber., 1926, **59**, [*B*], 2825—2826).—6-Methoxyquinoline has b. p. 153°/12 mm., 284°/749 mm., m. p. 26·5°. The discoloration observed when it is preserved is caused

by light, particularly ultra-violet rays, and not by air. H. WREN.

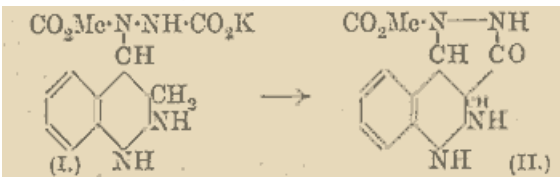
Quinoline derivatives. VI. 2-Phenylquinoline-4-carboxylic acid. H. JOHN [with V. FISCHL and E. WÜNSCHE] (Ber., 1926, 59, [*B*], 2709—2712).—Dry distillation of barium 2-phenylquinoline-4-carboxylate yields 2-phenylquinoline, m. p. 84°, and, apparently, *di-2-phenylquinolyl*, m. p. 303° (*hydrochloride*; *sulphate*; *nitrate*; additive *compound* with mercuric chloride; *chloroplatinate*, which does not melt below 300°; *picrate*, m. p. 234°). The product of high m. p. is also obtained by distillation of the lithium, ammonium, sodium, potassium, calcium, strontium, aluminium, and tin salts, but not from the magnesium, iron, copper, silver, zinc, cadmium, lead, or bismuth compounds. 4-Chloro-2-phenylquinoline is converted by copper powder in boiling nitrobenzene into 2-phenylquinoline, whereas distillation with zinc dust transforms it into the substance, m. p. 303°, in poor yield. H. WREN.

Behaviour of 2-substituted 8-methoxy-3-arylsulphonylquinolines towards nascent hydrogen. J. TRÖGER and F. KRÜCKEBERG (J. pr. Chem., 1926, [ii], **114**, 249—268).—The reactivity of 2-amino-3-arylsulphonylquinolines is decreased by the introduction of an 8-methoxyl group. Further study of the 2-amino-8-methoxy-3-arylsulphonylquinolines (cf. A., 1926, 68) shows that they do not form methiodides, that their *hydrochlorides* and *nitrates* decompose when heated at 105—120°, and that their *hydrogen sulphates* are hydrolysed by water. 2-Amino-8-methoxy-3-benzenesulphonylquinoline is converted by nitrous acid into 2-*hydroxy*-8-*methoxy*-3-*benzenesulphonylquinoline*, m. p. 250°. When the latter is heated at 150° with phosphorus pentachloride, it yields the corresponding 2-*chloro*-derivative, m. p. 195°. This does not react with metallic benzenesulphinates or thio-*p*-tolyloxides (cf. *ibid.*, 1924, i, 556), but with aniline, potassium hydrosulphide, and sodium ethoxide it affords 2-*anilino*-, m. p. 185°, 2-*thiol*-, m. p. 183°, and 2-*ethoxy*-8-*methoxy*-3-*benzenesulphonylquinoline*, m. p. 191°, respectively. The following derivatives are prepared by analogous methods: of 8-methoxy-3-*p*-toluenesulphonylquinoline: 2-*hydroxy*-, m. p. 262°; 2-*chloro*-, m. p. 197°; 2-*anilino*-, m. p. 187°; 2-*thiol*-, m. p. 186°; of 8-methoxy-3-*p*-chlorobenzenesulphonylquinoline: 2-*hydroxy*-, m. p. 275°; 2-*chloro*-, m. p. 212°; of 8-methoxy-3-*o*-anisolesulphonylquinoline: 2-*hydroxy*-, m. p. 237°; 2-*chloro*-, m. p. 188°; 2-*anilino*-, m. p. 184°; 2-*thiol*-, m. p. 189°; of 8-methoxy-3-*p*-phenetolesulphonylquinoline: 2-*hydroxy*-, m. p. 269°; 2-*chloro*-, m. p. 174°, and 2-*hydroxy*-8-*methoxy*-3-p-*bromobenzenesulphonylquinoline*, m. p. 262°. When reduced with tin and concentrated hydrochloric acid, these compounds behave in the usual way (cf. A., 1926, 524), the 2-substituent being removed in combination with hydrogen, the 3-arylsulphonyl-group as the corresponding arylthiophenol (75—80% yield), whilst the quinoline nucleus remains as 8-*methoxy*-1 : 2 : 3 : 4-*tetrahydroquinoline hydrochloride*, m. p. 220° (decomp.) (*benzoyl* derivative, m. p. 136°). The 2-hydroxy-8-methoxy-3-arylsulphonylquinolines, however, do not give a tetrahydroquinoline derivative. In this case, the methoxycarbostyril first produced probably resists further reduction. H. E. F. NOTTON.

Derivatives of acenaphthpyridine. I. S. U. NAIR and J. L. SIMONSEN (J.C.S., 1926, 3140—3143).—Whilst α-naphthylamine itself fails to condense with paracetaldehyde, its derivatives substituted in the 4-position readily undergo this reaction (cf. A., 1926, 1154). 5-Aminoacenaphthene reacts with paracetaldehyde in presence of hydrochloric acid to give 2-*methylacenaphthpyridine*, m. p. 131° (*hydrochloride*; *hydrobromide*; *picrate*, decomp. 225—226°; *chloroplatinate*, decomp. 251—252°), converted by reduction with sodium and ethyl alcohol into 2-*methyl*-1 : 2 : 3 : 4-*tetrahydroacenaphthpyridine*, m. p. 88—89°, b. p. 215—217°/14 mm. (*hydrochloride*, decomp. 260—261°; *benzoyl* derivative, m. p. 187—188°). 5-Aminoacenaphthene condenses with ethyl acetoacetate in alcoholic solution in presence of a trace of piperidine, giving *ethyl* β-5-*acenaphthylaminocrotonate*, m. p. 83—84°. When heated at 220°, this compound is converted into 4-*hydroxy*-2-*methylacenaphthpyridine*, m. p. above 330°. Condensation of 5-aminoacenaphthene and ethyl acetoacetate at 170° gives, besides a small quantity of s-*di*-5-*acenaphthylcarbamide*, m. p. 318°, β-5-*acenaphthylaminocroton*-5-*acenaphthylamide*, m. p. 189—190°, which is hydrolysed by dilute hydrochloric acid to 5-*acetoacetamidoacenaphthene*, m. p. 142—143°. This compound is converted by treatment with concentrated hydrochloric acid into 2-*hydroxy*-4-*methylacenaphthpyridine*, m. p. above 350° (*hydrochloride*). The hydroxy-compound reacts with phosphorus pentachloride to give 2-*chloro*-4-*methylacenaphthpyridine*, m. p. 200—201°, which yields on reduction with sodium and ethyl alcohol 4-*methyl*-1 : 2 : 3 : 4-*tetrahydroacenaphthpyridine*, m. p. 87—88° (*hydrobromide*). M. CLARK.

Causes of the "azo-ester reaction." O. DIELS and K. ALDER (Annalen, 1926, 450, 237—254; cf. Diels and others, A., 1925, i, 976).—An investigation of the 1 : 4 addition of azodicarboxylates to conjugated unsaturated hydrocarbons, a reaction which is considered to be a test for the presence of partial valencies in the 1 : 4 position. With isoprene, ethyl azodicarboxylate gives *ethyl* 5-*methyl*-1 : 2 : 3 : 6-*tetrahydro*-1 : 2-*pyridazine*-1 : 2-*dicarboxylate*, b. p. 115°/0·15 mm., which reacts violently with bromine. Ethyl azodicarbamidoacetate, $(CO_2Et{\cdot}CH_2{\cdot}NH{\cdot}CO{\cdot}N{:})_2$ (Blom., Diss., Kiel, 1923), gives the corresponding 1 : 2-*dicarbamidoacetate*, m. p. 158°, which with bromine forms *ethyl* 4 : 5-*dibromo*-4-*methylhexahydro*-1 : 2-*pyridazine*-1 : 2-*dicarbamidoacetate*, m. p. 175°. Myrcene reacts with methyl azodicarboxylate to give *methyl* 5-δ-*methyl*-Δ$^{\gamma}$-*amylidene*-1 : 2 : 3 : 6-*tetrahydropyridazine*-1 : 2-*dicarboxylate*, b. p. 145°/0·2 mm.; this reacts readily with bromine or with permanganate. With styrene, the conjugated system is continued in the benzene ring; addition of methyl azodicarboxylate occurs, but the product at the same time regains benzenoid character by reducing and combining with a second molecule of the azo-ester to give *methyl* 4-*hydrazino*-1 : 2 : 4 : 4-*tetrahydrocinnoline*-N : N′ : N″ : N‴-*tetracarboxylate* [*methyl* 4-*hydrazino*-1 : 2 : 4 : 4-*tetrahydro*-1 : 2-*benzdiazine*-N : N′ : N″ : N‴-*tetracarboxylate*], m. p. 178°, which gives no reactions

of an unsaturated compound. Hydrolysis of this by potassium hydroxide gives *potassium 4-carbomethoxyhydrazinotetrahydrocinnoline-ω-carboxylate* (I), m. p. 146—147° (decomp.), which on treatment with acetic acid yields *methyl* ar-*hexahydrocinnolo*-1 : 2 : 3-*pyrazolone*-1-*carboxylate* (II), m. p. 183° (decomp.).



In contrast to styrene, stilbene does not react with ethyl azodicarboxylate. It is thus assumed that a 1 : 4 conjugated system is required for the condensations. Correspondingly, *as*-diphenylethylene adds on 2 mols. of the methyl ester to give the unsaturated compound *methyl di-*[*o-hydrazinophenyl*]-*ethylene*-N : N′ : N″ : N‴-*tetracarboxylate*, $CH_2{:}C[\cdot C_6H_4\cdot N(CO_2Me)\cdot NH(CO_2Me)]_2$, m. p. 188°. γ-Phenylpropene yields a product which is probably *methyl* γ-2 : 6-*dihydrazinophenylpropenetetracarboxylate*, $CHMe{:}CH\cdot C_6H_3[N(CO_2Me)\cdot NH(CO_2Me)]_2$, m. p. 142°. β-Phenylpropene yields *methyl* β-*o-hydrazinophenylpropene*-N : N′-*dicarboxylate*, m. p. 82°. This gives by catalytic hydrogenation the corresponding *propane* derivative, m. p. 62°, and by addition of bromine the αβ-*dibromopropane* derivative, m. p. 164°; ozonisation yields *o-dicarbomethoxyhydrazinoacetophenone*, m. p. 104° (*phenylhydrazone*, m. p. 156°).

Indene combines with 1 mol. of the ethyl ester to give a product which is probably *ethyl* 2-*hydrazinoindene*-N : N′-*dicarboxylate*, m. p. 107°.

Substituted butadienes give rise to compounds which are regarded as pyridazine derivatives: thus *trans*-1 : 4-diphenylbutadiene gives *methyl* 3 : 6-*diphenyl*-1 : 2 : 3 : 6-*tetrahydropyridazine*-1 : 2-*dicarboxylate*, m. p. 182°. This adds on bromine to give *methyl* 4 : 5-*dibromo*-3 : 6-*diphenylhexahydropyridazine*-1 : 2-*dicarboxylate*, m. p. 183—184°. It is hydrolysed by methyl-alcoholic potassium hydroxide to 3 : 6-*diphenyl*-1 : 2 : 3 : 6-*tetrahydropyridazine*, m. p. 157°, feebly basic (*hydrochloride*, m. p. 185°), which is reduced by zinc and hydrochloric acid to 1 : 4-diamino-1 : 4-diphenyl-Δ^{β}-butene (picrate, decomp. 230°, cf. Wieland and Stenzl, A., 1908, i, 518).

Phenylacetylene and diphenylacetylene scarcely react with the azo-ester.

Considering the addition of the azo-ester to heterocyclic compounds containing a co-ordinated system, pyrrole reacts violently and forms a complex grey amorphous substance, derived from at least 3 mols. of ethyl azodicarboxylate to 1 mol. of pyrrole.

Thiophen is inert towards the azo-ester, but furan reacts very readily, indicating that ring oxygen co-ordinates much less readily with free partial valencies than does sulphur. E. W. Wignall.

Synthesis of 1-acylindazoles [and related substances]. K. von Auwers and E. Frese (Annalen, 1926, 450, 273—303).—Derivatives of *o*-aminobenzaldoxime of the formula $R'\cdot CO\cdot NH\cdot C_6H_4\cdot CH{:}N\cdot O\cdot CO\cdot R$ when heated, yield nitriles, $R'\cdot CO\cdot NH\cdot C_6H_4\cdot CN$; when heated with anhydrous sodium carbonate, the nitriles are obtained if R=alkyl, but 1-acylindazoles, $C_6H_4{:}(\cdot CH{:}N\cdot N\cdot COR')$ if R=alkoxyl. Thus *o*-acetamidoacetylbenzaldoxime, m. p. 131—132° (cf. Gabriel and Meyer, A., 1882, 188), when heated alone or with sodium carbonate, is converted into *o*-acetamidobenzonitrile. *Methyl* o-*aminobenzaldehyde*-N-*carboxylate*, m. p. 89—90°, which is obtained from *o*-aminobenzaldehyde and methyl chloroformate, and when treated with sodium carbonate gives various products, including a *substance*, $C_{14}H_{12}ON_2$, m. p. 132—134° (decomp.), gives an *oxime*, m. p. 129°, which is converted by acetic anhydride into an *isomeride*, m. p. 121—123°. The corresponding *methyl* o-*aminobenzaldoxime*-ON-*dicarboxylate*, m. p. 135—136°, which is obtained from *o*-aminobenzaldoxime and methyl chloroformate, yields, when heated alone, *methyl* o-*aminobenzonitrile*-N-*carboxylate*, m. p. 94·5—95·5°, but in presence of sodium carbonate, methyl indazole-1-carboxylate, m. p. 59—60°, b. p. 151—152°/13 mm. (cf. A., 1921, i, 808; 1925, i, 1460).

The following were similarly prepared, using ethyl chloroformate: *ethyl* o-*aminobenzaldoxime*-N-*carboxylate*, m. p. 115—116°; *ethyl* o-*aminobenzaldoxime*-ON-*dicarboxylate*, m. p. 88·5—89°, which yields *ethyl* o-*aminobenzonitrile*-N-*carboxylate*, m. p. 103—104°, and ethyl indazole-1-carboxylate (see above); *methyl* o-*amino*-O-*carbethoxybenzaldoxime*-N-*carboxylate*, m. p. 78·5—79·5°, which yields methyl *o*-aminobenzonitrile-*N*-carboxylate, and methyl indazole-1-carboxylate.

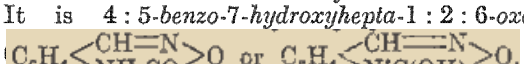
Methyl o-*aminoacetylbenzaldoxime*-N-*carboxylate*, m. p. 104·5—105·5°, is converted by alcoholic alkali into a heptaoxadiazine (see below); when heated alone, it gives methyl *o*-aminobenzonitrile-*N*-carboxylate; with sodium carbonate, unidentified products were obtained.

Methyl o-*acetamidobenzaldoxime*-O-*carboxylate*, m. p. 122—123° (decomp.), from *o*-acetamidobenzaldoxime, yields o-*acetamidobenzonitrile* and 1-acetylindazole. o-*Chloroacetamidochloroacetylbenzaldoxime*, m. p. 156·5—157·5°, converted by alcoholic alkali into an octaoxadiazine (see below), is hydrolysed by alcoholic hydrochloric acid to o-*chloroacetamidobenzaldoxime*, m. p. 182—183°. *Ethyl* o-*chloroacetamidobenzaldoxime*-O-*carboxylate*, m. p. 120—120·5°, obtained from the latter, yields o-*chloroacetamidobenzonitrile*, m. p. 115—116°, and with alkali, 1-chloroacetylindazole. *o*-Aminobenzaldoxime is benzoylated to a mixture of 5 parts of *o*-benzamidobenzaldoxime and 1 part of o-*benzamidobenzoylbenzaldoxime*, m. p. 141—143°; *ethyl* o-*benzamidobenzaldoxime*-O-*carboxylate*, m. p. 129—130°, obtained from the former, yields *o*-benzamidobenzonitrile and 1-benzoylindazole.

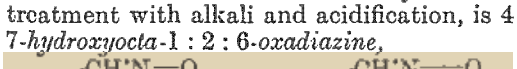
By the action of potassium cyanate on *o*-aminobenzaldoxime in acetic acid, *o*-carbamidobenzaldoxime, m. p. 161° (which gives an *ethyl* O-*carboxylate*, m. p. 166°), and a *substance*, $C_{16}H_{15}O_4N_5$, m. p. 216—217° (decomp.), are obtained. Using phenylcarbimide, the product is o-*benzamidobenzaldoxime*, m. p. 174—176° (*acetyl* derivative, m. p. 141—142°). Attempts to convert this by the action of potassium carbonate into 1-carbamylindazole have given no pure product. 2-*Carbamylindazole*, prepared from indazole and potassium cyanate, is labile, melting at

132—133°, resolidifying and melting again at 155°, being largely converted into 1-*carbamylindazole*, m. p. 166—167°.

o-*Benzamidoacetophenoneoxime*, m. p. 40—50°, gives an O-*carbomethoxy*-derivative, m. p. 93—94°, which, when heated with potassium carbonate in light petroleum gives some o-*benzamidoacetophenoneoxime benzoate*, m. p. 133°, and 1-*benzoyl*-3-*methylindazole*, m. p. 66—67°, identical with that prepared from 3-methylindazole.

The heptaoxadiazine mentioned above can also be obtained by heating *o*-carbomethoxyamidobenzaldoxime with dilute sodium hydroxide and acidifying, It is 4 : 5-*benzo*-7-*hydroxyhepta*-1 : 2 : 6-*oxadiazine*,  giving a *dihydrate*, decomp. 242—243°. This forms with ethyl chloroformate an O(?)-*carbethoxy*-derivative, m. p. 60—70° (decomp.), hydrolysed by alkali, but partly converted into a N(?)-*carbethoxy*-derivative, m. p. 181—182° or up to 193° (decomp.), according to the temperature at which heating begins; this substance may be obtained quantitatively by prolonged heating in benzene.

Acetic anhydride converts the heptaoxadiazine into *o*-acetamidoacetylbenzaldoxime, but by careful treatment, evaporating with methyl or with ethyl alcohol, *methyl* or *ethyl* o-*acetamidobenzaldoxime*-N-*carboxylates*(?), $CO_2R{\cdot}NAc{\cdot}C_6H_4{\cdot}CH{:}N{\cdot}OH$, m. p. 158—159° (decomp.) and 164—164·5°, are respectively obtained. The free N-*carboxylic acid* (?), m. p. 153—154°, is obtained by slow evaporation without alcohol; it is converted by sodium carbonate into the heptaoxadiazine. Action of hydroxylamine on the latter yields o-ω-*hydroxycarbamidobenzaldoxime*, m. p. 205° (decomp.).

The octaoxadiazine mentioned above, obtained from *o*-chloroacetamidochloroacetylbenzaldoxime by treatment with alkali and acidification, is 4 : 5-*benzo*-7-*hydroxyocta*-1 : 2 : 6-*oxadiazine*,  251—252° (*acetyl* derivative, decomp. 197—198°).

In an attempt to prepare labile 2-acylindazoles, *o*-aminobenzyl alcohol was diazotised and treated first with sodium sulphite, and then with (*a*) zinc and acetic acid; the product was a substance of high m. p. containing sulphur; or (*b*) sodium hydroxide, which gives a crystalline *sodium* salt, decomposed by acid to indazole and sulphuric acid, and thus an *indazole*-N-*sulphonate*.

o-Nitrobenzylamine (obtained in varying yields by the Gabriel reaction) gives o-*tolu*-o-*nitrobenzylamide*, m. p. 131—132°, which is reduced by ammonium sulphide to o-*tolu*-o-*hydroxylaminobenzylamide*, m. p. 114—115°; this on heating or treatment with alcoholic alkali loses water to form an *anhydro*-derivative, $C_{30}H_{30}O_3N_4$, m. p. 189—190°, and a *substance*, m. p. 110—112°.

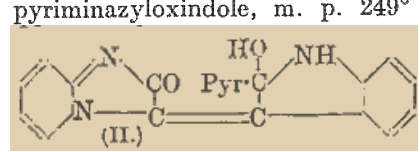
o-Hydrazinocinnamic acid, m. p. 196—197°, is better obtained by the method of Fischer and Kuzel (A., 1884, 440) than by that of Fischer and Tafel (*ibid.*, 1885, 540). The colour changes reported by these authors have not been confirmed. Attempts to acetylate this acid to a pure derivative from which a 2-acetylindazole might be obtained have not been successful.

E. W. WIGNALL.

Products of the action of aromatic aldehydes or pyriminazol-2-one and cyclic 1 : 2-dicarbonyl compounds. F. REINDEL and A. VON PUTZER-REYBEGG (Ber., 1926, **59**, [*B*], 2926—2932).—*Pyriminazol*-2-*one*, m. p. 169° (decomp.), is prepared by addition of barium chloride to an aqueous solution of the sodium salt and decomposition of the *barium* salt by carbon dioxide. The corresponding hydrochloride is converted by benzaldehyde in boiling, absolute alcoholic suspension into 3-*benzylidenepyriminazol*-2-*one hydrochloride*, m. p. 253° (decomp.), from which the free *base*, m. p. 233°, is derived; if the latter compound is crystallised from alcohol in presence of a little sodium salt, a *substance*, $C_{28}H_{26}O_3N_4$, m. p. 233° (decomp.) after becoming yellow at 190°, is obtained. Catalytic hydrogenation of the benzylidene derivative yields 3-*benzylpyriminazolone hydrochloride*, m. p. 216° (decomp.) [corresponding *picrate*, m. p. 189° (decomp.)]. Bromine converts the benzylidene compound into the *perbromide*, $C_{14}H_{10}ON_2Br_2$, m. p. 171—173° (decomp.). The following derivatives of pyriminazol-2-one are prepared analogously; 3-o-*nitrobenzylidene*, m. p. 214° (decomp.); *hydrochloride*, m. p. 239° (decomp.); 3-m-*nitrobenzylidene*, *sulphate*, m. p. 236° (decomp.); 3-o-*hydroxybenzylidene*, *hydrochloride*, m. p. 245° (decomp.): 3-p-*hydroxybenzylidene*, m. p. 278° (decomp.); *sulphate*, m. p. 237° (decomp.); *sodium* salt: 3-p-*dimethylaminobenzylidene*, m. p. 275° (decomp.); *hydrochloride*, m. p. 256° (decomp.). The pyriminazole ring appears to have chromophoric properties similar to those of the indole ring.

3-Benzylidenepyriminazolone hydrochloride is transformed by boiling aqueous sodium acetate into benzaldehyde and (?) *di*-2-*keto*-2 : 3-*dihydro*-3-*pyriminazylphenylmethane*, m. p. 207° (decomp.), which is converted into a *substance*, m. p. 248° (decomp.), when crystallised from alcohol. Both substances are converted by phenylhydrazine into benzaldehydephenylhydrazone and by concentrated sodium hydroxide into a crystalline *sodium* salt converted by benzoylation into the *dibenzoyl* derivative of the methane, m. p. 204° (slight decomp.). Direct benzoylation of the substances, m. p. 207° and 248°, affords the benzoyl derivative of pyriminazolone, whereas oxidation of them with potassium ferricyanide gives *di*-2-*keto*-2 : 3-*dihydro*-3-*pyriminazylphenylmethene*, m. p. 207° (decomp.) (*sodium* salt). *Di*-2-*keto*-2 : 3-*dihydro*-3-*pyriminazyl*-2′-*hydroxyphenylmethane* ($+H_2O$), m. p. 216° (decomp.), is oxidised by ferricyanide to a red, non-crystalline methene.

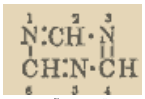
In cold alcoholic suspension, isatin and pyriminazolone hydrochloride afford 3-*pyriminazyl*-3′-*dioxindole*, m. p. 170° (decomp.) (*hydrochloride*, m. p. 230°), whereas in boiling suspension and with an increased proportion of the hydrochloride, di-3 : 3-pyriminazyloxindole, m. p. 249° (decomp.) (*hydrochloride*), is obtained. The latter compound is isomerised in boiling alcohol or converted by sodium hydroxide to the *dye* (II), m. p.


(II.)

281° (decomp.) (*dibenzoyl* derivative, m. p. 241°). Analogous *dyes* are prepared from 5 : 7-dibromoisatin, 5-bromoisatin, and acenaphthaquinone, and have m. p. (decomp.) 294°, 287°, and 280°, respectively.

H. WREN.

Cyanurin group. O. DIELS and R. LICHTE (Ber., 1926, **59**, [*B*], 2778—2784).—It is proposed to base the nomenclature of all cyanuric compounds on "cyanurin," $C_3H_3N_3$. Cyanuric acid itself



is therefore 2 : 4 : 6-trihydroxycyanurin. *iso*Cyanuric compounds are regarded as hydrogenated cyanurins; thus, *iso*cyanuric acid is designated 2 : 4 : 6-triketohexahydrocyanurin.

Acetylcarbamide, obtained in 80% yield by the acetylation of carbamide in presence of a small amount of sublimed aluminium chloride, is converted by formaldehyde in presence of concentrated sulphuric acid at −15° into *methylenediacetylcarbamide*, $CH_2(NH{\cdot}CO{\cdot}NHAc)_2$, m. p. 255°, which is hydrolysed by concentrated aqueous potassium hydroxide to *methylenedicarbamide*, m. p. 207°. The latter substance is transformed by concentrated hydrochloric acid into 2 : 4-*diketohexahydrocyanurin*, m. p. 245°, the salts of which are readily hydrolysed by water. Acetylthiocarbamide and formaldehyde afford *methylenediacetylthiocarbamide*, m. p. 167°, from which *methylenedithiocarbamide*, m. p. 152°, and 2 : 4-*dithiohexahydrocyanurin* are successively derived; the *silver*, *cuprous*, and *mercurous* (decomp. 230°) salts of the latter compound are described. The mercurous compound adds methyl iodide at the three nitrogen and two sulphur atoms, whilst the imino-group between the two CS groups is also methylated, thus giving the *compound* $C_9H_{20}N_2S_2I_5Hg_2$, m. p. 101°; ethyl iodide affords the analogous *substance* $C_{15}H_{32}N_3S_2I_5Hg_2$, m. p. 73°. The compounds are readily hydrolysed by water with separation of mercuric iodide. 2 : 4-Dithiohexahydrocyanurin and methyl iodide give the *substance* $C_7H_{16}N_3I_3S_2$, m. p. 115°.

Thioacetanilide and methyl iodide yield the *compound* NHPh·CMe:SMeI, m. p. 135—137°.

H. WREN.

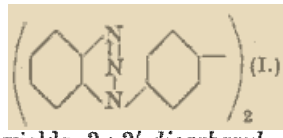
Condensations of unsaturated compounds with diazomethane. R. ROTTER (Monatsh., 1926, **47**, 353—356).—Freshly-distilled (unimolecular) carbodianil combines with diazomethane in ethereal solution to yield 5-anilino-1-phenyltriazole, m. p. 142° (cf. Dimroth, A., 1909, 269).

G. M. BENNETT.

Syntheses with azoimide and mechanism of the reactions. E. OLIVERI-MANDALÀ (Mem. R. Accad. Lincei, 1926, [vi], **2**, 132—150).—A summary is given of the syntheses effected by addition of azoimide to (1) compounds with two contiguous double linkings in the molecule, such as carbodiphenylimide, carbimides, and thiocarbimides, ketens, carbon disulphide, and nitrous acid, (2) compounds containing bivalent carbon, such as carbylamines and fulminic acid, (3) the nitrilic linking, (4) the ethylenic linking, and (5) the acetylenic linking, the mechanism of the reaction being discussed in each case.

T. H. POPE.

Dicarbazyls. I. Synthesis of 3 : 3′-dicarbazyl. S. H. TUCKER (J.C.S., 1926, 3033—3038).—NN′-*Di*-o-*nitrophenylbenzidine*, m. p. 240° (NN′-*diacetyl* derivative $+2C_6H_6$, m. p. 80—85°; +EtOH, m. p. 120°; $+MeCO_2H$, m. p. 100—105°; +MeOH, m. p. 125—130°), is obtained, together with a little N-o-*nitrophenylbenzidine* (N′-*acetyl* derivative, m. p. 222°), by condensation of benzidine and *o*-chloronitrobenzene, or, alternatively, by oxidation of *o*-nitrodiphenylamine with sodium dichromate. Reduction gives NN′-*di*-o-*aminophenylbenzidine*, m. p. 218° (*dihydrochloride* becoming greenish-blue at 230—260°), converted by treatment with nitrous acid into 4 : 4′-*di*-1″ : 2″ : 3″-*benztriazolyldiphenyl* (I), m. p. 299°, which, when heated above its m. p., yields 3 : 3′-*dicarbazyl*, m. p. above 350° (9 : 9′-*diacetyl* derivative, m. p. 247—249°).

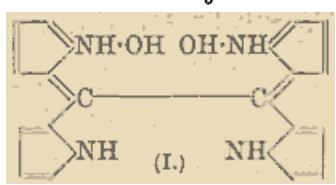

(I.)

M. CLARK.

So-called "substituted dihydropentazines" of Chattaway and Parkes. R. STOLLÉ (J. pr. Chem., 1926, [ii], **114**, 348—349).—Since α-hydrazinobenzaldehydebenzylideneazine, $CHPh{:}N{\cdot}N{:}CPh{\cdot}NH{\cdot}NH_2$, is converted by nitrous acid into 1-benzylideneamino-5-phenyltetrazole (A., 1914, i, 750), the product obtained in a similar way from α-hydrazinobenzaldehyde-2 : 4-dibromophenylhydrazone by Chattaway and Parkes (*ibid.*, 1926, 308) is probably 1-dibromoanilino-5-phenyltetrazole, and not 1-dibromophenyl-5-phenyl-1 : 4-dihydropentazine.

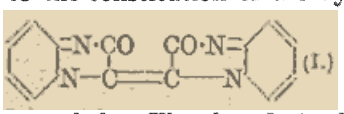
H. E. F. NOTTON.

Action of ethyl oxalate on magnesium pyrryl iodide. T. N. GODNEV and N. A. NARYSCHKIN (Ber., 1926, **59**, [*B*], 2897—2898; cf. A., 1926, 183).—The isolation of "tetra-2-pyrrylethylene glycol" as a blackish-brown powder indicates that it is the true dye base (I).


(I.)

H. WREN.

Constitution of the dye obtained by oxidation of pyriminazol-2-one with potassium ferricyanide. F. REINDEL and H. RAUCH (Ber., 1926, **59**, [*B*], 2921—2925; cf. A., 1924, i, 1235; 1925, i, 438; Tschitschibabin, *ibid.*, 1925, i, 158).—In relation to the constitution of the dye, inconclusive attempts to synthesise a substance (I), by the action of ethyl dibromomaleate on 2-aminopyridine are recorded. The dye derived from 3 : 3-dibromopyriminazol-2-one and pyriminazol-2-one is not identical with that described previously. The yellow sodium salt obtained by the action of air on the sodium salts of pyriminazol-2-one (Reindel, *loc. cit.*) is not an intermediate product in the formation of the dye, since the latter cannot be produced from it by oxidation with potassium ferricyanide in alkaline solution. Treatment of the yellow salt with a little hydrochloric acid gives a *compound*, $C_{14}H_{10}O_3N_4,HCl,2H_2O$, m. p. 176° (decomp.), which is transformed by boiling water into pyriminazolone and a *substance*, decomp. 215—220°, giving 2-aminopyridine and oxalic acid when treated with sodium hydroxide.


(I.)

H. WREN.

Action of cyanogen halides on phenylhydrazine. X. Derivatives of oxadiazole. G. PELLIZZARI (Gazzetta, 1926, **56**, 695—700).—α-Cyanophenylhydrazine reacts in boiling benzene solution with acyl chlorides to give imino-oxadiazole derivatives. With benzoyl chloride the product is 2-*imino*-3 : 5-*diphenyloxa*-3 : 4-*diazole*, m. p. 124° (*benzoyl* derivative, m. p. 165°; *acetyl* derivative, m. p. 111°; *nitroso*-derivative explodes at about 80°), soluble in acids and converted by nitrous acid in boiling solution into the 3 : 5-diphenyloxa-3 : 4-diazol-2-one, m. p. 113°, of Freund and Goldsmith (A., 1888, 1187). In the same way, acetyl chloride yields the corresponding 2-imino-3-phenyl-5-methyloxa-3 : 4-diazole (Freund and Kuh, A., 1890, 1442) [*hydrochloride*, m. p. 190° (decomp.), and *picrate*, m. p. 174°, described], hydrolysed to the oxadiazolone, m. p. 93—94°. Ethyl chloroformate reacts to give 2-*imino*-5-*ethoxy*-3-*phenyloxa*-3 : 4-*diazole*, m. p. 75°, which has weak basic and acidic properties, and is hydrolysed by aqueous sodium hydroxide to 2-*imino*-5-*hydroxy*-3-*phenyloxa*-3 : 4-*diazole*, m. p. 262—263° (decomp.). G. M. BENNETT.

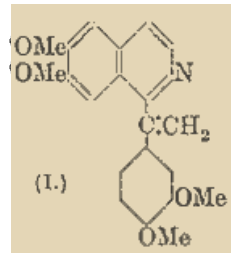
1 : 3-Benzoxazines. II. Conversion of *iso*-nitrosocoumaranones into derivatives of 1 : 3-benzoxazine. E. MAMELI (Gazzetta, 1926, **56**, 759—772).—The conversion of an *iso*nitrosocoumaranone derivative, by means of the Beckmann transformation, into a diketo-1 : 3-benzoxazine (A., 1922, i, 669) has been extended to a number of other cases. 2-*iso*Nitrosocoumaran-3-one yields 2 : 4-diketo-1 : 3-benzoxazine (m. p. 227°), and 2-*iso*nitroso-6-methylcoumaran-3-one is converted into 7-*methyl*-2 : 4-*diketo*-1 : 3-*benzoxazine*, m. p. 232° (*potassium* and *silver* salts described), which is hydrolysed by sodium hydroxide to the amide (m. p. 182°) of 2-hydroxy-*p*-toluic acid. 2-*iso*Nitroso-5-methylcoumaran-3-one yields 6-*methyl*-2 : 4-*diketo*-1 : 3-*benzoxazine*, m. p. 233°, which is hydrolysed by alkali to the amide (m. p. 178°) of 2-hydroxy-5-methylbenzoic acid. 2-iso*Nitroso*-7-*methylcoumaran*-3-*one*, m. p. 194°, obtained by the action of nitrite in acetic acid solution on 7-methylcoumaranone, is converted by the Beckmann reaction into 8-*methyl*-2 : 4-*diketo*-1 : 3-*benzoxazine*, m. p. 207° (*potassium* and *silver* salts described), which is hydrolysed by alkali to the amide (m. p. 112°) of 2-hydroxy-3-methylbenzoic acid. Contrary to statements in the literature (*e.g.*, J.C.S., 1920, **117**, 1534), better yields of these coumaranones are obtained from the phenols by the action of sodium acetate on the *o*-hydroxyphenyl chloromethyl ketone than by the action of aluminium chloride on the phenoxyacetyl chloride. G. M. BENNETT.

Synthesis of coniine. G. KOLLER (Monatsh., 1926, **47**, 393—396).—α-Trichloro-γ-2-pyridylpropan-β-ol, from picoline and chloral, is reduced with zinc dust in aqueous methyl alcohol to α-propenylpyridine (picrate identical with the picrate of Ladenburg's "allylpyridine"). Reduction of this base by means of hydrogen and colloidal platinum, followed by sodium and ethyl alcohol, gives *dl*-coniine, b. p. 59—63°/17 mm. (*m*-nitrobenzoyl derivative and nitrosoamine, oils; hydrochloride, m. p. 211—212°), from which *d*-coniine hydrogen tartrate, m. p. 53—54°, is obtained. G. M. BENNETT.

Yohimba alkaloids. L. SPIEGEL (Ber., 1926, **59**, [*B*], 2706—2707).—It appears doubtful whether justification exists for assigning to yohimbine the composition $C_{21}H_{26}O_3N_2$ (cf. Field, J.C.S., 1923, **123**, 3003) instead of $C_{22}H_{28}O_3N_2$ suggested by the author. Criticism is directed against the observations of Hahn and Brandenberg and of Warnat (A., 1926, 1263). The identity of *iso*yohimbine with *meso*yohimbine and with corynanthine is regarded as impossible. H. WREN.

Corydalis alkaloids. VII. Syntheses of corybulbine and *iso*corybulbine. E. SPATH and H. HOLTER (Ber., 1926, **59**, [*B*], 2800—2805; cf. A., 1925, i, 1085).—Corydaline is partly demethylated by treatment with hydrochloric acid (*d* 1·19) at 100°, and the separated mixture of phenolic bases is preserved in methyl-alcoholic solution, when corybulbine, m. p. 242—243°, $[\alpha]_D^{19}$ +304·9° in chloroform, separates in 8% yield. The residue from the corybulbine is dissolved in ether and fractionally extracted with aqueous hydrochloric acid; the final fractions afford *iso*corybulbine, m. p. 187·5—188·5°, $[\alpha]_D^{15}$ +301° in chloroform, in small amount. H. WREN.

Opium alkaloids. V. ψ-Papaverine and methylenepapaverine. E. SPATH and N. POLGAR (Ber., 1926, **59**, [*B*], 2787—2790).—Direct comparison of Hesse's ψ-papaverine (cf. A., 1903, i, 773) and papaverine, their hydrochlorides, m. p. 225—226° (decomp.), hydrobromides, m. p. 213—214° (slight decomp.), picrate, m. p. 186—186·5°, hydrogen oxalates, m. p. 201·5—202° (decomp.), and *chloroplatinates*, m. p. 212—213° (decomp.), establishes the identity of the alkaloids. The name ψ-papaverine should be deleted from the literature. Methylenepapaverine has the constitution (I), since it is oxidised by permanganate to papaveraldine and catalytically reduced to *methylenedihydropapaverine*, m. p. 154°. *Methylenepapaverine methiodide* is described.

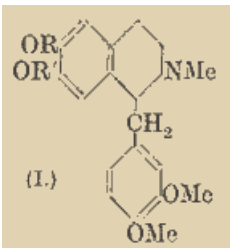


(I.)

H. WREN.

Opium alkaloids. VI. Constitution of codamine and ψ-laudanine. E. SPATH and H. EPSTEIN (Ber., 1926, **59**, [*B*], 2791—2890).—Contrary to the observations of Hesse, codamine, m. p. 126°, has the composition $C_{20}H_{25}O_4N$; it contains one hydroxyl and three methoxyl groups. When treated with diazomethane, it affords *d*-laudanosine. To determine the position of the free hydroxyl group, codamine is transformed into its ethyl ether and the latter oxidised by permanganate, whereby veratric acid is obtained, thus indicating the position 6 or 7 for the hydroxyl group in the *iso*quinoline nucleus. To establish the course of the mild oxidation of laudanosine derivatives, *r*-laudanosine is treated with permanganate in faintly alkaline solution under definite conditions, whereby 6 : 7-dimethoxy-1-keto-2-methyl-1 : 2 : 3 : 4-tetrahydro*iso*quinoline, m. p. 125—126°, is obtained (cf. Pyman, J.C.S., 1909, **95**, 1617). The synthesis of this substance is accomplished by converting β-3 : 4-dimethoxyphenylethylamine into the corresponding formyl derivative, and thence, by

means of phosphoric oxide in the presence of toluene, into 6 : 7-dimethoxy-3 : 4-dihydro*iso*quinoline (*picrate*, m. p. 204—206°). The base is converted into the corresponding *methiodide*, m. p. 202° (decomp.), and thence into the chloride, from which 6 : 7-dimethoxy-1-keto-2-methyl-1 : 2 : 3 : 4-tetrahydro*iso*quinoline is obtained by oxidation. Similarly, 7-methoxy-6-ethoxy-3 : 4-dihydro*iso*quinoline (cf. Späth and Dobrowsky, A., 1925, i, 1085) is transformed into the *methiodide*, m. p. 187—189° after softening, the methochloride, and 7-*methoxy*-6-*ethoxy*-1-*keto*-2-*methyl*-1 : 2 : 3 : 4-*tetrahydroisoquinoline*, m. p. 97—97·5°, whereas 6-methoxy-7-ethoxy-3 : 4-dihydro*iso*quinoline (*loc. cit.*) affords successively the *methiodide*, m. p. 170—172°, *methochloride*, and 6-*methoxy*-7-*ethoxy*-1-*keto*-2-*methyl*-1 : 2 : 3 : 4-*tetrahydroisoquinoline*, m. p. 120—121°. Oxidation of ethylated codamine affords the product, m. p. 120—121°, thus establishing the constitution (I) for codamine (R=Me, R′=H).

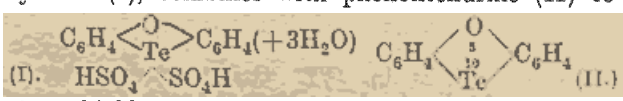


(I.)

Methylation of *ψ*-laudanine by diazomethane affords *r*-laudanosine in good yield. Energetic oxidation of ethylated *ψ*-laudanine yields veratric acid and the methyl ethyl ether of nor-*m*-hemipinic acid, thus establishing the presence of the free hydroxyl group in the *iso*quinoline nucleus, whereas mild oxidation affords 7-methoxy-6-ethoxy-1-keto-2-methyl-1 : 2 : 3 : 4-tetrahydro*iso*quinoline, m. p. 95—96°. The constitution (I) (R=H, R′=Me) is therefore established for *ψ*-laudanine. H. Wren.

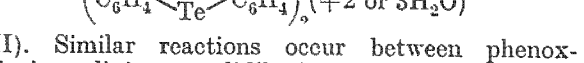
Determination of morphine in opium. F. C. M. J. Hollman.—See B., 1927, 58.

Cyclic organo-metallic compounds. II. Tellurylium compounds, a new series of intensely coloured tellurium derivatives. Migration of anions in solids. H. D. K. Drew (J.C.S., 1926, 3054—3071).—Phenoxtellurine dibisulphate trihydrate (I), combines with phenoxtellurine (II) to



(I). (II.)

give a highly-coloured violet compound formulated as diphenoxtellurylium dibisulphate di- or tri-hydrate



(III.)

(III). Similar reactions occur between phenoxtellurine dinitrate, didihydrogen phosphate, or diperchlorate and various organic tellurides or sulphides. In these salts, the tellurium is satisfied with one polar and three non-polar linkings, but in the case of phenoxtellurine dichloride, dibromide, or diacetate, the compounds are non-polar and do not give rise to coloured complexes with tellurides.

A development of intense colour occurs when (I) is rubbed with iron or other base metal. Explanations for the colour changes are offered. The following compounds are described: *phenoxtellurine* 10 : 10-*dinitrate*, m. p. 258° (decomp.); 2-*nitrophenoxtellurine* 10 : 10-*dinitrate*, m. p. 196—197° (decomp.); 2 : 8-*dinitrophenoxtellurine* 10 : 10-*dinitrate*, m. p. 259° (decomp.); 4-*nitro*-10-*hydroxyphenoxtellurine* 10-*nitrate monohydrate* (?), m. p. 243°; 4 : 8-*dinitro*-10-*hydroxyphenoxtellurine* 10-*nitrate monohydrate* (?), violent decomp. 237—239°.

After cautious addition of water to a solution of phenoxtellurine in concentrated sulphuric acid, red crystals of *diphenoxtellurylium dibisulphate disulphuric acid trihydrate* (IV), decomp. near 165°, are slowly deposited. This compound is converted, on exposure to moist air, into *diphenoxtellurylium dibisulphate di-* or *tri-hydrate* (III), in which the conditions of drying determine the final degree of hydration. Dilution of the red solution of phenoxtellurine in concentrated sulphuric acid with a greater proportion of water gives a violet precipitate, crystallising from glacial acetic acid as *diphenoxtellurylium hydroxybisulphate monohydrate* (V). This compound loses colour gradually at 205—245°, giving phenoxtellurine and a white solid unmelted at 300°.

Each of the compounds (III), (IV), and (V) is decomposed into its constituents by an excess of water. *Phenoxtellurine* 10 : 10-*diacetate*, m. p. 205—207° (decomp.), is obtained by the action of aqueous hydrogen peroxide on a solution of phenoxtellurine in hot glacial acetic acid. Excess of hydrogen peroxide reacts to give *phenoxtellurone*. When a solution of the diacetate in boiling water is treated with sulphuric acid, a crystalline sulphate separates, giving, on recrystallisation from sulphuric acid, crystals the composition of which depends on the concentration of acid present. With the minimum of acid necessary to cause precipitation, *phenoxtellurine sulphate* is obtained. From more strongly acid solutions, a complex *compound* is deposited, containing two molecular proportions of phenoxtellurine hydroxybisulphate, and one of phenoxtellurine dibisulphate + 1 mol. of water. When the crude sulphate is dissolved in warm concentrated sulphuric acid, and a relatively small proportion of water added, crystals of *phenoxtellurine dibisulphate trihydrate* (I) are obtained. M. Clark.

Organic compounds of arsenic. IV. Reaction between the Grignard reagent and arsenic trisulphide. K. Matsumiya and M. Nakai (Mem. Coll. Sci. Kyoto, 1926, **10**, 57—66; cf. A., 1925, i, 1339).—Magnesium *p*-tolyl bromide and arsenic trisulphide react to form tri-*p*-tolylarsine, di-*p*-tolylarsenious sulphide, and tri-*p*-tolylarsine sulphide, the relative amounts varying greatly according to the mode of preparation of the sulphide. These differences are not shown in the corresponding reaction using magnesium phenyl bromide. Magnesium α-naphthyl bromide reacts with the sulphide to form only *di-α-naphthylarsenious sulphide*, m. p. 185—186°; which was also prepared from hydrogen sulphide and di-α-naphthylarsenious oxide or di-α-naphthylchloroarsine. *Triphenylarsine sulphide mercurichloride*, m. p. 239—241°, and *tri-p-tolylarsine sulphide mercurichloride*, m. p. 227—229°, were also prepared.

B. W. Anderson.

Manufacture of solutions of aminoaryldichloroarsines or aminoarylarsenious oxides. G. Newbery, and May & Baker, Ltd.,—See B., 1927, 29.

Decomposition of unsymmetrical mercuri-organic compounds: a method of establishing the degree of electronegativity of organic radicals. M. S. KHARASCH and R. MARKER (J. Amer. Chem. Soc., 1926, 48, 3130—3143; cf. A., 1925, i, 1107).—The failure of Hilpert and Grüttner (A., 1915, i, 729) to obtain unsymmetrical mercuri-organic compounds was due to their use of too large an excess of Grignard reagent, and non-recognition of the instability of these derivatives towards heat. Thus *mercuryphenyl* p-*tolyl*, obtained by the action of 1 mol. of mercuric *p*-tolyl chloride on 2 mols. of magnesium phenyl bromide in ether at 5°, is almost completely decomposed into mercury diphenyl and mercury di-*p*-tolyl if the ethereal reaction mixture be boiled for 30 min. If the proportions of the reactants and the temperature be carefully controlled, the unsymmetrical derivatives can be readily prepared, and the following compounds containing the groups mentioned attached to mercury obtained in this way are described: *phenyl methyl* (liquid), *phenyl cyclohexyl* (solid), *phenyl butyl* (liquid), *benzyl methyl* (liquid), *phenyl naphthyl* (solid, decomp. 110—115°), *α-naphthyl ethyl* (liquid), *methyl butyl* (liquid), *phenyl o-anisyl* (solid), cyclo*hexyl methyl* (liquid), *ethyl benzyl* (liquid), *phenyl mesityl* (solid, decomp. 110—120°), *methyl mesityl* (solid), *propyl butyl* (liquid), and *butyl-mercury* iso*amyl*. The decomposition of the unsymmetrical derivatives, HgR_1R_2, by hydrogen chloride, according to the equation $HgR_1R_2+HCl=R_1HgCl+R_2H$, the great rapidity of which precludes the possibility of side reactions, proceeds in a manner determined by the relative electronegativity of R_1 and R_2, the more electronegative radical combining with the hydrogen atom. It is assumed that the more electronegative radical dissociates first from the mercury and then combines with the hydrogen ion in solution. Examination of the products obtained by the action of hydrogen chloride on a series of unsymmetrical mercury derivatives thus enables the relative electronegativity of the radicals concerned to be determined, and from the results so far obtained the following radicals are listed in the order of their decreasing electronegativity: cyanogen; α-naphthyl, *p*-anisyl, and mesityl; *p*-tolyl; phenyl; methyl; ethyl and *n*-propyl; *n*-butyl; *iso*amyl; benzyl; *cyclo*hexyl and *n*-hexadecyl. Diphenylyl is more electronegative than phenyl, and α-naphthyl than β-naphthyl. Hydrogen chloride converts a mercury dialkyl in which the two radicals are of approximately equal electronegativity into both the possible hydrocarbons in a fixed ratio. Thus, mercury propyl butyl affords 74·2% of mercuric butyl chloride and 25·8% of mercuric propyl chloride, whilst mercury benzyl ethyl yields 94·1% of mercuric benzyl chloride and 5·9% of mercuric ethyl chloride, with a variation of not more than ±1% in each case. The bearing of the above results on the electronic conception of valency is discussed (cf. Kharasch and Sher, A., 1925, ii, 636) and an explanation is offered for the existence of free radicals, according to which the extent of the dissociation of the hexa-arylethanes is determined by by electronegativity of, and is independent of the mass and complexity of, the radicals attached to the methyl carbon atoms. F. G. WILLSON.

Mercuration of aromatic substances. III. *p*- and *m*-Nitrotoluenes. S. COFFEY (J.C.S., 1926, 3215—3224; cf. A., 1926, i, 629).—When excess of *p*-nitrotoluene is heated with mercuric acetate at 140°, a mixture of 2- and 3-acetoxymercuri-4-nitrotoluenes, in which the latter compound may constitute as much as 80% of the product, is obtained. The pure individual products could not be isolated from the mercuration mixture. The proportions of the two substances were determined by conversion through the chloromercuri-*p*-nitrotoluenes into a mixture of 2- and 3-bromonitrotoluenes, the composition of which was determined by comparison with the f.-p. curve obtained from mixtures of the pure bromonitrotoluenes. Improved methods of preparation for these substances are described.

2-*Chloromercuri*-4-*nitrotoluene*, m. p. 230—231° (corr.), is obtained when 4-*nitrotoluene*-2-*sulphinic acid*, m. p. 127—128° (*sodium* salt $+2H_2O$; *ferric* salt), prepared from the corresponding sulphonyl chloride by warming with sodium sulphite, is boiled with a 50% aqueous-alcoholic solution of mercuric chloride. 3-*Chloromercuri*-4-*nitrotoluene*, m. p. 226—227° (corr.), is synthesised by the following method: 4-Nitro-*o*-toluidine yields, on sulphonation with chlorosulphonic acid, 4-*nitro*-2-*aminotoluene*-5-*sulphonic acid* (*ammonium* and *potassium* salts), the constitution of this substance being proved by reduction to 2 : 4-tolylenediamine-5-sulphonic acid. The *diazonium* derivative of the sulphonic acid is extremely stable. The diazonium group is eliminated by means of copper powder and formic acid, yielding 4-*nitrotoluene*-3-*sulphonic acid*, isolated as the *potassium* salt. The sulphonic acid is converted into the corresponding *sulphinic acid*, m. p. 112—113° (*ferric* and *ammonium* salts), and thence into 3-chloromercuri-4-nitrotoluene.

When *m*-nitrotoluene is heated with mercuric acetate for 12 hrs. at 140°, it yields a mixture of acetoxymercuri-*m*-nitrotoluenes. After conversion into the corresponding chloromercuri-derivatives, 4-*chloromercuri*-3-*nitrotoluene*, m. p. 210° (corr.), and 6-*chloromercuri*-3-*nitrotoluene*, m. p. 294° (corr.), can be isolated from the mixture. The constitution of these substances is proved by conversion into the corresponding bromonitrotoluenes. The presence of 6-chloromercuri-3-nitrotoluene is demonstrated by the isolation of 6-bromo-*m*-toluidine from the mixture of amino-compounds obtained by reducing the bromonitrotoluene product derived from the mixture of chloromercuri-derivatives. M. CLARK.

Colloidal organomercuric compounds. G. ROSSI and C. BOCCHI (Gazzetta, 1926, 56, 817—821; cf. A., 1925, i, 601).—*Tetramercuri*-α-*acetonaphthalide acetate*, $NHAc\cdot C_{10}H_3(Hg\cdot OAc)_4$, prepared by heating an intimate mixture of mercuric acetate (4 mols.) free from mercurous salts with α-acetonaphthalide, decomposes at 220°, and forms aqueous solutions which froth abundantly when shaken, are highly viscous, cannot be dialysed, coagulate when heated, and are acid owing to the presence of acetic acid; if much acetic acid is present, coagulation of the solution does not take place. This compound does not yield mercuric oxide when treated with potassium hydroxide. T. H. POPE.

Organo-tin compounds. K. K. LAW (J.C.S., 1926, 3243).—*Hexabenzyldistannane*, $Sn(CH_2Ph)_3 \cdot Sn(CH_2Ph)_3$, m. p. 147—148°, obtained by heating tribenzylstannic chloride (*ibid.*, 1912, **101**, 2557) with sodium in toluene solution, is decomposed by iodine in benzene solution, giving tribenzylstannic iodide. Dibenzylethylstannic iodide reacts with excess of an ethereal solution of magnesium *n*-butyl bromide, giving, when the product is afterwards heated at 140°, *dibenzylethylbutylstannane*, $SnEtBu(CH_2Ph)_2$, b. p. 207—209°/9 mm. *Benzylethyldibutylstannane*, $SnEtBu_2 \cdot CH_2Ph$, b. p. 175—180°/9 mm., is obtained as a by-product from benzylethylstannic iodide present as impurity. M. CLARK.

Structure of complex carbohydrates and proteins. M. BERGMANN (Kolloid-Z., 1926, **40**, 289—295, and Ber., 1926, 59, [*B*], 2973—2981).—A lecture on the structure of compounds of high mol. wt. E. S. HEDGES.

Structure of proteins. E. WALDSCHMIDT-LEITZ (Kolloid-Z., 1926, **40**, 295—300, and Ber., 1926, **59**, [*B*], 3000—3007).—A lecture on the structure of proteins studied from the point of view of the products of enzyme action. E. S. HEDGES.

Partial hydrolysis of globin. F HAUROWITZ (Z. physiol. Chem., 1926, **162**, 41—62).—Globin is partly hydrolysed by sulphuric acid (70 vol.-%) after some days at 40°. After 5 days, no free histidine is present in the hydrolysate, but a histidine-rich peptide (containing 68% of its nitrogen as histidine-nitrogen) may be precipitated by mercuric sulphate. Leucine and proline are present, but neither arginine nor lysine. Kirbach's "globinokyrin" is a mixture of peptides. H. D. KAY.

Composition and characterisation of genuine proteins. S. P. L. SØRENSEN (J.C.S., 1926, 2995—3009).—Hugo Muller Lecture, delivered on Oct. 28, 1926.

Colorimetric determination of tryptophan in proteins. J. TILLMANS and A. ALT (Biochem. Z., 1926, **178**, 243—244).—A reply to the criticisms by Fürth (A., 1926, 633) of the author's method (*ibid.*, 189). J. PRYDE.

Sources of error in organic elementary analysis. II. The combustion tube. J. LINDNER (Ber., 1926, **59**, [*B*], 2806—2812; cf. this vol., 66).—Complete freedom of the current of air from carbon dioxide can be attained only with extreme difficulty and by particular precautions. Many hard glass tubes appear to evolve traces of carbon dioxide when strongly heated, but the amount is insufficient to be of practical importance. The entry of traces of organic matter into the combustion tube from the air aspirator and system is facilitated by the heat from the furnace. Technical copper oxide "for analysis" may contain alkaline impurities which are of much greater importance in micro- than in macro-analysis. H. WREN.

Meulen's catalytic method for the determination of nitrogen in organic compounds. F. L. SMITH and A. P. WEST (Philippine J. Sci., 1926, **31**, 265—275).—A modification of the method (A., 1925, ii, 66) is described involving the separation of the mixture of asbestos fibre and nickel catalyst, by means of asbestos plugs, into four sections, the first of which is heated to dull redness and acts as a preheater to the rest of the catalyst, which is maintained at 350°. This arrangement is claimed to obviate the tendency in the original method for solid compounds to distil unchanged through the reduction tube. E. HOLMES.

Influence of chlorides on Denigès' reaction for citric acid. I. M. KOLTHOFF (Pharm. Weekblad, 1926, **63**, 1453—1455; cf. Wagenaar, A., 1926, 1226).—Small proportions of chlorine do not affect the reaction in aqueous solution. If, however, other organic acids be present, chlorides interfere strongly. The test can be carried out without removing chlorides if manganous sulphate be added. S. I. LEVY.

Stahre's reaction for citric acid. N. SCHOORL (Pharm. Weekblad, 1926, **63**, 1455—1458).—The detection of citric acid by oxidation with permanganate and treatment with bromine, which gives a white precipitate of pentabromoacetone, is not affected by the presence of other organic acids, or of chlorides, unless these are in great excess. S. I. LEVY.

Determination of aniline, especially in dilute solutions. A. V. PAMFILOFF.—See B., 1927, 7.

Determination of antimony in organic compounds. W. H. GRAY.—See this vol., 143.

Biochemistry.

Regulation of respiration. VI. Continuous electrometric methods of recording changes in expired carbon dioxide and oxygen. R. GESELL and D. A. MCGINTY (Amer. J. Physiol., 1926, **79**, 72—90).—The "carbon dioxide electrode" consisted of a fine manganese dioxide electrode resting on a peritoneal membrane moistened with potassium chloride solution in connexion with a calomel electrode. The "carbon dioxide electrode" was exposed to a steady stream of expired air and responded to changes in carbon dioxide tension by changes in acidity, the resulting changes in *E.M.F.* being balanced potentiometrically and recorded mechanically. The changes in oxygen tension were measured by supplying to a Bunsen burner a constant mixture of gas and expired air. The changes in heat of the flame were impressed on a constant flow of water and measured and recorded by a thermopile in the same way as with the "carbon dioxide electrode." *In vitro* and *in vivo* experiments demonstrating the accuracy of the methods are recorded and rapid means of calibration described. R. K. CANNAN.

Prolonged alterations of oxygen pressure in the inspired air with special reference to tissue oxygen tension, tissue carbon dioxide tension, and hæmoglobin. J. A. CAMPBELL (J. Physiol., 1927, 62, 211—231).—Rabbits were exposed for about 6 weeks to oxygen pressures varying from 60% below to 200% above the normal, the barometric pressure being kept constant. There was no effect on the oxygen consumption. Reduced oxygen pressure depressed the carbon dioxide and oxygen tensions of the tissues notably and increased the hæmoglobin content of the blood. With increased oxygen pressure, inverse effects to the above were noted. In both cases, pronounced after-effects indicated mechanisms concerned with acclimatisation. These, however, did not serve to restore the normal oxygen tension of the tissues. Rabbits, previously acclimatised, tolerated for 10 days an atmosphere containing only 7·5% of oxygen. The carbon dioxide and oxygen tensions of the tissues are regulated by the oxygen content of the arterial blood. Excessive thyroid feeding was without effect on the tension of oxygen or of carbon dioxide in the tissues. R. K. CANNAN.

Comparative capacity of the blood and of the tissues to absorb carbonic acid. L. A. SHAW (Amer. J. Physiol., 1926, 79, 91—99).—Cats were caused to breathe air containing 7·5% of carbon dioxide until the carbon dioxide uptake was complete. From this, by subtracting the carbon dioxide in the blood independently determined, the carbon dioxide taken up by the tissues was calculated. This accounted for 87·4% of the total, corresponding with 10 volumes per 100 g. of tissue. The buffering capacity of the blood against a rise in carbon dioxide tension in the inspired air is about twice as great as that of the same weight of tissue. The respiratory quotient was about the same after saturation of the body with carbon dioxide at the increased tension as before the experiment. R. K. CANNAN.

Rate of distribution of dissolved gases between the red blood-corpuscle and its fluid environment. I. Rate of uptake of oxygen and carbon monoxide by sheep's corpuscles. H. HARTRIDGE and F. J. W. ROUGHTON (J. Physiol., 1927, 62, 232—242).—The authors' method of determining the velocity of very rapid reactions was employed. Control experiments established that the observed rate of increase in the concentration of oxyhæmoglobin was to be attributed to the rate of the actual reaction within the corpuscle. The effects on the velocity of varying the concentration of dissolved oxygen, the temperature, and the sodium chloride are given. Under parallel conditions, the rate of uptake of carbon monoxide was about half that of oxygen. R. K. CANNAN.

Pyramidone in testing for blood. M. ELZAS and L. M. LANSBERG (Pharm. Weekblad, 1927, 64, 19—22).—By addition of 1 drop of a solution, containing 1 part of blood in 60,000 parts, to 3 c.c. of a 5% solution of pyramidone in alcohol, to which a little acetic acid and hydrogen peroxide have been added, a violet coloration develops on keeping. The test compares well in sensitiveness with the ordinary tests for blood. Comparative tests on blood in fæces are described. S. I. LEVY.

Existence of "pinnaglobin." M. HENZE (Z. physiol. Chem., 1926, 162, 136—138).—The liquid obtained from *Pinna squamosa* by Griffiths, and believed by him to be blood, is in fact the pericardial fluid. From this fluid a pigment may be isolated which is not of a protein nature and has no respiratory functions, but contains manganese in organic combination. "Pinnaglobin" does not exist. H. D. KAY.

Distribution of diffusible and non-diffusible calcium in blood-serum of normal animals. H. UPDEGRAFF, D. M. GREENBERG, and J. W. CLARK (J. Biol. Chem., 1926, 71, 87—117).—A number of determinations of diffusible and non-diffusible calcium in the blood-serum of man and of various animals have been made by a modification of the method of Moritz (A., 1925, i, 995), whose results are criticised on the ground that he neglected to allow for the diffusible calcium remaining in the collodion sacs. It is found that, of the two fractions, the non-diffusible is the more constant; the non-diffusible calcium is not in equilibrium with the total diffusible calcium, but may be in equilibrium with a small fraction of the latter. Since, in the different sera, the concentration of non-diffusible calcium runs parallel with that of the protein, it is probable that these two are in chemical combination. C. R. HARINGTON.

Colorimetric determination of chlorides, inorganic sulphates, and inorganic phosphates in small amounts of blood. S. YOSHIMATSU (Tohoku J. Exp. Med., 1926, 7, 553—559).—The blood (5—10 c.c.) is deproteinised by alcohol, heat, and "dazol," aliquot parts being used for the determination of sulphate (*ibid.*, 1926, 7, 11), phosphate (Sato, A., 1918, ii, 406), and chloride (Isaacs' method, *ibid.*, 1922, ii, 716, author's modification). CHEMICAL ABSTRACTS.

Determination of non-protein sulphur compounds of blood. Determination of sulphur compounds in urine. W. DENIS and L. REED (J. Biol. Chem., 1926, 71, 191—204, 205—208).—Proteins are removed from blood with trichloroacetic acid. Inorganic sulphate is determined by precipitation with barium chloride in presence of gelatin, and nephelometric comparison of the resulting solution with a similarly treated solution of a known amount of potassium sulphate. Application of the method to further portions of the blood filtrate after acid hydrolysis and after incineration with a mixture of zinc nitrate, sodium chloride, and ammonium chloride yields figures for the total sulphates and total sulphur, respectively. The error of the method, as compared with gravimetric determinations, is −10 to +7%. The above method has been applied successfully to suitably diluted urine. C. R. HARINGTON.

Colorimetric determination of blood-sugar. Correction. B. GLASSMANN (Z. physiol. Chem., 1926, 162, 145—147).—Many specimens of resorcinol, even in absence of dextrose, give a yellow colour when heated with 25% hydrochloric acid. A method of

correcting for this possible error in the author's method (A., 1926, 192) is described. H. D. KAY.

Determination of dextrose in blood. A. HANSEN (Dansk Tiddsk. Farm., 1927, **1**, 195—205).—Blood is deproteinised and the alkaline ferricyanide oxidation conducted as in the Hagedorn and Jensen method. The ferrocyanide formed is determined by oxidation with 2 c.c. of 0·005*N*-potassium dichromate in presence of 5 c.c. of 10% hydrochloric acid; the excess of dichromate is determined by addition of 3 c.c. of 0·005*N*-sodium arsenite containing 1% of sulphuric acid, and excess of arsenite is titrated with 0·005*N*-potassium bromate in presence of potassium bromide, using 0·0004% methyl-orange as indicator. The stock solutions used are more stable than those in the Hagedorn and Jensen method, but the same results are obtained with both methods. L. F. HEWITT.

Co-zymase. IX. Determination of co-zymase in blood. H. VON EULER and R. NILSSON (Z. physiol. Chem., 1926, **162**, 63—71).—Co-zymase, measured by its effect in restoring fermenting power to washed, dried yeast, is present in considerable quantities in human blood. It is present entirely in the red cells, from which it may be extracted by boiling with water. Bird's blood contains more co-zymase than the blood of mammals. The co-zymase content of the blood in man in diabetes, and in the mouse in rickets, remains normal.

H. D. KAY.

Reversible hæmolysis. K. FUKUSHIMA (J. Biochem. [Japan], 1926, **6**, 315—322).—Reversion of hæmolysis is attributed to the action of electrolytes which apparently combine with the hæmoglobin and either penetrate into or adhere to the stroma.

CHEMICAL ABSTRACTS.

Anticoagulating action and nuclear origin of a substance extracted from the mesenteric ganglion. M. DOYON and I. VIAL (Compt. rend., 1926, **183**, 1123—1124).—The isolation from the mesenteric ganglions of a bullock of a phosphorus-free nucleoside which, *in vitro*, has a powerful inhibiting action on blood coagulation, is described. It consists essentially of a carbohydrate–purine compound, is acid to litmus, and, after hydrolysis, reduces Fehling's solution. J. W. BAKER.

Lactacidogen in heart-muscle. H. PERGER (Z. physiol. Chem., 1926, **162**, 122—135).—Heart-muscle contains lactacidogen, which is diminished in quantity when the isolated organ is allowed to beat for a considerable time in a non-nutrient solution before the determination is made. Heart-muscle is able to re-synthesise inorganic phosphate into organically combined phosphoric acid in presence of sodium fluoride. This ability is diminished in the heart-muscle of a sick animal. Potassium cyanide also brings about this synthesis in presence of heart-muscle. Within certain limits, alanine will replace glycogen in the lactacidogen synthesis in presence of sodium fluoride. H. D. KAY.

Non-existence of uncombined adrenaline in fresh suprarenal capsules. G. MOURIQUAND and A. LEULIER (Compt. rend., 1926, **183**, 1353—1355).—The suprarenal capsule (guinea-pig) gives practically no adrenaline reaction with mercuric chloride and sodium acetate directly after removal from the body, but after keeping for 24 hrs., a strong reaction is given. It is suggested, therefore, that adrenaline exists in the capsule in a combined state.

L. F. HEWITT.

Fixed oil of the kidney fat of the emu (*Dromaius novæ-hollandiæ*). F. R. MORRISON (J. Proc. Roy. Soc. New South Wales, 1926, **60**, 113—118).—The oil obtained from the fatty tissue surrounding the kidneys of the emu has m. p. 30—31°, 0·915, n_D^{20} 1·4700, acid value 1·7, saponification value 195·2, iodine value 95·5, and consists of glycerides of oleic, linolenic, palmitic, and stearic acids. In addition, 0·2% of unsaponifiable matter which gives the colour reactions of cholesterol and a small amount of a mixed glyceride of palmitic and stearic acids (probably glyceryl β-stearate-αγ-dipalmitate) were isolated.

J. W. BAKER.

Nickel and cobalt content of the pancreas. G. BERTRAND and M. MÂCHEBŒUF (Bull. Soc. chim., 1926, [iv], **39**, 1646—1648).—See A., 1926, 869.

Chemistry of the ovary. XI. Fat of ovarian residue. D. TOURTELOTTE and M. C. HART (J. Biol. Chem., 1926, **71**, 1—13).—From 247 g. of the acetone-soluble portion of the ethereal extract of ovarian residue there were obtained 100 g. of free fatty acids, 95 g. of fatty acids present as neutral fat, and 46·3 g. of unsaponifiable matter, of which 30·76 g. was cholesterol. The mixed fatty acids comprised 0·4% myristic, 32·4% palmitic, 10·4% stearic, 55·3% oleic, 0·7% arachidonic acids, together with a trace of linoleic acid and 0·7% of an acid, $C_{20}H_{31}O_2$, yielding a *hexabromide*, m. p. 220° (decomp.).

C. R. HARINGTON.

Investigation of asparaginase in the testicles of the calf. M. MARIO (Arch. Farm. sper. Sci. aff., 1926, **41**, 216—218).—Contrary to the statement of Lang (A., 1904, ii, 427), calves' testicles contain no enzyme capable of deaminating asparagine.

T. H. POPE.

Shark's fins. K. H. LIN (J. Biochem. [Japan], 1926, **6**, 323—333).—Commercial, prepared shark's fins are free from fat or carbohydrate; the ash content is 0·84% (of which 0·70% is sulphur) and the nitrogen content 17·18%. Hence it is an incomplete protein, lacking in tryptophan; one third of the total amount of amino-acids consists of arginine, histidine, and lysine. CHEMICAL ABSTRACTS.

Oil from *Mesoplodon bidens*. E. ANDRÉ and H. CANAL (Compt. rend., 1926, **183**, 1063—1065).—Oil from the cetacean *Mesoplodon bidens* had the following properties: d_0^{15} 0·8694, n_D^{15} 1·4650, α_D −0·85°, saponification value, 103·4, iodine value (Hanus) 81·5. When saponified, 51% of fatty acids and 49% of unsaponifiable matter were obtained, together with 0·7% of glycerol. From the unsaponifiable matter, m. p. 20—25°, iodine value, 83·4, acetyl index (André) 184, were isolated cetyl alcohol and oleyl alcohol. In the fatty acid fraction, an acid similar to *iso*pelargonic acid is present to the extent of about 1%; oleic acid predominates, together with gadoleic acid and erucic acid. In general, the oil is similar to cachalot oil. L. F. HEWITT.

Chemical composition of the jellyfish *Velella spirans*. F. HAUROWITZ and H. WAELSCH (Z. physiol. Chem., 1926, **161**, 300—317).—A quantitative investigation of the ash, ether-, alcohol-, water-, hydrochloric acid-soluble and insoluble fractions and of the enzymes of the dried jellyfish. P. W. CLUTTERBUCK.

Comparative chemical investigation of *Holothuria* and *Actinia*. F. HAUROWITZ and H. WAELSCH (Z. physiol. Chem., 1926, **161**, 318).—Tests for carbamide, uric acid, creatine, and creatinine in extracts of *Holothuria tubulosa* and *Actinia equina* were negative. Differing from *Velella spirans*, the entire framework of the above is completely digested by pepsin–trypsin treatment, and is free from cellulose, chitin, and scleroprotein. P. W. CLUTTERBUCK.

Composition of the spawn from *Hemifusus tuba*, Gmel. Y. KOMORI (J. Biochem. [Japan], 1926, **6**, 129—138).—From 2 kg. of the fluid from the egg-sac, 160 g. of " crude vitellin " were obtained, having the following amino-acid composition : alanine 0·71, valine 0·27, leucine 10·29, proline 1·1, phenylalanine 0·22, aspartic acid 1·6, tyrosine 0·8, arginine 3·73, lysine 0·86, tryptophan 1·49%. Glycine, *iso*-leucine, glutamic acid, serine, and histidine were absent. CHEMICAL ABSTRACTS.

Amylolytic power of certain digestive secretions in relation to the time of glandular activity. V. ZAGAMI (Arch. Farm. sper. Sci. aff., 1926, **41**, 151—169).—Human saliva, obtained under the influence of an acid stimulus such as 0·1*N*-hydrochloric acid or lemon juice, is secreted in almost uniform quantities during the succeeding periods of intense glandular activity, whilst the amylolytic power increases rapidly during the first 15 min. and subsequently diminishes slowly and continuously. The pancreatic juice of the dog, obtained under the action of various mixed foods and then of 0·4% hydrochloric acid, is secreted in almost uniform quantities during succeeding periods of intense glandular activity, and maintains constant amylolytic power. The enteric juice of the dog, obtained by stimulation with 5% sodium chloride solution, is formed in quantities diminishing almost to zero, whilst its amylolytic power increases to four times the original value. T. H. POPE.

Iodine as a biological element. IV. Iodine content of colostrum and normal milk. E. MAURER and S. DIEZ (Biochem. Z., 1926, **167**, 161—166).—Both in the cow and in the human the iodine content of colostrum diminishes steadily during the first five or six days of lactation until normal milk is produced. J. PRYDE.

Carbon dioxide tension of cerebrospinal fluid. A. T. SHOHL and S. KARELITZ (J. Biol. Chem., 1926, **71**, 119—126).—For cerebrospinal fluid, the term pK' of the Henderson–Hasselbalch equation is found, both by analysis of the fluid after equilibration with a known tension of carbon dioxide and by calculation from the ionic strength of the fluid, to be $6·13 \pm 0·03$. Assuming equal values for p_H and hydrogen carbonate in blood plasma and cerebrospinal fluid, the carbon dioxide tension in the latter is the higher by 5—7 mm. of mercury. The carbon dioxide tension of the cerebrospinal fluid does not in general, however, bear a definite relation to that of the blood plasma. C. R. HARINGTON.

Gallodeoxycholic acid from the bile of chickens and its influence on pancreatic lipase activity. S. YONEMURA (J. Biochem. [Japan], 1926, **6**, 287—296).—Crude bile acid, obtained by boiling fresh bile with potassium hydroxide and precipitating with hydrochloric acid, was kneaded with cold water, dissolved in alcohol, and freed from fatty acids with light petroleum. The dry residue was then boiled with alcoholic sodium ethoxide, acidified with dilute sulphuric acid, and extracted with light petroleum, and this process repeated. *Gallodeoxycholic acid*, prepared from the *barium* salt, $C_{48}H_{78}O_8Ba$, has m. p. 112° (softening at 95°), $[\alpha]_D$ +13·23°. When boiled with chromium trioxide in glacial acetic acid, it affords *gallodehydrodeoxycholic acid*, $C_{24}H_{66}O_4$, m. p. 153—154°. Boiling with concentrated nitric acid affords gallodeoxybilianic acid, m. p. 89—90°, identified as a trimethyl ester of deoxybilianic acid. Gallodeoxycholic acid increases the activity of pancreatic lipase as also does cholic acid. CHEMICAL ABSTRACTS.

Presence of amino-acids in the gall from a bile duct cyst. T. TAKAKI (J. Biochem. [Japan], 1926, **6**, 27—29).—Bile (1500 c.c.) from a one-year-old child yielded tyrosine (0·03 g.), leucine (0·43 g.), arginine (0·18 g.), and lysine (0·06 g.). CHEMICAL ABSTRACTS.

Isotopes of chlorine in urine. L. AMBARD and A. CHRÉTIEN (Bull. Soc. Chim. biol., 1926, **8**, 1103—1105).—After injection of sodium chloride, the urinary chloride, purified by fractionation, gave values for the atomic weight of chlorine identical with the normal value. The two isotopes therefore pass through the body and the ratio remains constant. A. WORMALL.

Determination of urea. B. GLASSMANN (Z. physiol Chem., 1926, **162**, 148).—A correction to the author's volumetric method. H. D. KAY.

Determination of cellulose in human fæces and the digestion of food cellulose. T. KOHMOTO and S. SAKAGUCHI (J. Biochem. [Japan], 1926, **6**, 61—76).—The sample (3—5 g.) is digested for 1 hr. with 2·5% potassium hydroxide solution (200 c.c.), acidified with sulphuric acid, diluted, again heated for 1 hr., and filtered hot through fine linen on an asbestos pad. The residue, after being washed with water, alcohol, and alcohol–ether mixture, is mixed with water to 100 c.c., 6 c.c. of 5% sodium hypochlorite are added with stirring, the mixture is filtered after 15 min. through a tared paper, washed, treated with 1% acetic acid, washed with water, alcohol, and ether, and dried at 105°. The loss of cellulose is 5·8%. Persons whose food contained 8·5% of cellulose digested and absorbed 75% of the quantity. Air-dried foods contain cellulose as follows : rice 0·465, bread 0·318, hard bread 0·334, potato 1·904, sweet potato 2·694, beans 5·2%. CHEMICAL ABSTRACTS.

Extraction of total ether-soluble material from fæces. R. G. FREEMAN, jun., and E. G. MILLER, jun. (Arch. Pediatrics, 1926, **43**, 421—422).—

For the determination of total lipins, the material (1—5 g.) is triturated with concentrated hydrochloric acid (1—3 c.c.) and then with anhydrous sodium sulphate (35—40 g. per g. of fæces), and the mass repeatedly extracted with ether at the ordinary temperature, the residue after evaporation being dried at 98—100°. The free fatty acids are determined by solution in benzene and titration with 0·1*N*-sodium ethoxide solution. Soaps are determined by difference. CHEMICAL ABSTRACTS.

Lactacidogen metabolism in diabetic muscle. H. LANGE (Arch. exp. Path. Pharm., 1926, **118**, 115—120).—In diabetic muscle, the enzymic processes resulting in the formation and decomposition of lactacidogen proceed under the same conditions with considerably less speed than in normal muscle. W. ROBSON.

Diazo-urine. I. Chemical composition of the diazo-urine in tuberculosis. Y. KOMORI (J. Biochem. [Japan], 1926, **6**, 297—305).—Fifty litres of urine from advanced tuberculous patients contained: antoxyproteic acid 67·33 g., oxyproteic acid 10·79 g., *l*-proline 0·15 g., aspartic acid 0·37 g., glutamic acid 0·024 g., serine 0·04 g., arginine 2·39 g., lysine 3·05 g.; histidine and phenylalanine were present. CHEMICAL ABSTRACTS.

Metabolism during fasting in the human subject. W. G. LENNOX (J. Clin. Invest., 1926, 2, 609).—The oxygen consumed increases during fasting and runs parallel with the nitrogen excretion. CHEMICAL ABSTRACTS.

Role of acetaldehyde in animal metabolism. A. P. BRIGGS (J. Biol. Chem., 1926, **71**, 67—73).—After administration of acetaldehyde and of alcohol, the former substance could be detected in the expired air and in the urine; no acetaldehyde was excreted after administration of pyruvic acid. C. R. HARINGTON.

Action of the sympathetic system on the carbohydrate metabolism of muscle. H. E. BUTTNER (Z. physiol. Chem., 1926, **161**, 282—299).—By section of the rami communicantes in the frog, the muscle lactic acid is increased by about 40% and the glycogen content by 34%, whereas the lactacidogen content is decreased by 18%. The lactic acid content of the muscle is increased on the operated side when the aorta is ligatured immediately after the operation. Lactic acid formation after injection of caffeine is greater by 50% in the muscle, the sympathetic innervation of which is cut, than in the normal muscle. After injection of carbamide in large doses, the lactic acid content of the muscle becomes 8—10 times the normal value, and that of the muscle, the rami of which are cut, is increased by 44%. P. W. CLUTTERBUCK.

Specific dynamic action of gelatin hydrolysates. D. RAPPORT (J. Biol. Chem., 1926, **71**, 75—86).—When gelatin is administered together with the products of its acid or tryptic hydrolysis, the specific dynamic effect obtained is equal to the sum of that of the gelatin and that of the hydrolysate; if, on the other hand, the protein or its hydrolysate be administered simultaneously with glycine (the latter being given either orally or intravenously), the normal specific dynamic action of the glycine is neutralised. The specific dynamic action of the mixed hydrolytic products of a protein is therefore a property of the original protein, and does not depend on the amount of any given amino-acid which is present. C. R. HARINGTON.

Value of cocoa and chocolate as sources of protein in the diet. H. H. MITCHELL, J. R. BEADLES, and M. H. KEITH (J. Biol. Chem., 1926, **71**, 15—31).—Rats were fed on a diet containing 8% of protein, the whole of which was supplied in the form of cocoa. Under these conditions, the protein was digested to the extent of 38% on the average, and its biological value (*i.e.*, % of absorbed nitrogen which was retained in the body) was 37; neither of these values was altered by the substitution of milk for half the cocoa. Neither by itself nor in combination with milk, therefore, can cocoa be regarded as an important source of food protein. Cocoa was found to contain 0·55% of creatinine and 0·24% of creatine, and the excretion of these compounds was increased in the animals on the cocoa diet. C. R. HARINGTON.

Effect on the kidney of long-continued administration of diets containing an excess of certain food elements. I. Excess of protein and cystine. II. Excess of acid and alkali. T. ADDIS, E. M. MACKAY, and L. L. MACKAY (J. Biol. Chem., 1926, **71**, 139—156, 157—166).—I. At the end of a year on a diet containing 70% of protein, rats showed, as compared with control animals on a diet with 17% of protein, a general deficiency of body-fat, a decrease in the weight of the liver, and an increase in that of the kidneys; these changes were less marked, or absent, in rats on the low-protein diet with the addition of 1% of cystine. Renal lesions were not observed.

II. Rats fed for a year on an " acid diet " containing 2% of calcium chloride showed a reduction in body-weight and a decreased excretion of protein in the urine as compared with normal rats, but no pathological changes in the kidney; on a diet containing 4% of sodium hydrogen carbonate, however, large amounts of blood appeared in the urine, and 30% of the rats so treated showed hydronephrosis. C. R. HARINGTON.

Chemical nature of substances required for cell multiplication. A. CARREL and L. E. BAKER (J. Exp. Med., 1926, **44**, 503—521).—The presence in embryo juice of a hormone that stimulates cell division is improbable. Proteoses separated from peptic digests of fibrin by sodium sulphate determine a more abundant and prolonged multiplication of fibroblasts than that produced by embryo juice. Peptones and smaller split products furnish some nutrient material, but are sometimes toxic. Possibly the effect of embryo juice is due to the splitting of the protein of the juice into proteoses by the cell enzyme, or by other enzymes activated by the presence of living cells. CHEMICAL ABSTRACTS.

Comparative biochemistry. II. Behaviour of aromatic fatty acids and of pyridine in the organism of lower animals. Y. KOMORI, Y. SENDJU, J. SAGARA, and M. TAKAMATSU (J. Biochem. [Japan], 1926, **6**, 21—26).—Frogs eliminate subcutaneously administered benzoic, phenylacetic, and

phenylpropionic acids in the urine as hippuric acid. Turtles eliminate benzoic acid as hippuric acid and pyridine as methylpyridylammonium hydroxide. CHEMICAL ABSTRACTS.

Comparative biochemistry. III. Behaviour of nicotinic acid in the organism of mammals and birds. Y. KOMORI and Y. SENDJU (J. Biochem. [Japan], 1926, 6, 163—170).—Nicotinic acid, neutralised with sodium carbonate and fed to dogs, is eliminated in the urine partly unchanged and partly as nicotinuric acid and as trigonelline. Trigonelline does not appear in the urine of rabbits given nicotinic acid; birds eliminate the whole of the nicotinic acid unchanged. CHEMICAL ABSTRACTS.

Behaviour of *o*-nitrobenzaldehyde, *o*-aminobenzaldehyde, and anthranil in the animal organism. T. HOSODA (J. Biochem. [Japan], 1926, 6, 171—177).—When *o*-aminobenzaldehyde is administered to rabbits, especially subcutaneously, anthranilic acid appears in the urine. Injections of *o*-amino- and *o*-nitro-benzaldehyde do not produce a reducing urine. The urines contain *o*-nitrobenzoic acid. Anthranil caused the appearance of anthranilic acid in the urine. CHEMICAL ABSTRACTS.

Action of carnosine on gastric secretion. I. P. RASENKOW, G. W. DERWIES, and S. E. SSEWERIN (Z. physiol. Chem., 1926, 162, 95—102).—Administration of carnosine, either subcutaneously or *per os*, has no effect on the secretion of gastric juice. Only when injected intravenously does carnosine act as a weak stimulator of gastric secretion. Meat extract owes its activity only in the slightest degree to carnosine. Krimberg's results (A., 1926, 752) are probably due to impurities present in his carnosine fractions, and not to the base itself. H. D. KAY.

Production of alcohol in the animal body. II. Amount of alcohol in the blood and liver of asphyxiated animals. M. AOKI (J. Biochem. [Japan], 1926, 6, 307—314).—The blood and tissues of asphyxiated fowls contain an increased amount of alcohol. CHEMICAL ABSTRACTS.

Distribution of iodine in nature and its physiological significance in vegetable and animal organisms. J. STOKLASA [with DVOŘAK, BARES, ŠILHAVÝ, and ŠTRUPL] (Z. angew. Chem., 1927, 40, 20—27).—Analyses of many different kinds of rocks show that iodine is widely distributed, especially in volcanic rocks and the more recent rocks which contain the fossilised remains of animal- or plant-life. In the case of volcanic rocks, the content varies from 0·458 to 0·984 mg. of iodine per kg. in recent rocks to 0·295—0·428 mg. per kg. in plutonic rocks. The fossils of the silurian and carboniferous formations are especially rich in iodine, some of them containing as much as 1·94 mg. per kg. (*Caulopteris*). The fact that fossilised plants have a relatively high content of iodine indicates that this element played an important part in their growth, and tests made on many plants grown in various soils both with and without an iodine supply substantiate this. Iodine promotes the growth of the nitrifying bacteria in a similar way to radioactive substances, and the simultaneous presence of iron and iodine in a soil causes a much more intensive assimilation of nitrogen, a greater growth of the plant, a larger yield of seed, and a much greater development of the germ, thus resulting in greater fertility. Thus iodine must be considered as an essential biogenic element in the synthesising processes of the living cell. Radishes, tomatoes, and, to a smaller extent, potatoes are particularly rich in iodo-oxydases and are therefore a valuable source of iodine for human food. A. R. POWELL.

Trimethylamine oxide as biological hydrogen acceptor. D. ACKERMANN, K. POLLER, and W. LINNEWEH (Ber., 1926, 59, [*B*], 2750—2751).—Trimethylamine oxide behaves as hydrogen acceptor towards substances containing the thiol group united to carbon, provided the mol. wt. of these substances is not too large, but not towards a variety of compounds such as dextrose, adrenaline, amino-acids, albumin, globulin, hæmoglobin, and ovalbumin. The oxide is indifferent towards hydrogen except in presence of palladised charcoal or other carrier. H. WREN.

Influence of bile acids on the protein metabolism of the sex glands and the significance of choleic acid. R. KARASAWA (J. Biochem. [Japan], 1926, 6, 139—159).—Cholic, and particularly deoxycholic, acids inhibit the proteolysis in autolysing testes, the effect depending on the amount as well as on the concentration. The amount of nitrogen from mono- and di-amino-acids becomes both absolutely and relatively smaller as the quantity of bile acid increases, whilst the cleavage of nucleoproteins is actually stimulated. CHEMICAL ABSTRACTS.

Relation between bile acids, snake venom, and cholesterol. I. S. YONEMURA and M. FUJIHARA (J. Biochem. [Japan], 1926, 6, 91—100).—Cholic and deoxycholic acids have a strong hæmolytic effect on rabbit red blood-cells, and act plasmolytically on leucocytes. When injected intravenously into rabbits, cholic and deoxycholic acids, like the poison of *Trigocephalus*, reduce the blood cholesterol and the number of leucocytes. CHEMICAL ABSTRACTS.

Effect of parasympathetic poisons on blood-sugar. Problem of the parasympathetic hyperglycæmia. T. SAKURAI (J. Biochem. [Japan], 1926, 6, 211—236).—Subcutaneous, but not oral, administration of choline to fasting rabbits produces slight hyper- or hypo-glycæmia, according to the dose (0·1—0·01 g. per kg.). Eserine (1 mg. per kg.) and pilocarpine (5—10 mg. per kg.), injected subcutaneously, produce hyperglycæmia, the hyperglycæmic effect being inhibited by atropine. Eserine does not inhibit the effect of insulin, but the reverse is true. CHEMICAL ABSTRACTS.

Influence of hydrazine and its derivatives on metabolism. II. Non-protein nitrogen of blood and metabolism of glycine in hydrazine intoxication. H. B. LEWIS and S. IZUME. **III. Mechanism of hydrazine hypoglycæmia.** S. IZUME and H. B. LEWIS (J. Biol. Chem., 1926, 71, 33—49, 51—66).—II. After subcutaneous injection into rabbits of 130 mg. per kg. of hydrazine sulphate, the amino-acid nitrogen of the blood was always increased; the total non-protein nitrogen and urea nitrogen of

the blood were markedly increased only in those cases in which renal lesions were produced in addition to the hepatic lesions which are a constant effect of the hydrazine. Injection of glycine into rabbits poisoned with hydrazine leads to an abnormal rise in the concentration of amino-acid nitrogen in the blood and no simultaneous increase in the urea; the hyperglycæmia and increased deposition of glycogen in the liver, which follows large doses of glycine in the normal rabbit, did not take place during hydrazine poisoning.

III. In rabbits poisoned with hydrazine the hyperglycæmia following administration of dextrose or of sodium lactate was abnormally great, whilst no deposition of glycogen took place. It therefore appears that the hepatic injury induced by hydrazine interferes both with the process of deamination and with the synthesis of glycogen. It is suggested that the hypoglycæmia produced by a simple injection of hydrazine is due to a failure in the conversion of non-carbohydrate materials into dextrose, with resulting deficiency in the latter substance.

C. R. Harington.

Biothermic action of organic compounds. E. Mameli and E. Filippi (Annali Chim. Appl., 1926, 16, 556—602).—Investigation of about 80 compounds (cf. A., 1925, i, 466) shows that, in general, only few functional groups or molecular groupings impart a distinct and constant biothermic function to the molecules of which they form part. Most of the organic compounds examined exhibit varied thermic behaviour, not only as regards doses, but also in relation to other experimental conditions, such as the character of the solvent used or the mode of suspension, and the method of administration. The carboxyl group in aliphatic chains is predominantly athermic, the acetamido-group mostly hypothermic, and the hydroxyacetyl group hyperthermic. Certain vitamins also have a hyperthermic effect. Glycollic acid and various coumaranone derivatives act similarly to the phenoxyacetic acids, and the hyperthermic effects are neither preceded nor followed by marked or rapid hypothermia, such as is observed with carbazole and certain other compounds, and do not exhibit the considerable oscillations during the rise of temperature which follow the administration of non-toxic doses of strychnine. T. H. Pope.

Rate of sedimentation of red blood cells and shifting in the plasma proteins in animals injected with India ink. S. Tsunekawa (J. Biochem. [Japan], 1926, 6, 237—260).—Injection of the ink is followed by a sudden increase in the fibrinogen content of the plasma, with return to the normal level after 7—10 days. The albumin/globulin quotient similarly diminishes and becomes normal. The absolute and relative increase of the globulin is not always parallel to the change in fibrinogen content. The rate of sedimentation of red cells is greatly increased. Chemical Abstracts.

Chemotherapy. I. Physiological action of leuco-dyes of the triphenylmethane series. M. Coplans and A. G. Green (J. Pharm. Exp. Ther. 1926, 30, 101—119).—The leuco-compounds of brilliant-green, xylene-blue, sulphato-green, and sulphato-violet are much less toxic and less active bactericidal agents than the corresponding dyes themselves. The dyes themselves, however, have no effect on toxins, whilst the leuco-compounds detoxicate diphtheria and tetanus toxins both *in vitro* and *in vivo*. For detoxication *in vitro*, incubation for several hours at 37° is necessary. Lethal doses of toxins thus treated do not produce toxic symptoms or death of the animal. Simultaneous injection of toxin and leuco-dye, or injection of the leuco-dye within a short time of injection of toxin and in the same place, also results in "neutralisation" of the toxin. Previous injection of leuco-compound has no effect. In the case of cobra-venom, detoxication of the toxin could be obtained *in vivo*, but not *in vitro*. In some cases, toxic symptoms were manifested in the animal some days after the introduction of the detoxicated toxin. Hæmoglobin prevents the neutralisation of the toxin by the leuco-compound, owing, it is suggested, to catalytic oxidation of the latter through the agency of the hæmoglobin. The more basic the leuco-compound the greater is its activity in neutralising toxins. The name "contra-toxins" is suggested for such compounds. L. F. Hewitt.

Relation between chemical constitution and therapeutic action. E. Fourneau (Compt. rend. 6me. Conference intern. chim., 1925, 72—211).—A review, chiefly devoted to protozoocidal and spirillicidal substances. A number of dyes, and organic derivatives of mercury and arsenic, are considered, and some general rules are deduced.

Chemical Abstracts.

Pharmacology of iron. E. Starkenstein (Arch. exp. Path. Pharm., 1926, 118, 131—191).—Ferrous compounds are not precipitated in the highest concentrations of protein solutions or in blood-serum, nor do they agglutinate or dissolve washed erythrocytes. They have neither an irritating nor an astringent action on subcutaneous or intravenous injection. Ferric salts are precipitated by very dilute protein solutions, and agglutinate and dissolve washed erythrocytes. The hæmolytic action of ferric salts of organic acids is stronger than that of inorganic ferric salts, whilst as protein precipitants the inverse holds. Ferric salts of hydroxypolycarboxylic acids (at least two carboxyls and one hydroxyl) behave likewise. Their acid-reacting solutions may be neutralised or made slightly alkaline without the separation of ferric hydroxide. These neutral solutions do not precipitate protein, and the iron forms part of a complex anion. These iron-containing acids exist only within a limited range of p_H; they form insoluble calcium and lead salts. The analogous ferrous salts of these acids behave similarly to other ferrous salts. Only the ferro-ions are toxic. After larger doses, the toxic effects are first similar to those of magnesium narcosis, from which the animals recover only to relapse later in convulsions. The toxicity of the ferrous salts is analogous to the behaviour of calcium salts with differing anions. In descending order of toxicity are chloride, sulphate, nitrate, acetate, lactate, indicating that the anion determines the degree of toxicity. The ferric ion is inactive in the organism. The complex salts of the

above-mentioned ferrous and ferric hydroxypolycarboxylic acids are formed in the organism after the administration of the ferrous or ferric salts of the corresponding acids. They are stable on account of the buffering action of the organism. In the animal body, the ferro-acids are oxidised to ferri-acids. Ferrous salts and the complex iron-containing anions are rendered non-toxic by calcium chloride.

W. Robson.

Elimination of lead by the secretion of the digestive glands. F. Bricker (Arch. exp. Path. Pharm., 1926, **119**, 129—139).—After the administration of a single dose of white lead (0·4—0·6 g.) to a dog *per os*, a small amount of white lead is eliminated in the bile on the following day and a smaller amount in the pancreatic juice. With long-continued feeding (0·2—0·3 g. of white lead per day), the cessation of lead treatment may give rise to two types of results. Excretion in the bile may persist for some time and then cease, or may cease after a very short time, followed by excretion of traces later. Excretion in the pancreatic juice continues for some time after the lead feeding has stopped, and then ceases. The quantity excreted over an extended period is very small, and thus the liver and pancreas play no significant role in eliminating lead. No renewal of lead excretion in the bile can be produced by stimulants, whilst various foodstuffs or hydrochloric acid have no effect on excretion in pancreatic juice.

A. Wormall.

Methods of destroying organic matter in the chemical and biological analysis of poisons. M. A. Mancini (Arch. Farm. sper. Sci. aff., 1926, **41**, 170—184).—The various methods suggested for destroying animal tissue in the investigation of cases of poisoning are discussed. Tryptic digestion serves well for this purpose and effects no change in the chemical or biological properties of alkaloids, glucosides, antipyrin, veronal, trional, or acetanilide.

T. H. Pope.

Ionic changes in the blood with narcotics and stimulants. E. Brauchli and O. Schnider (Arch. exp. Path. Pharm., 1926, **119**, 240—253).—Earlier experiments with dogs showing the changes in blood calcium and potassium in narcosis (cf. Cloetta and Brauchli, A., 1926, 431) are confirmed and applied to man with similar results. A reduction in the calcium content takes place whenever sleep ensues, but the fall is not quite so great if the dog has previously been accustomed to the narcotic by doses *per os* over an extended period. Some relationship thus exists between the condition of sleep and the fall of calcium content of plasma. Caffeine, tetrahydro-β-naphthylamine, and camphor produce a definite rise in plasma calcium, but strychnine gives varying results. The alterations in the potassium content are less constant. In narcosis there is a rise, in light sleep the results vary, and with caffeine, tetrahydro-β-naphthylamine, and camphor there is a tendency for the blood potassium to fall.

A. Wormall.

Toxicological investigation of veronal. G. Sensi (Annali Chim. Appl., 1926, **16**, 510—519).—The viscera (or urine), rendered acid by acetic acid, are extracted with ethyl acetate until a small portion of the solvent leaves no appreciable residue on evaporation. The extract is evaporated and the residue boiled with water and filtered hot. The filtrate is evaporated to dryness on a water-bath and the remaining impure veronal dissolved in boiling alcohol and the solution filtered. The filtrate is treated for 24 hrs. with 7% of activated aluminium, prepared by immersing strips of aluminium sheet for 3 min. in 1% mercuric chloride solution, the filtered liquid being then evaporated to dryness and the residue of highly pure veronal weighed.

T. H. Pope.

Solvent action of carbon disulphide on biliary calculi *in vivo*. G. Galata (Arch. Farm. sper. Sci. aff., 1926, **41**, 185—201).—Carbon disulphide, ingested in oil by a dog for 25 days in daily doses of 1 c.c. of 10% solution per kg. body-weight, and also injected subcutaneously in daily doses of about 0·8 c.c. per kg., effected no diminution in the weight of two cholesterol calculi deposited in the gall-bladder 25 days previously. Further, daily ingestion for 15 days of a 10% solution of carbon disulphide in oil at the rate of 2 c.c. per kg. body-weight caused no appreciable modification in the volumes of two calculi of cholesterol or of four fragments of calculi encysted under the skin; these calculi were, however, partly dissolved by subsequent subcutaneous injection of carbon disulphide in the same doses, although the injections were made at points distant from the encysted calculi.

T. H. Pope.

Specificity of enzymes. S. Kostytschev (Z. physiol. Chem., 1926, **162**, 139—144).—A reply to Neuberg (A., 1926, 1173). The author restates his criticism of Neuberg's theory of fermentation.

H. D. Kay.

Alteration of liver arginase activity through external factors. S. Hino (J. Biochem. [Japan], 1926, **6**, 335—366).—A temperature of 4—8° does not diminish the activity of a solution of liver arginase even after 10 days; the destructive effect of a higher temperature varies according to the hydrogen-ion concentration. The presence of phosphates does not make liver arginase thermolabile (?). The inhibitory influence of sodium fluoride is a linear function of the logarithm of its concentration. Potassium bromide, cyanide, and iodide are without effect over a wide range of concentration, but free iodine is strongly inhibitory or destructive.

Chemical Abstracts.

Action of enzymes on γ-methylglucoside. R. Kuhn and T. Wagner-Jauregg (Z. physiol. Chem., 1926, **162**, 103—121).—γ-Methylglucoside (1 : 4 ?) has been prepared by a modification of Fischer's method, and from a consideration of the simultaneous polarimetric and titrimetric changes observed during its hydrolysis by dilute hydrochloric acid it is concluded that it is a mixture of the two isomerides. Free γ-glucose cannot be detected in the reaction mixture during this hydrolysis. If γ-glucose plays a large part in carbohydrate metabolism, it might be expected that enzymes capable of hydrolysing γ-glucosides would be widely distributed in nature. This is not the case. Of a large number of enzyme preparations and organ extracts examined, only autolysed yeast and an aqueous extract of pig's liver

have a slight hydrolytic effect, the remainder being inactive. H. D. Kay.

Biochemical synthesis of β-5-chlorosalicylglucoside. P. Delauney (Compt. rend., 1926, **183**, 990—992).—5-Chlorosaligenol and dextrose dissolved in aqueous acetone are treated with emulsin, when β-5-chlorosalicylglucoside (lævorotatory) is formed. L. F. Hewitt.

Biochemical oxidation of ferrous malate. J. Wolff and J. Loiseleur (Compt. rend., 1926, **183**, 1134—1136).—The effect of varying conditions on the oxidation of ferrous malate in the presence of ferrase (Wolff, A., 1926, 322) has been studied. The oxydase effects complete oxidation in air (not in a vacuum) between 20° and 50° (at 95° the ferrase is destroyed). At p_H 5 oxidation is rapid, and still proceeds, but more slowly, at p_H 3. Dialysis of an aqueous extract of ferrase from *Lactarius piperatus* or *Agaricus campestris* causes a large diminution in its activity, but reactivation occurs on the addition of a small quantity of manganese sulphate. J. W. Baker.

Nature of ferrase and certain oxydases. G. Bertrand (Compt. rend., 1926, **183**, 1136—1137).—The author does not agree that the observed facts (cf. preceding abstract) constitute sufficient evidence for the real existence of a new oxydase, ferrase, in extracts from the tissues of fungi, but believes that the oxidising power is due to the presence of a small quantity of a quinonoid derivative, volatile or readily destroyed by heat, forming a complex system with laccase (cf. Bertrand, A., 1896, i, 534).
J. W. Baker.

Methylglyoxal as a decomposition product of dextrose. E. Toenniessen and W. Fischer (Z. physiol. Chem., 1926, **161**, 254—264).—Hexosephosphoric acid (but neither glycogen nor dextrose) is converted by a mixture of muscle and pancreas pulp or by the mixed extracts of these pulps into methylglyoxal by an enzyme present in the muscle, the aldehyde being not further converted into lactic acid owing to the restraining action of the antiglyoxalase of the pancreas. This is regarded as proof of the view that methylglyoxal is an intermediate in carbohydrate metabolism.
P. W. Clutterbuck.

Hydrolysis of phosphoric esters in the surviving liver and the influence of drugs on the reaction. Liver lactacidogen. O. Riesser (Z. physiol. Chem., 1926, **161**, 149—177).—Liver pulp of frog and rabbit in 2% sodium hydrogen carbonate solution at 43—45° readily eliminates phosphoric acid, the amounts, for frog 0·174%, for rabbit 0·219% of the dry weight, being of the same order of magnitude as the lactacidogen phosphoric acid. An amount of lactic acid equal to or greater than that of the phosphoric acid is simultaneously formed. Hexosediphosphoric acid added to an alkaline solution under the same conditions gives rise to phosphoric, but no lactic acid, whereas added to muscle pulp it gives considerable amounts of phosphoric and a little lactic acid. Liver of frog and rabbit, on keeping in physiological saline, readily splits off phosphoric acid in the first hour, the maximum being reached for frog in Ringer's solution in 3 hrs. and for rabbit in Locke's solution at 39° in 2 hrs. The simultaneous formation of lactic acid is small. In isotonic calcium chloride solution, phosphoric acid formation is inhibited, and in isotonic sodium fluoride solution it is either inhibited completely or may be decreased (indicating synthesis of phosphoric esters). Alcohol, chloroform, adrenaline, and insulin do not affect the rate of spontaneous phosphoric acid formation, and quinine appears slightly to inhibit. P. W. Clutterbuck.

Function of a phosphatase in bone formation. H. D. Kay (Brit. J. Exp. Path., 1926, **7**, 177—180).—Normal blood plasma contains a small quantity of an acid-soluble phosphoric ester which is hydrolysable by bone phosphatase. The phosphatase content of whole bone is high in the fœtus, diminishing as the rate of bone formation decreases. In the kidney, the phosphatase is lowest in the fœtal stage.
Chemical Abstracts.

Synthetic action of pepsin. T. Oda (J. Biochem. [Japan], 1926, **6**, 77—89).—In digests of egg-white, edestin, and fibrin treated with pepsin, the synthesis (measured by changes in the amount of nitrogen unprecipitated by trichloroacetic acid) is complete after incubation for 2 days, and is most rapid at p_H 4. The synthetic process is not affected by lecithin or cholesterol, or by various electrolytes. The free amino-nitrogen is unaltered.
Chemical Abstracts.

Adsorption of pepsin. K. Kikawa (J. Biochem. [Japan], 1926, **6**, 275—286).—Pepsin is best absorbed on animal charcoal at p_H 1 or 2; it is removed by a phosphate (p_H 6·8) or citrate (p_H 5) solution, but not by a mixture of citrate and hydrochloric acid at p_H 1·8. The charcoal with the adsorbed pepsin digests caseinogen at p_H 1·8, much pepsin being removed. The leaching effect of protein is not due to the lowering of surface tension or to its viscosity; amino-acids, peptone, and diketopiperazine do not show the same effect. Chemical Abstracts.

Auto-digestion. II. Trypsin and "antitrypsin." H. Necheles and F. Fernando (Amer. J. Physiol., 1926, **79**, 9—27).—The sera of the chicken, duck, goose, and pigeon and saline extracts of the earthworm were found to have "antitryptic" titres of the same order as that of dog's serum. Injection of pancreas, pancreatic juice, or trypsin did not change the titre. Agents having possible effects on the permeability of the intestine were without effect on the titre. It is concluded that trypsin does not act as an antigen and that antitrypsin is not an antibody. It is suggested that the "antitryptic titre" is the product of the action of a protease and of a trypsin-inhibiting substance. R. K. Cannan.

Trypsin. XV. Enzymes of the pancreas. R. Willstatter, E. Waldschmidt-Leitz, S. Dunaiturria, and G. Künstner (Z. physiol. Chem., 1926, **161**, 191—209).—A number of improvements of the gelatin method for determination of trypsin are given, rendering it sufficiently accurate for the determination of the enzyme in fresh pancreas and in glycerol extracts thereof. A new method of preparation of trypsin is given, aiming at the complete separation of accompanying enzymes. Although trypsin is not adsorbed from acid solution by the stable γ-form

of aluminium hydroxide, it is readily adsorbed by the unstable β modification. A new method for the determination of trypsin by caseinogen is described which is regarded as superior to the gelatin method.
P. W. CLUTTERBUCK.

Enzymic cleavage of dipeptides. III. Activation and inhibition of peptidases. H. VON EULER and K. JOSEPHSON (Z. physiol. Chem., 1926, **161**, 270—281).—The hydrolysis of glycylglycine by erepsin (see A., 1926, 388, 1174) is inhibited by calcium chloride at concentrations of 0·02—0·03*M* upwards. Phosphate inhibits the enzyme of fresh glycerol extracts, but does not inhibit if the extract has been kept. Changes in activity of intestinal and yeast erepsin during dialysis are followed. In the crude enzyme, some substance is present which slightly activates the enzyme, but its effect is small.
P. W. CLUTTERBUCK.

Enzymic hydrolysis of dipeptides. IV. Intestinal erepsin. K. JOSEPHSON and H. VON EULER (Z. physiol. Chem., 1926, **162**, 85—94).—It has been shown previously that in the formation of the enzyme-substrate complex between a peptide and intestinal erepsin which precedes hydrolysis, the free amino-group of the α-amino-acid present in the peptide combines with the enzyme. Evidence is now adduced that the group in the enzyme molecule which combines with the free amino-group of the peptide is an aldehyde group. Phenylhydrazine, potassium cyanide, and sodium sulphite, all of which combine with aldehydes, strongly inhibit the hydrolysis of glycylglycine by erepsin. H. D. KAY.

Effect of amino-acids and other compounds on the activity of urease. W. J. HUSA (J. Amer. Chem. Soc., 1926, **48**, 3199—3201; cf. A., 1923, i, 351).—The promoter effect of α-amino-acids on urease has been confirmed, and is not affected by the introduction of a methyl group in the α-position. δ-Amino-*n*-valeric acid has no promoter effect, thus supporting the previous conclusion that the degree of the effect is determined by the proximity of the amino- and carboxyl groups. Quinine hydrochloride and ethyl 3-amino-4-hydroxymethylbenzoate slightly decrease the activity of urease. The enzyme is completely inactivated by "Mercurochrome 220 Soluble." F. G. WILLSON.

Enzymic conversion of aldehydes. II. K. MYRBÄCK and W. JACOBI (Z. physiol. Chem., 1926, **161**, 245—253).—The Cannizzaro reaction with acetaldehyde is accelerated by both fresh and dried yeast. The enzyme is not, but an activator is, removed by washing. By addition of the wash-water, the washed yeast is reactivated. This activator cannot be definitely said to be identical with co-zymase or co-reductase. P. W. CLUTTERBUCK.

Oxidoreductase in yeast. A. N. LEBEDEV (J. Russ. Phys. Chem. Soc., 1926, **58**, 184—195).—The power of yeast extract to decolorise methylene-blue was studied quantitatively. Variously treated samples of extract boiled, heated at different temperatures (35°, 60°) with and without addition of chemical reagents and fresh enzyme, were used. Experiments were also performed with maceration extract. Boiled extract was inert, but on autolysis it again became very active. This was shown not to be due to the formation of xanthine substances. Extract heated at 60° was moderately active, but did not ferment, like the fresh extracts, sugar or glyceric acid solutions, although its effect on pyruvic acid was greater. The results confirm the presence of a vigorous oxidoreductase in yeast, but not its participation in fermentation reaction.
M. ZVEGINTZOV.

Bacteria. XI. Development of a systematic analytical method for the comparative study of bacterial cells. T. B. JOHNSON (Amer. Rev. Tuberculosis, 1926, **14**, 164—171).
CHEMICAL ABSTRACTS.

General properties of cryptotoxins; tetanus cryptotoxin. H. VINCENT (Compt. rend., 1926, **182**, 1307—1310).—Cryptotoxins are formed by treating bacterial toxins with soaps, *e.g.*, sodium palmitate. The toxic properties of the toxin are destroyed, but the immunising properties remain. The toxin of tetanus is destroyed by treatment with 0·5% of a 0·2% solution of sodium palmitate at 38° for 10—16 hrs., but the toxic properties are partly recovered by treating the cryptotoxin with dilute hydrochloric acid. The immunising properties of the toxin are not destroyed by treatment with soaps, and the local reaction caused by the first injection disappears after repeated injections. Sodium palmitate is an efficient bactericidal agent for typhoid, paratyphoid A and B, and cholera bacilli, for Shiga's and Flexner's bacilli, *B. coli communis*, and streptococci, but is not hæmolytic. L. F. HEWITT.

Chemistry of insulin. H. PENAU and L. BLANCHARD (Bull. Soc. Chim. biol., 1926, **8**, 383—450).—An account of the preparation, properties, and physiological action of insulin.

Effect of various sugars (and of adrenaline and pituitrin) in restoring the shivering reflex. G. J. CASSIDY, S. DWORKIN, and W. H. FINNY (Amer. J. Physiol., 1926, **77**, 211—218).—Dihydroxyacetone, lævulose, mannose, and galactose restore the shivering reflex in cats in which it has been abolished by insulin hypoglycæmia. Maltose, sucrose, and lactose are also sometimes effective by reason of the products of their hydrolysis. All these substances, with the exception of sucrose and lactose, also abolish insulin convulsions. Adrenaline and pituitrin cause shivering to reappear in hypoglycæmic cats. R. K. CANNAN.

Effect of prolonged administration of parathyroid extract on excretion of phosphorus and calcium. I. GREENWALD and J. GROSS (J. Biol. Chem., 1926, **68**, 325—333).—Prolonged administration of parathyroid extract to a dog led to an increase in the total excretion of calcium and phosphorus; the increase in the excretion of calcium was so large as to indicate that it must have been due, in part at least, to removal of calcium from the bones.
C. R. HARINGTON.

Influence of diet and sunlight on the amount of vitamin-*A* and vitamin-*D* in the milk afforded by a cow. H. CHICK and M. H. ROSCOE (Biochem. J., 1926, **20**, 632—649).—The vitamin-*A* content of milk is at a maximum when the cow is fed on fresh

green food, and least when the animal is on a winter ration of cereals and roots; exposure of the cow to sunlight does not affect this vitamin in the milk. The antirachitic value of milk, on the other hand, depends on the degree of insolation of the cow as well as on the character of the diet. Milk contains a maximum amount of both fat-soluble vitamins when the cow is out at pasture in summer. Butter made from milk possessing antirachitic potency preserves this property after storage in the frozen condition for more than 2 years. S. S. ZILVA.

Difference in chemical composition of the skeletons of young rats fed (1) on diets deprived of fat-soluble vitamins and (2) on a low-phosphorus rachitic diet, compared with those of normally nourished animals of the same age. H. CHICK, V. KOVENCHEVSKY, and M. H. ROSCOE (Biochem. J., 1926, **20**, 622—631).—A condition of osteoporosis found in the bones of young rats kept on a diet deprived of fat-soluble vitamins is characterised by (1) a proportion of alcohol- and (fat) ether-soluble material in excess of the normal, (2) a proportion of ash (A) less than the normal, (3) a normal proportion of organic material, cartilage and connective-tissue, etc. (R), (4) a value of the A/R ratio of about 0·9—1·2, the normal value being about 1·5. In the osteoporotic bone, the percentage of calcium, reckoned on the dry weight of the bones, is frequently very low (12—16%), and is found to approach much nearer to the normal if the calculation is made on the fat-extracted bone.

Rachitic bones of rats kept on McCollum's low-phosphorus rickets-producing diet are characterised by (1) a content of mineral ash (A) much below the normal, (2) a water content much above the normal, (3) a very low value of the A/R ratio, *i.e.*, from 0·4 to 0·8, as compared with 1·0, the value found for the bones of rats which receive cod-liver oil in addition to this diet. The value of the A/R ratio is the best chemical criterion in the diagnosis of rickets.

S. S. ZILVA.

Value of egg-yolk in supplementing diets deficient in calcium. E. TSE (Amer. J. Physiol., 1926, **77**, 192—198).—Contrary to McCollum, it is found that small quantities of egg-yolk effectively supplement diets poor in calcium. This is due to a vitamin-like substance economising available calcium.

R. K. CANNAN.

Relation of certain soil algæ to some soluble carbon compounds. B. M. B. ROACH (Ann. Bot., 1926, **40**, 149—201).—A number of species of algæ have been isolated from the soil and the nutrition of the organisms has been studied in pure culture. The majority of the species show greatly increased growth when provided with dextrose or other suitable soluble organic compounds; and some, at least, are able to develop saprophytically in complete darkness, and must therefore be taken into account in regard to the biological and chemical changes taking place in the soil. A few soil species seem to be completely autotrophic in nutrition. A method for the quantitative study of unicellular algæ is described, involving daily measurements of the size of the cells and the number of cells per unit volume of the culture fluid, and the calculation from these data of the bulk of algal protoplasm present. In media favourable to growth, the logarithmic values of the bulk, plotted against time for a limited period of growth, lie on a straight line within the limits of experimental error, indicating growth at a uniform rate. Deviations from the straight line are still further reduced if the cultures are continuously aerated and the illumination is controlled. The relative average rates of growth of the species *Scenedesmus costulatus*, Chod., var. *chlorelloides*, in media containing mineral salts with 1% of various soluble organic compounds, taking the rate with dextrose as 100%, are: maltose, 100%, with an initial "lag" period; galactose, 94%; sucrose, 84%; lævulose, 73%; mineral salts alone, 60%; mannitol, 13%; xylose, 0%. Xylose is definitely toxic. C. T. GIMINGHAM.

Chlorosis of fruit trees. I. Composition of apple leaves in cases of lime-induced chlorosis. T. WALLACE and C. E. T. MANN (J. Pomology, 1926, **5**, 115—123).—Normal apple leaves contain more dry matter and less ash in the dry matter than chlorotic leaves. The percentages of potassium and sodium are always much higher, and of calcium definitely lower, in the ash of chlorotic leaves than in that of normal leaves; the differences are especially great in the case of potassium. Differences in the amounts of magnesium, iron, aluminium, phosphorus, and silica are not so definite. The soils on which chlorosis of apple trees occurred all contained high percentages of carbonates. Spraying chlorotic foliage with a solution of ferrous sulphate restored the normal green colour in several cases. C. T. GIMINGHAM.

Waxes of perfumed flowers. I. Wax of *Rosa Druscky*. A. D'AMBROSIO (Annali Chim. Appl., 1926, **16**, 443—451).—This rose contains a yellow wax, m. p. 57—58°. The portion extracted by cold alcohol contains oleic acid and other substances. That extracted by hot alcohol is colourless, m. p. 71—72°, and contains *rosilic acid*, $C_{18}H_{36}O_3$, m. p. 73°. This is ι-hydroxystearic acid, since chromic acid oxidation yields azelaic acid, and probably sebacic acid, whilst hydriodic acid yields *ι-iodostearic acid*, m. p. 56—57°, which is reduced to stearic acid. With the rosilic acid there is present an *acid*, m. p. 70°, forming a *barium* salt which indicates a mol. wt. of 1438. As hydrolysis gives rosilic acid, it is considered that the new acid consists of five rosilic acid molecules united by condensation of the hydroxyl group of one with the carboxyl group of the next and so on (cf. Bougault and Baudier, A., 1909, i, 82).

The portion of the wax insoluble in alcohol has m. p. 57—58°; it is yellow, and contains sulphur compounds, and also 0-hydroxyheptadecane (dinonylcarbinol, Kipping, J.C.S., 1893, **63**, 457). This is the alcohol which would be obtained by loss of carbon dioxide from rosilic acid. E. W. WIGNALL.

Flower waxes. Rose wax. H. PROPHÈTE (Bull. Soc. chim., 1926, [iv], **39**, 1600—1610).—See A., 1926, 981, 1281.

BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

MARCH, 1927.

POLITECHNIKI

General, Physical, and Inorganic Chemistry.

Infra-red spectrum of hydrogen. A. H. Poetker (Nature, 1927, **119**, 123—124).—The secondary spectrum of hydrogen has been extended to 9300 Å., about 170 lines being measured in addition to those observed by Allibone (A., 1926, 873). In a practically pure monatomic spectrum, the fourth, fifth, sixth, seventh, and eighth members of the Paschen series were obtained, the wave-lengths agreeing with those calculated from the Bohr formula.

A. A. Eldridge.

Fine structure of the Balmer lines of hydrogen. N. A. Kent, L. B. Taylor, and H. Pearson (Nature, 1927, **119**, 163).—Values of $\Delta\lambda$ were obtained as follows: (25 milliamp./cm.^{2}) H_α 0·1370, 0·0791, H_γ 0·0669 Å.; (13 milliamp./cm.^{2}) H_α 0·1391 Å. A third component on the longer wave-length side of λ' is also present.

A. A. Eldridge.

Continuous spectrum of hydrogen. O. Oldenberg (Z. Physik, 1927, **41**, 1—7).—The continuous spectrum obtained from a discharge tube filled with hydrogen is shown to be due to hydrogen, and not to water vapour. The addition of argon suppresses this continuous spectrum while simplifying the bands in the Schumann region, thus showing the two spectra to be independent. Pressure variation, addition of helium and neon, variation of current density, and effect of a magnetic field show the spectrum to be homogeneous and probably due to a homogeneous elementary process. A minimum intensity at 4000° Å. is observed in canal rays and is explained as being due to the superposition of the limit of the series spectrum of the atom.

W. E. Downey.

Absorption coefficient of helium for its own radiation. A. Wolf and B. B. Weatherby (Physical Rev., 1927, [ii], **29**, 135—140).—The mass absorption coefficient of helium for its own radiation in the extreme ultra-violet is $1{\cdot}24(\pm 0{\cdot}02)\times 10^7$ in the pressure range 0·016—0·040 mm. Below 0·016 mm., the coefficient increases rapidly with decrease in pressure.

A. A. Eldridge.

Structure of the third order spectra of oxygen (O III). C. Mihul (Compt. rend., 1927, **184**, 89—91).—Four multiplets of the same system of triplets and four multiplets of a system of quintuplets are added to those previously found for the third order spectrum of oxygen (this vol., 3). The wave-lengths and intensities of the various combinations are given in full.

J. Grant.

Hyperfine structure in the neon spectrum. G. Hansen (Nature, 1927, **119**, 237).—All neon lines which arise from an *s*-term have a component of shorter wave-length, of separation varying according to the term concerned, apparently due to a multiplicity in the *s*-levels. There are also evidences of a fine structure in the *pd* series lines.

The mercury line 4916 Å. consists of five components of separation +0·098 cm.$^{-1}$ (2), +0 056 (4), ±0 (10), −0·066 (3), −0·121 (5).

The components $^3P_2$ and $^3P_1$ of the helium line 5876 Å. have been resolved; the frequency differences are: $^3P_2-{}^3P_1$ 0·075 cm.$^{-1}$; $^3P_1-{}^3P_0$ 0·98 cm.$^{-1}$

A. A. Eldridge.

Electric field near the surface of the atoms of certain elements as deduced from the doublet separations of their spectra. N. R. Sen (Phil. Mag., 1927, [vii], **3**, 209—213).—By an extension of the results of Lande (A., 1924, ii, 711) to the doublet series of aluminium, gallium, indium, and thallium and to the triplet series of zinc and cadmium, it has been shown that the effective charge influencing the electron orbits near the aphelion is practically the same for all six elements. With zinc and cadmium, the aphelion of the *p*-orbit must be under the influence of the one electron moving in the *s*-orbit. From the constancy of the results and the agreement with the other four elements, it is concluded that in their cases the first *p*-orbit is influenced by only one of the two electrons moving in the *s*-orbits.

A. E. Mitchell.

Series of the argon spectrum. K. W. Meissner (Z. Physik, 1927, **40**, 839—875; cf. A., 1926, 766, 1186).—A continuation of the former work, giving wave-lengths and combinations from the extreme ultra-violet, 797·68, down to 9766·58 Å.

E. B. Ludlam.

Extension of doublet laws in the first long period to chromium and manganese. R. C. Gibbs and H. E. White (Proc. Nat. Acad. Sci., 1926, **12**, 675—677).—The regular and irregular doublet laws of stripped atoms have been shown (A., 1926, 874) to hold for the *N*-doublets for K I, Ca II, Sc III, Ti IV, and V V. Recent data on chromium and manganese in the extreme ultra-violet have made it possible to extend these laws to include Cr VI and Mn VII. Further measurements confirm the choice of lines for the V V doublet.

J. S. Carter.

Arc and spark spectra of iron in the extreme ultra-violet. L. Bloch and E. Bloch (Ann. Physique, 1926, [x], **6**, 409—451).—A more detailed account of work already published (A., 1926, 650).

Resonance radiation of zinc. P. Soleillet (Compt. rend., 1927, **184**, 149).—It has been shown

that each of the resonance radiations of zinc 3076 ($1S-2p_2$) and 2139 ($1S-2P$) excites only radiations of the same wave-length (cf. A., 1926, 766). Similar confirmatory results have been obtained for cadmium. J. GRANT.

Spark spectra of bromine. L. BLOCH and E. BLOCH (Compt. rend., 1927, **184**, 193—195).—The method previously described (A., 1925, ii, 611) has been applied to the analysis of the spark spectra of bromine between the red and extreme ultra-violet regions. A few arc rays of long wave-length and numerous spark rays extending into the extreme ultra-violet region were observed. The latter fall into two distinct groups (the wave-lengths and intensities of which are given in full), and are attributed to the ionised atoms Br II and Br III. A few of the rays observed in the same region are due to a higher degree of excitation. J. GRANT.

Spectrum of krypton in the extreme ultra-violet. L. B. TAYLOR (Proc. Nat. Acad. Sci., 1926, **12**, 658—659).—The following wave-lengths are recorded: 1235·87, 1164·90, 1074·32, 1067·11, 1051·97, 1041·38, and 1003·46 Å., the first two being resonance lines. The frequency difference for the resonance pair is 4930, a value repeated in other parts of the spectrum. J. S. CARTER.

Flash arc spectrum of rubidium. F. H. NEWMAN (Phil. Mag., 1927, [vii], **3**, 229—235).—With an applied voltage of 120 volts and at a pressure below 10^{-3} mm., an intermittent arc could be struck between an iron anode and a rubidium cathode. The radiation from this arc comprised 69 lines from 6517 to 3081·6 Å., and included most of the enhanced lines of rubidium as well as the ordinary arc lines. All the spark lines, with the exception of those at 3851·9, 3833·94, 3492·5, 3321·61, and 3286·6 Å., noted by Exner and Haschek, and all the induction spectral lines noted by Dunoyer (A., 1922, ii, 729), appear in the flash arc spectrum. A bright line at 4763 Å. has not been reported by previous experimenters. The optical centre of the group of enhanced lines developed in the flash arc is in the neighbourhood of 4070 Å. The spectrum is analogous to the red krypton arc spectrum and points to a similarity in structure between the ionised rubidium and the normal krypton atoms. A. E. MITCHELL.

Intensity-ratio for the doublets in the principal series of the alkali metals. H. KORN and H. JAKOB (Physikal. 1926, **27**, 819—825).—The relative intensities of the components of doublets in the principal series of rubidium and cæsium have been measured when the lines are excited in a flame. The results do not agree with the values expected on the basis of the Burger–Dorgelo relationships between intensity and inner quantum numbers. The question is discussed as to whether the number of centres concerned in line emission from the flame is so small that the relative intensity of the doublet components is unaffected by the characteristic absorption. The "line absorption" has been investigated for the components at the same time as the brightness of the line. When the line absorption becomes very small, the observed intensity ratio of the doublet components corresponds with the "true" ratio for a very small number of centres. The line absorption does not, however, become zero, and the Gouy–Ladenburg–Reiche relations between line absorption and number of centres can be compared with experiment. The intensity ratio is not constant at 2 : 1, but increases with increasing term number in the principal series (cf. A., 1922, ii, 6, 194, 242). R. A. MORTON.

Intensity-ratio for the doublets in the principal series of the alkali metals. C. FÜCHTBAUER and H. MEIER (Physikal. Z., 1926, **27**, 853—856).—Both in respect of the shape of the curve and the ratio of half-breadths, the broadening of the *D*-lines of sodium through the presence of foreign gases (hydrogen, argon, nitrogen) resembles the broadening for the 2537 line of mercury under similar conditions. It is shown by experiments on the broadening of absorption lines in the principal series of cæsium by foreign gases that the intensity ratio of the doublets does not conform with the expected 2 : 1 value. The ratio actually increases to 5·6 : 1 for the third pair in the series. R. A. MORTON.

1*s*—*md* Series of cæsium and the other alkali metals. G. M. SHRUM, N. M. CARTER, and H. W. FOWLER (Phil. Mag., 1927, [vii], **3**, 27—31).—It has been shown that the 1*s*—*md* combination lines of the alkali metals can be excited directly by means of a direct-current arc between carbon electrodes well coated with a salt of the alkali metal. By this means, six members of the 1*s*—*md* series of cæsium between 6894·7 and 3391 Å., not previously observed in emission, have been obtained. The measurements are in good agreement with the values calculated from Fowler's "Report on Series Spectra." The observed wave-lengths are approximately the same as those obtained by Sowerby and Barratt (A., 1926, 213) in absorption experiments. It is suggested that the great differences, found by Sowerby and Barratt, between observed and calculated values have arisen from the omission by these authors of the ordinary vacuum correction for their calculated wave-lengths. A. E. MITCHELL.

Regularities in the arc spectrum of lanthanum. W. F. MEGGERS (J. Washington Acad. Sci., 1927, **17**, 25—35).—The relative terms, comprising 48 levels in the La I spectrum, the corresponding energies, level separations, and term combinations have been tabulated from data, shortly to be published by the author and by King and Carter, relating to the arc spectrum of lanthanum. The spectrum of lanthanum is compared with the spectra of scandium and of yttrium. R. W. LUNT.

Arc spectrum of europium. Measurements made at normal pressure between 3100 and 2200 I.Å. S. PINA DE RUBIES (Compt. rend., 1927, **184**, 87—89; cf. A., 1926, 986).—A list of rays belonging to europium and their intensities is given for wave-lengths of range 3100—2200 I.Å. Urbain's pure europium gave more lines than Auer's mixed europium. Lines obtained by previous investigators which were not found by the author are enumerated and attributed to impurities, particularly iron. J. GRANT.

Continuous spectrum of mercury. H. VOLKRINGER (Compt. rend., 1927, **184**, 150—151).—A

relation between the intensity of radiation of the continuous spectrum of mercury and the frequency is deduced mathematically from the author's hypothesis of the distribution of energy in the visible portion of the continuous spectrum of mercury vapour. The curve obtained is in satisfactory agreement with that given by the experimental results. The theory postulates the existence of vibrators composed of groups of atoms, formed as a result of atomic excitation by the spectral rays, and subsequent production of a dipole capable of uniting with a neutral or other excited atom. J. GRANT.

Line spectra of the isotopes of mercury and chlorine. F. A. JENKINS (Physical Rev., 1927, [ii], 29, 50—58).—The lines 5461, 4359, 4078, and 4047 Å. of two sample-pairs of mercury of at.-wt. differences 0·124 and 0·180, respectively, showed no shift greater than 3×10^{-4} Å., and the first two showed no differences in the relative intensities of the satellites. With chlorine, shifts of the order of 0·001 Å. were obtained, the at.-wt. difference of the sample-pair being 0·097. For chlorine, the discharge tube was provided with a trough-shaped platinum cathode on which silver chloride was fused; the tube was then highly evacuated and filled with hydrogen at 1 mm. pressure.
A. A. ELDRIDGE.

Intensity changes in the lines of a mercury triplet. S. ESKELAND (Physikal. Z., 1927, 28, 89—92).—The triplet 5461 ($2p_3$—$2s$), 4358 ($2p_2$—$2s$), 4047 ($2p_1$—$2s$) has been investigated. The relative intensities of the lines are not changed when the applied voltage is changed from 120 to 460. On the other hand, at temperatures of 37° and 83°, which correspond with pressures of mercury in the ratio 1 : 25, the intensities are affected as follows: at 37°, 4·9, 24·4, 3·0; at 83°, 5·8, 18·4, 3·3, for λ 5461, 4358, and 4047, respectively. The middle component decreases in intensity, whilst the extreme lines increase as the temperature is increased. R. A. MORTON.

[Intensity changes of the lines of a mercury triplet.] L. VEGARD (Physikal. Z., 1927, 28, 92—93; cf. preceding abstract).—The significance of Eskeland's results is pointed out. The intensity-distribution within the triplet certainly varies, but whether the effect of pressure is to be ascribed to collisions or to absorption is not yet clear.
R. A. MORTON.

Magnetic separation of the mercury line 5770 into a nonet of special type. H. NAGAOKA and T. MISHIMA (Proc. Imp. Acad. Tokyo, 1926. 2, 479—480).—When resolved in a field of 27,000 gauss, the p-components consist of a triplet in which the separation amounts to ±0·083 Å., and in which the n-components are symmetrically situated about the initial position of the line, and consist each of three components separated from the initial line by ±1 0, ±1·083, and ±1·66 Å. R. W. LUNT.

Auroral green line 5577 A. D. A. KEYS (Nature, 1927, 119, 162).—The results of McLennan, McLeod, and McQuarrie (A., 1926, 985), indicating that the line is primarily due to oxygen, are confirmed.
A. A. ELDRIDGE.

Intensity and width of spectral lines. B. TRUMPY (Z. Physik, 1926, 40, 594—617; cf. A., 1926, 101; Holtsmark, *ibid.*, 102).—Results with mercury vapour instead of sodium, as in the earlier experiments, lead to the same conclusions. Different foreign gases were introduced, the total pressure being kept constant whilst the pressure of mercury vapour was varied. The total widening is satisfactorily accounted for as the sum of the effects due to collisions and the coupling of the electric fields of the molecules.
E. B. LUDLAM.

Spectral series of bismuth. V. THORSEN (Z. Physik, 1926, 40, 642—647).—With the help of some new lines, the terms and combinations of the spectrum are worked out and a scheme is constructed.
E. B. LUDLAM.

Wave-length of ruthenium $K\beta_1$. F. H. LORING (Chem. News, 1927, 134, 49).—The wave-length of this line has been determined from the values assigned by Auger and Dauvillier to the K lines, from the exact values of $K\alpha_1$ and $K\alpha_2$, and from the values of $(\nu R^{-1})^{\frac{1}{2}}$ of the K series. The mean of these and of the author's experimental value (cf. this vol., 87) is 0·57158 Å. R. W. LUNT.

Satellites of lines of X-rays. D. COSTER and M. J. DRUYVESTEYN (Z. Physik, 1927, 40, 765—774).—A new X-ray tube is described for fluorescence observations, with which satellites could be observed on the hard side of the lines, although the intensity was less than that obtained by cathode-ray excitation. The existence of these satellites indicates the simultaneous ejection of two electrons from the inner ring of the atom. The satellites on the soft side of the lines possessed normal intensity. Their interpretation is discussed. E. B. LUDLAM.

Absorption in the region of soft X-rays. E. R. LAIRD (Physical Rev., 1927, [ii], 29, 41—49).—The energy of soft X-rays from a tungsten-coated nickel target varies approximately as the square of the potential from 40 to 610 volts. Experiments with thin celluloid films support the view that the absorption varies as the cube of the wave-length, and that K-absorption discontinuities in celluloid occur between 300 and 600 volts. Values of μ/ρ for air are corrected (cf. Laird and Barton, *ibid.*, 1920, [ii], 15, 303) to 6·0, 6·25, 7·0, $7·6 \times 10^3$ at 600, 500, 400, 300 volts, respectively; for hydrogen, μ/ρ is about $1·8 \times 10^4$. A. A. ELDRIDGE.

Anomalous Zeeman effect of the mercury line 5791 and its satellite 0·124. H. NAGAOKA and T. MISHIMA (Proc. Imp. Acad. Tokyo, 1926, 2, 383—386).—The behaviour of the line 5791 and its satellite 0·124 has been examined by an interferential spectroscope in fields up to 32,000 gauss. R. W. LUNT.

Stark patterns observed in helium. J. S. FOSTER (Proc. Roy. Soc., 1927, **A**, 114, 47—65; cf. A., 1924, ii, 511, 798; 1925, ii, 831).—Four Stark patterns, each constant within its appropriate spectral series, have been found in parhelium and orthohelium. A detailed analysis of these effects supports the Bohr perturbation theory of the Stark effect as developed by Kramers, which predicts corrections between the fine structure of the hydrogen lines and the components observed in high fields. The general characteristics of the Stark effect in both

hydrogen and helium are reviewed, and found to differ mainly in the range of field strength at which the more interesting features appear. The work may be regarded as an extension to the observations of Stark and Nyquist, but definite reasons are advanced for an extensive revision of the analyses reported by Takamine and Kokubu (A., 1919, ii, 379). A modified Lo Surdo discharge tube is described.

L. L. Bircumshaw.

Dielectric constant and Stark effect for polyatomic dipolar gases with symmetrical molecules according to the wave-mechanics. C. Manneback (Physikal. Z., 1927, **28**, 72—84).—Mathematical. The wave-mechanics and the matrix mechanics lead equally to the conclusion that the dielectric constant of an ideal polyatomic gas with two equal principal moments of inertia approaches the values indicated for high temperatures by the classical theory of Langevin and Debye.

R. A. Morton.

Stark-Lunelund effect. A. Weigl (Ann. Physik, 1927, [iv], **82**, 1—15).—The light emitted by hydrogen canal rays is polarised so that the component vibrating in a direction parallel to the direction of motion is 30% stronger than the component at right angles. The polarisation is due to the moving atoms. An increased potential or pressure causes a changed intensity of the polarisation induced in this way. The polarisation persists in spite of collisions between moving and stationary atoms. Canal rays in nitrogen and in oxygen exhibit no polarisation.

R. A. Morton.

Polarisation of canal-ray light. R. Dopel and R. von Hirsch (Ann. Physik, 1927, [iv], **82**, 16—24).—Hydrogen canal rays in air exhibit a polarisation of 1·12 for H_β which is independent of pressure, whilst for the nitrogen 4709 band the value is 1·00.

For air canal rays in hydrogen, there is no polarisation. For atomic hydrogen in molecular hydrogen the value falls from 1·37 at 3600 volts to 1·11 at 32,000 volts. For hydrogen in oxygen, the value $1·16 \pm 0·01$ is independent of pressure and voltage. These and other results indicate that the polarisation of the emitted light depends on the nature of both the gases present and is in general absent in the absence of an exciting gas.

R. A. Morton.

Intensities in the Stark effect of helium. J. M. Dewey (Physical Rev., 1926, [ii], **28**, 1108—1124).—The observed intensities of the helium lines $2P-nM$, $2P-nm$, and $2S-4M$, where $n=4, 5, 6, 7$; $M=P, D, F$, etc., are in agreement with values calculated by application of the quantum theory of dispersion to the Stark effect.

A. A. Eldridge.

Critical potentials and the heat of dissociation of hydrogen as determined from its ultra-violet band spectrum. E. W. Witmer (Physical Rev., 1926, [ii], **28**, 1223—1241).—See A., 1926, 552.

Electron collisions in carbon monoxide. F. L. Mohler and P. D. Foote (Physical Rev., 1927, [ii], **29**, 141—144).—The authors' values of the critical potentials for electron impact in carbon monoxide ("Origin of Spectra," 1922, 188) are correlated with recent analyses of the carbon monoxide band spectrum. The resemblance of carbon monoxide to metals of the second periodic group is in accord with the spectral classification which makes the 6-volt level a ^3P state and the 8-volt level a ^1P state.

A. A. Eldridge.

Photo-electric electron emission and the optical absorptive power of potassium in relation to the gas content of the metal. R. Fleischer (Ann. Physik, 1927, [iv], **82**, 75—86).—The selective photo-electric emission of electrons is connected with the use of light so polarised that the electric vector is parallel to the plane of incidence of the component. Outgassed potassium exhibits a maximum of selective absorption and of photo-electric emission at 313 μμ under these conditions, whereas if the metal is allowed to absorb hydrogen, the selective emission and absorption occur near 436 μμ. When the photo-electric emission is plotted against the absorption at different wave-lengths, there is no selectivity for the outgassed metal, but with the hydrogen containing potassium, the maximum is enhanced. When the electric vector is perpendicular to the plane of incidence, both the photo-electric electron emission and the light absorption show no selectivity. If instead of a plane mirror a black body-cell is used, the outgassed metal exhibits the normal photo-electric emission, whereas if hydrogen is present, the maximum occurs at 436 μμ. This selective effect also occurs with unpolarised light if hydrogen is present.

R. A. Morton.

Experimental evidence of the thermal ionisation of elements. M. N. Saha, N. K. Sur, and K. Mazumdar (Z. Physik, 1926, **40**, 648—651).—Metal vapour was distilled from a small silica furnace into a graphite vacuum furnace which could be maintained at 2000°. A potential of 1 volt across two graphite plates in the latter furnace produced no current for mercury, zinc, or cadmium, but for sodium or potassium a current was obtained large enough to be measured with a milliammeter.

E. B. Ludlam.

Thermionic experiments with a new source of positive ions. C. H. Kunsman (Proc. Nat. Acad. Sci., 1926, **12**, 659—662; cf. A., 1926, 218, 685, 769).—A further study of the positive ion and the electron emission from reduced iron oxide–alkali or alkaline-earth oxide mixtures. Both types of emission satisfy Richardson's equation over a considerable temperature range. As before, the surface is defined in terms of ϕ_+ and ϕ_-, the equivalent voltages of the work function for the vaporisation of a positive ion and an electron, respectively. For cæsium and potassium, the values of ϕ_+ are 1·96 and 2·10 volts, respectively. Measurements with thoroughly reduced iron–barium mixtures show that the hot surface is a constant source of positive ions when used as anode, and of electrons when used as cathode, the values of ϕ_+ and ϕ_- being 2·12 and 3·49 volts, respectively. Somewhat similar results were obtained with calcium and strontium. Whenever it was found possible to measure both positive ion and electron currents for the same surface, ϕ_- was found to be greater than ϕ_+. At high temperatures, an appreciable vaporisation of iron occurs, but only in the form of neutral atoms. It is concluded that when an element is vaporised from a surface, the

vaporisation will be in the form of positive ions if the electron work function ϕ_- of the surface is greater than the potential tending to hold the outer electron to the atom vaporised. With barium–iron mixtures, ϕ_- is not sufficient to remove both outer electrons, since no doubly-charged ions were observed in mass-spectrograph studies. Positive ion emission is largely an interface phenomenon and confined to a small part of the total surface. J. S. CARTER.

Continuity of existence [of electrons]. D. B. MAIR (Nature, 1927, **119**, 199).—The theory of relativity indicates that the existence of electrons is discontinuous. A. A. ELDRIDGE.

Orbits and radiations of hydrogen electrons. T. ENGSET (Ann. Physik, 1927, [iv], **82**, 143—154, 184—190).—Theoretical. R. A. MORTON.

Deformation of electronic orbits in crystalline salts. K. FAJANS (Rocz. Chem., 1926, **6**, 396—403).—Examples are given where measurements of the refraction of alkaline-earth fluorides indicate various degrees of deformation of electronic orbits. R. TRUSZKOWSKI.

Electrical discharge and the radiations emitted by gases and solids bombarded by slow electrons. A. DAUVILLIER (J. Phys. Radium, 1926, [vi], **7**, 369—389).—A detailed account of work published earlier (cf. A., 1926, 330, 1196), to which is added a section on the bombardment of solids. Slow electrons give rise to a spectrum showing a feeble continuous background and intense characteristic lines, as found in the region of short-wave *X*-rays. The continuous spectrum appears to be governed by a different law. Various precautions are outlined which increase the accuracy of measurements of critical emission potentials, so that a new method is available for determining the principal levels of low energy for both light and heavy elements. Seven elements from boron to thorium have been studied in this way. R. A. MORTON.

Attribution to the secondary electrons of the action of *X*-rays on micro-organisms. J. J. TRILLAT (Compt. rend., 1927, **184**, 170—172).—Results of experiments show that the bactericidal action of secondary *X*-rays is due almost entirely to the bombardment of the microbes by the electrons arising from the radiator. W. ROBSON.

Cross-sectional curve of hydrogen chloride for slow electrons and its comparison with the argon curve. E. BRÜCHE (Ann. Physik, 1927, [iv], **27**, 25—38).—The curve cross-sectional area–electron velocity in volt$^{1/2}$ for hydrogen chloride shows a maximum at 3 volt$^{1/2}$. A special apparatus has been devised and a new source of error in the change of cross-section with time is disclosed. In general character, the curves for hydrogen chloride and argon are closely similar and show maxima at velocities of 3 volt$^{1/2}$ and 3·5 volt$^{1/2}$, respectively. Hydrogen shows a maximum at 1 volt$^{1/2}$, and it does not appear to affect the curve for hydrogen chloride. The argon curve corresponds with that due to the other rare gases, and the effect is ascribed to the completed outer shell of eight electrons. The comparison of argon with hydrogen chloride with its similarly completed octet supports this view if the resemblance between the curves is not fortuitous. R. A. MORTON.

Ionic mobilities in ammonia–hydrogen mixtures and an anomalous effect of ammonia. L. B. LOEB (Proc. Nat. Acad. Sci., 1926, **12**, 677—684; cf. A., 1925, ii, 7; 1926, 219; this vol., 86; Erikson, A., 1925, ii, 6).—Traces of ammonia in hydrogen and air attach themselves to positive ions to form a protective cluster of one or more molecules, which prevents the attachment of other bulky molecules and raises the mobility of the positive ion by as much as 30% without affecting the negative ion. In the presence of ether, however, the ether molecule is preferentially attached, and the observed mobility is that due to the superposed retarding effect of ether and ammonia molecules in hydrogen or air on a positive ion carrying an ether molecule (or molecules). The mobilities of both ions in ammonia–hydrogen mixtures decrease with increasing concentration of ammonia, the decrease following no simple law. The results are discussed and the importance of minute traces of foreign gases in work of this type is emphasised. J. S. CARTER.

Ionisation of gases and the Saha equation. G. HOMÈS (Bull. Acad. roy. Belg., 1926, [v], **12**, 422—428).—Mathematical. The application of the Saha equation to the ionisation and excitation of gas molecules is considered. C. H. D. CLARK.

Phenomenon of ionisation of mercury vapour at low pressures. R. MOENS (Bull. Acad. roy. Belg., 1926, [v], **12**, 429—436).—Experiments have been conducted on the ionisation currents set up when mercury ions, produced by the impact of electrons from a heated filament, fall on suitably placed anodes, the relation between applied *P.D.* and current being determined. It is found that no appreciable currents are detected until the ionisation potential is reached, after which the current increases rapidly with increasing *P.D.* If a primary stage of increasing *P.D.* is followed by a second stage of decreasing *P.D.*, a marked hysteresis occurs, the current being always stronger for a given *P.D.* during the second than during the primary stage. A subsequent temporary increase of current is generally observed during the second stage. C. H. D. CLARK.

Distribution of intensity in a positive-ray spectral line. I. M. C. JOHNSON (Ann. Physik, 1926, [iv], **81**, 666—680; Proc. Physical Soc., 1926, **38**, 324—334).—The extreme faintness of the light emitted by positive rays has hitherto required the use of instruments of low resolving power, so that the Stark and Doppler effects have been difficult to investigate for positive rays.

A technique has been developed employing interference analysis, the Merton wedge method for determining intensity distribution, and a relatively intense light source. The design of the tube and cathode necessary for an intense positive-ray light and the control of the intensity ratio of the Balmer and many-lined spectra are discussed in detail. The new technique discloses a line structure differing from that observed in ordinary discharge tube spectra.

The explanation of the structure in terms of Doppler and Stark components is compared with the theory of broadened lines in ordinary discharge tube spectra. R. A. MORTON.

Distribution of intensity in a positive-ray spectral line. II. M. C. JOHNSON (Proc. Physical Soc., 1926, **39**, 26—38; cf. preceding abstract).—Work is continued with the apparatus described previously. The direction of observation is here longitudinal, in order to isolate the Doppler effect in the "moving" spectrum; accordingly, a 6-prism spectrograph is substituted for the echelon previously used. The results are added to those of Stark, Paschen, Wilsar, and Krefft on the same spectrum, and the uncertainties in identifying atomic and molecular carriers are analysed. The distribution of velocities among the particles contributing to the "moving" spectrum is compared with the distribution of velocity in positive rays measured by the electromagnetic method. The appearance of the many-lined spectrum of hydrogen in the positive rays and the ratio of intensity of the "moving" and "resting" spectra are considered. The inverse square law of probability of electron capture, and some consequences of the work of Wien and Rüchart, are the most likely controlling factors in the several phenomena. C. J. SMITHELLS.

Scattering-absorption of hydrogen positive rays on passage through hydrogen. G. P. THOMSON (Z. Physik, 1926, **40**, 652; cf. Conrad, A., 1926, 990).—Conrad's criticisms are answered and the improbability that his results are accurate is indicated. E. B. LUDLAM.

Passage of positively-charged particles through helium. A. J. DEMPSTER (Phil. Mag., 1927, [vii], **3**, 115—127).—A study of the passage of very slow positively-charged particles through helium has shown that protons having velocities corresponding with *P.D.* between 14 and 900 volts pass through a large number of helium atoms without neutralisation and with only slight changes in velocity or direction. The loss of energy in penetrating the atom is probably less than that corresponding with 0·5 volt per collision. When hydrogen is mixed with helium, hydrogen-molecule ions are dissociated with a free path for dissociation about nine times the free path calculated on the kinetic theory for 900-volt protons. Helium ions are neutralised after about the first collision. A. E. MITCHELL.

Mobility of ions in solution with particular reference to the separation of isotopes. E. R. JETTE (Phil. Mag., 1927, [vii], **3**, 258—269).—Available theoretical and experimental material on the possibility of separating isotopes by methods depending on an assumed influence of the different masses of isotopic ions on their mobilities in solution, is examined. It is concluded that an experimental detection of a difference in the mobility of isotopic ions in solution is impossible by any method at present available. A. E. MITCHELL.

Seventh report of the German committee on the determination of atomic weights. M. BODENSTEIN, O. HAHN, O. HONIGSCHMID, and R. J. MEYER (Ber., 1927, **60**, [*B*], 1—20).—The report comprises a criticism of measurements of atomic weight by physico-chemical methods [mainly a reply to Moles (A., 1926, 654)] and by chemical gravimetric processes, and discussion of the progress in the isotope question as far as ordinary, non-radioactive elements are concerned. Alterations in the German atomic weight table of 1926 are not suggested. H. WREN.

Weight of the litre and atomic weight of argon. E. MOLES (Ber., 1927, **60**, [*B*], 134—138).—The atomic weight, A=39·88, adopted by the German Commission (1923) is based on the weight of the litre of crude argon, and is certainly low. The most probable weight of the litre of pure gas is 1·7833± 0·0001 g., from which the atomic weight A=39·94 is deduced; this is regarded as a minimal value. H. WREN.

Density, compressibility, and atomic weight of nitrogen. G. P. BAXTER and H. W. STARKWEATHER.—See this vol., 194.

Determination of the half-value period of polonium. M. A. DA SILVA (Compt. rend., 1927, **184**, 197—199; cf. A., 1926, 877).—A constant saturation-current in pure argon ionised by the α-particles from polonium is obtained at 50 volts. The polonium is best deposited on a silver plate and covered with a thin mica leaf. Measurements of the rate of fall of the saturation-current during 8 months gave a value for the half-value period of polonium of 140·2 days. This agrees with most recent determinations. J. GRANT.

Heat of radiation of radium. (MLLE.) A. DORABIALSKA and D. K. YOVANOVITCH (Rocz. Chem., 1926, **6**, 569—577).—The heat produced by the absorption of β- and γ-rays of radium by aluminium, copper, and lead is measured calorimetrically. The mean coefficient of absorption (μ/ρ) for β-rays in aluminium is 51·02, the values for the two different groups of β-particles, the heats of radiation of which are 10·4 and 3·0 g.-cal. per g. radium per hr., respectively, being 73·8 and 19·5. The heat of radiation due to α-particles is 129 g.-cal. R. TRUSZKOWSKI.

Comparison of the spectra of radon with those of uranium and thorium. H. NAGAOKA and T. FUTAGAMI (Proc. Imp. Acad. Tokyo, 1926, **2**, 390—394).—A table of the spectra of these substances from 6204 to 3089 Å. compiled from the data of Rutherford and Royds, Royds, Watson, and Nyswander, Lind and Moore. The results show that in the published spectra of uranium and of thorium, lines due to actinon and thoron have been included. R. W. LUNT.

Joachimstal pitchblende residues and their capacity for emanating. J. MARKL (Physikal. Z., 1927, **28**, 10—12).—Direct determinations of the radium content and of the evolution of radon in Joachimstal pitchblende residues are in agreement with those calculated from the uranium content and the known radium–uranium ratio. R. W. LUNT.

Anomalies associated with the γ-radiation of radium-*C*. K. W. F. KOHLRAUSCH (Physikal. Z., 1927, **28**, 1—10).—A review of the literature dealing with the γ-radiation of radium-*C* in which the photoelectric computation of the energy distribution in the

line spectrum of this radiation is discussed at length. It is shown that this distribution is in general agreement with observations on electron scattering; but the application of the Compton–Debye theory to the data relating to absorption and scattered radiation leads to considerable discrepancies. R. W. LUNT.

Scattering of gamma rays. L. H. CLARK (Nature, 1927, **119**, 121—122).—Confirmatory experiments show that a comparatively soft radiation is produced from air penetrated by gamma rays. The effect on numerical results of lining the electroscope is considered. A. A. ELDRIDGE.

Method of making H-particles audible. G. ORTNER and G. STETTER (Physikal. Z., 1927, **28**, 70—72).—A new arrangement, comprising an ionisation chamber, a system of valve amplification connected to a loud speaker, and devices to reduce acoustical and mechanical disturbances is described. The noises caused by the entry of α- and H-particles can be distinguished, and the method appears to possess advantages over the scintillation method and the ordinary ionisation chamber.

R. A. MORTON.

Synthesis and disintegration of atoms as revealed by the photography of Wilson cloud tracks. W. D. HARKINS and H. A. SHADDUCK (Proc. Nat. Acad. Sci., 1926, **12**, 707—714; cf. A., 1923, ii, 720; Blackett, *ibid.*, 1925, ii, 256).—A more detailed account of work previously published (this vol., 87).

Breakdown of atoms at high pressures. P. W. BRIDGMAN (Physical Rev., 1927, [ii], **29**, 188—191).—Thermodynamic evidence tends to indicate that in addition to atomic dissociation at high temperatures and comparatively low pressures, sufficiently high pressures are also capable at the ordinary temperature of reducing matter to an electrical gas of electrons and protons. A. A. ELDRIDGE.

Chemistry of lightning. J. ESTALELLA (Anal. Fís. Quím., 1926, **24**, 587—599).—The author discusses the chemistry of thunderbolts and lightning, and suggests that during the passage of the electric discharge the elements present in the air may suffer ultrachemical change, leading to the transitory formation of unstable atomic groupings.

G. W. ROBINSON.

Structure of nickel. H. COLLINS (Chem. News, 1927, **134**, 81—85).—Speculative.

Relation between the reciprocal impenetrability of matter and Pauli's exclusion principle. P. EHRENFEST (Nature, 1927, **119**, 196).—Mathematical. A. A. ELDRIDGE.

Spinning electrons and protons. H. S. ALLEN (Nature, 1927, **119**, 237—238).—It is postulated that the proton, as well as the electron, may be capable of a quantised spin. A spinning electron is one example of a magneton; a quantised magneton was first described by McLaren (*ibid.*, 1913, **92**, 165).

A. A. ELDRIDGE.

Theory of the spectra of diatomic molecules. L. LANDAU (Z. Physik, 1926, **40**, 621—627).—Formulæ are obtained, using the new quantum mechanics, for the frequencies of the band spectrum, for the intensities, and for the Stark and Zeeman effects.

E. B. LUDLAM.

Electronic states and band-spectrum structure in diatomic molecules. II. Spectra involving terms essentially of the form $B(j^2-\sigma^2)$. R. S. MULLIKEN (Physical Rev., 1926, [ii], **28**, 1202—1222).—Evidence is adduced to show that the AlH, He_2, and certain other bands involve rotational terms essentially of the form $B(j^2-\sigma^2)$, the chief empirical properties of which are discussed. Additional confirmation is afforded of Kratzer's interpretation of the violet CN bands. The AlH bands fall under the classification $^1S-{}^1P$; it is predicted that the fourth positive CO bands, designated $^1S-{}^1P$ by Birge, will have the corresponding structure and missing lines. The three-branch " series " bands of helium are of the $^1S-{}^1P$ type, the three-branch bands 6400 and 4546 of the $^1P-{}^1S$ type and the six-branch band 5733 of the $^1P-{}^1D$ type. Revised values are given of various constants of molecular helium in its different electronic states. The band spectra of the alkalis and the halogens are considered; the Na_2 absorption bands in the green, and probably most alkali metal bands, are probably $^1S-{}^1P$. The red CN, BO-α, and CO^+ comet tail bands probably have a structure essentially the same as that of the ZnH, CdH, and HgH bands, and characteristic of the transition $^2S-{}^2P_{1,2}$. The " combination " bands of BO and CO^+, the NO third positive bands, and presumably Jevons' SnCl bands probably have a similar structure characteristic of $^2P_{1,2}-{}^2S$ transitions. The OH, CH, and MgH bands are discussed. A. A. ELDRIDGE.

Interpretation of molecular spectra. F. HUND (Z. Physik, 1927, **40**, 742—764).—A qualitative expression for those features of band spectra which are due to the motions of the electrons is obtained. A system with one degree of freedom is examined, by the aid of quantum mechanics, of which the potential energy has several minima. The conditions for stationary states of such systems are considered, and an adiabatic correspondence is established between the states of two separated atoms or ions, of a diatomic molecule, and of a composite atom formed by the union of two atomic cores. These ideas are applied to the positively-charged hydrogen molecule, the neutral hydrogen molecule, and to polar molecules such as sodium chloride, of which the spectrum indicates dissociation into two oppositely-charged ions. E. B. LUDLAM.

Measurement of absorptive power. E. C. C. BALY and R. W. RIDING (Proc. Roy. Soc., 1927, **A**, **113**, 709—716).—The relative merits of the Hilger rotating sector photometric method and the Judd Lewis sector spectrophotometric method (J.C.S., 1919, **105**, 312) for the determination of extinction coefficients are discussed. The methods are compared by measuring, with both instruments, the absorptive powers of a thin glass plate, transmitting to about 254 $\mu\mu$, of a neutral-tinted glass plate, and of standard solutions of potassium chromate and potassium and barium nitrates. The results given between 436 and 254 $\mu\mu$ agree well within the limits of experimental error ($\pm 2\%$). In the visible region,

the photographic and von Halban's photo-electric methods (cf. A., 1921, ii, 145) agree with the visual methods. The error of the photographic method, which is ±2% in this region with the dispersion of a Hilger E_3 spectrograph, is probably greater than that shown by the photo-electric method and less than that of the visual method. In the region 240—330 μμ, the photo-electric method gives values which are uniformly smaller than those given by the two photometers. It is suggested that von Halban's results are subject to a wave-length error in this region. With solutions of barium and potassium nitrates, a new discrepancy is superimposed in the short-wave ultra-violet. L. L. Bircumshaw.

Oxygen bands in the ultra-violet. V. M. Ellsworth and J. J. Hopfield (Physical Rev., 1927, [ii], 29, 79—84).—A number of new bands have been observed, some of which have been measured and found to represent the $(n'—n'')$ 7—0, 8—0, 9—0, 10—0, 9—1, and 0—9 transitions as given by Birge's formula (*ibid.*, 1925, [ii], 25, 240).

A. A. Eldridge.

Absorption of light by ozone between 3050 and 3400 Å. J. Dutheil and (Mme.) M. Dutheil (J. Phys. Radium, 1926, [vi], 7, 414—416).—Ozone exhibits about 23 bands of low persistence in the region 3050—3400 Å. (Huggins' bands). The wave-lengths of maximum and minimum absorption and the corresponding absorption coefficients have been redetermined. The new data, when applied to the absorption of the atmosphere, yield results for the thickness of the ozone layer which are in agreement with results based on the great ultra-violet band (2550 Å.) of ozone. R. A. Morton.

Band spectra associated with silicon. W. H. B. Cameron (Phil. Mag., 1927, [vii], 3, 110—115).—When an arc was burned between silicon poles in air or oxygen at atmospheric pressure, the silicon oxide bands observed by de Gramont and de Watteville (A., 1908, ii, 909) were obtained. When the silicon arc was burned in a slow stream of oxygen at about 10 mm. pressure, the character of the radiation changed to an intense blue, and showed, in addition to the silicon oxide bands, a system of five or six bands with heads between 4393·4 and 4648·2 Å. It is suggested that this new band system has its origin also in the silicon oxide molecule When an uncondensed discharge was passed through the vapour of silicon tetrachloride at very low pressures and oxygen was added in slight excess, the colour of the discharge was dark green, and was found to comprise a series of bands with heads extending from 3960·2 to 5677·6 Å. Most of the bands were degraded towards the red, and in many cases the fine structure was clearly visible at a considerable distance from the head. It is suggested that this system is the analogue of the comet-tail and associated bands of carbon monoxide. A. E. Mitchell.

Spectrographic identification of certain elements and the possibility of determination by means of the arc spectrum. II. Uranium. C. Porlezza and A. Donati (Annali Chim. Appl., 1926, 16, 622—636).—The spectrum obtained when a small quantity of the oxide U_3O_8 is placed on the positive carbon of an arc exhibits an intense continuous foundation, especially in the green region, where also the density of the spectral lines is the greatest; all the possible lines cannot therefore be identified. The spectrum may be simplified and the continuous basis rendered less pronounced by mixing the oxide with a diluent. When mixed with silica, which forms the predominating gangue in various uraniferous minerals, uranium is detectable by its arc spectrum when present to the extent of 0·05%, whilst with tricalcium phosphate as diluent, 0·5% of uranium, and with silicates of calcium. aluminium, alkali metals, etc., intermediate proportions of the metal may be detected. By mixing a mineral such as autunite or carnotite with definite proportions of silica and comparing the spark spectrum with those of mixtures of the oxide with silica, the percentage of uranium in the mineral may be determined very approximately. (Cf. this vol., 124.)

T. H. Pope.

Band spectra of carbon monoxide. R. T. Birge (Physical Rev., 1926, [ii], 28, 1157—1181).—A critical discussion. The known band spectra of neutral carbon monoxide comprise the fourth positive group of carbon, the Ångstrom CO bands, the Cameron bands, and the third positive group of carbon; those of ionised carbon monoxide are the comet-tail bands, the first negative group of carbon, and the Baldet–Johnson combination bands. The relation of the various systems is shown in diagrammatic and tabular form, and possible correlation with magnesium is considered. An analysis of the fourth positive group of carbon is tabulated, and data on the Ångstrom bands are collected. There is probably a triple electronic level common to the third positive group and the Cameron bands. A. A. Eldridge.

Effect of water on the infra-red emission from the flame and explosion of carbon monoxide and oxygen. W. E. Garner and C. H. Johnson (Phil. Mag., 1927, [vii], 3, 97—110).—The infra-red spectrum of carbon monoxide burning in oxygen has been mapped for the flame and for the explosion between 1·3 and 6·1 μ. Small quantities of water vapour depress the infra-red emission from the explosion, whilst at the same time they increase the rate of reaction. It is suggested that the reduction in the intensity of the infra-red emission, brought about by the addition of water, is due to collisions of water molecules with the freshly-formed molecules of carbon dioxide, which are known to emit infra-red radiation at 2·8 and 4·4 μ. In the absence of water, the carbon dioxide molecules give up their excess of internal energy as infra-red radiation, whilst in the presence of water they lose part or all of this energy by collision. The result is then that more energy is retained in the system, and leads to the observed increase in the rate of reaction. In this case, water vapour is only a special example of a number of substances which are known to depress or to accelerate infra-red emission. The term " energo-thermic catalysis " is proposed for the action of those substances which retard or accelerate the rate of attainment of thermal equilibrium in a reacting gaseous system.

A. E. Mitchell.

Spectra of NH compounds. E. HULTHEN and S. NAKAMURA (Nature, 1927, **119**, 235—236).—The origin of the β-group of ammonia bands is referred to the NH dipole; new bands observed by Gleu (A., 1926, 992) are similarly referred. A ν–m diagram of the β-group is given. The initial state contains an electronic triplet, whilst the final state is a singulet; the final state, however, includes a rotational triplet of unknown nature. The nuclear spacing of the molecule in its final state is $r_0 = 1{\cdot}10 \times 10^{-8}$ cm. A $^3P \longrightarrow {}^1S$ transition is assigned to the β-group of the NH spectrum, where ^3P separations should agree in magnitude with those of carbon.

A. A. ELDRIDGE.

β Bands of nitric oxide. F. A. JENKINS, H. A. BARTON, and R. S. MULLIKEN (Nature, 1927, **119**, 118—119).—A comprehensive analysis of the β bands of nitric oxide has been made, and an interpretation put forward which is in agreement with theory. The internuclear distance in nitric oxide is computed to be, for the initial states, $1{\cdot}44$ and $1{\cdot}40 \times 10^{-8}$ cm., and for the final (normal) states $1{\cdot}16$ and $1{\cdot}14 \times 10^{-8}$ cm. A detailed account is promised.

A. A. ELDRIDGE.

Many-lined spectrum of sodium hydride. E. H. JOHNSON (Physical Rev., 1927, [ii], **29**, 85—96).—Several bands and branches between 3900 and 5100 Å. were identified in a many-lined spectrum; data are tabulated for bands at 4333 and 4655 Å. It is concluded that the carrier of the bands is the NaH dipole. There is evidence that several of the bands are members of the same system.

A. A. ELDRIDGE.

Quantum analysis of the band spectrum of aluminium oxide (5200—4650 Å.). W. C. POMEROY (Physical Rev., 1927, [ii], **29**, 59—78).—The frequencies and combination differences of all measured lines of the 0,0, 0,1, and 1,0 bands of AlO are tabulated. Numerical formulæ are given for the frequencies of individual band lines and for doublet separations. A direct method of locating band origins and verifying the combination principle is described. The moments of inertia of the AlO molecule for infinitely small vibration are $46{\cdot}02 \pm 0{\cdot}02 \times 10^{-40}$ and $43{\cdot}38 \pm 0{\cdot}02 \times 10^{-40}$ g. cm.^{2} for the initial and final states, respectively, the corresponding distances of nuclear separation being $1{\cdot}665$ and $1{\cdot}617$ Å.

A. A. ELDRIDGE.

Absorption spectra of alkali halides in aqueous solution and in the vapour state. L. A. MULLER (Ann. Physik, 1927, [iv], **82**, 39—66).—4N-Solutions of alkali halides show characteristic absorption maxima at 3567 Å. for iodides, 2800 Å. for bromides, and 2680 Å. for chlorides (Macbeth and Brannigan, J.C.S., 1916, **109**, 1277). The existence of these bands is not indicated in the dispersion. A series of 0·5N-solutions has now been investigated by means of an aluminium spark under water as light source, Hansen's step arrangement for intensity measurements, followed by photometric registration of the darkening of negatives. Sodium iodide shows a band $\lambda_{max.}$ 3153, $\epsilon_{max.}$ 0·07, and rubidium iodide exhibits somewhat more persistent absorption, $\lambda_{max.}$ 3245, $\epsilon_{max.}$ 0·07. Potassium iodide absorbs strongly, owing possibly to a trace of the tri-iodide. Cæsium chloride has a weak band at 2945 Å., but the remaining alkali halides examined all exhibit general absorption under the conditions: concentration 0·5N, range of extinction coefficient 0—0·26. The absorption increases in the order F⟶Cl⟶Br⟶I and Na⟶K⟶Cs⟶Rb except for potassium iodide.

It was hoped to determine electron affinity from measurements of the absorption spectra of the vapours, since this constant can be calculated from the long-wave limit of the continuous emission spectrum. Selective absorption became apparent at 700—800°, at which temperature the partial pressures, NaCl 3×10^{-4} atm., C 3×10^{-11} atm., Cl^- 5×10^{-14} atm., express the condition of the vapour.

The observed maxima due to undissociated alkali halide molecules are tabulated. The vapour bands are in all cases persistent and well defined.

The bands due to the halogens are shifted towards the red as the at. wt. of the metal increases, but cæsium is definitely anomalous in this respect. (Cf. Getman, A., 1925, ii, 837.)

R. A. MORTON.

Band spectrum of calcium hydride. E. HULTHÈN (Physical Rev., 1927, [ii], **29**, 97—111).—The spectrum of a calcium arc in hydrogen at low pressure contains many bands between 6000 and 7000 Å.; the A-group has heads at 7035, 7028, 6921, 6903 Å., and the B-group at 6389, 6382 Å. The C-group is a single band at 3533·6 Å. The lines of the bands A, B, A', B' (the overlapping faint bands in A and B) are tabulated in series. Values of the final and initial terms of rotation are also tabulated. The nuclear spacings in the CaH molecule are not in correlation with their vibration frequencies.

A. A. ELDRIDGE.

Constitution and absorption spectra of the nitrososulphides of iron. L. CAMBI and L. SZEGÖ (Atti R. Accad. Lincei, 1926, [vi], **4**, 491—497).—Compounds containing the grouping $\cdot S \cdot Fe \cdot N_2O_2$ or $\cdot S_2O_3 \cdot Fe \cdot N_2O_2$ give absorption spectra exhibiting certain analogies to those of the ferric compounds, $Fe(N_2O_2Ph)_3$ and $Fe(CNS)_3$. Just as is the case with the compound $FeSO_4 \cdot NO$, the absorption spectrum of the salt $KS_3Fe_4(NO)_7$ at great dilutions indicates the presence of ferrous iron. The absorption of light by solutions of the above nitrososulphides presents no characteristic justifying the hypothesis that they contain univalent iron.

T. H. POPE.

Possible cause of the changes of colour in vapours. (MRS.) F. LANGWORTHY (Chem. News, 1927, **134**, 20—21).—When illuminated by a spark, the vapour of mercuric chloride appears green, that of mercuric bromide blue, and that of the iodide violet. This is accounted for on the supposition that, as the halogen atom becomes more positive with increasing at. wt., the violet or more negative rays are more likely to be attracted to its vicinity. Elements in the same group of the periodic table become more positive with increasing at. wt., and the conclusion is reached that this increase of positivity is acquired in stages.

W. J. POWELL.

Bohr's model and the supposed coloration of the ions. G. MAGNANINI (Atti R. Accad. Lincei, 1926, [vi], 4, 530—532; cf. A., 1912, ii, 142).—That

the dissociated part of a coloured electrolyte has always the same absorption spectrum as the non-dissociated part follows both from experimental data and also from deductions based on the theory of Arrhenius. Since this is not in accord with Bohr's theory, it follows that either electrolytic dissociation is a spontaneous process having nothing in common with true dissociation, such as is caused by the spark discharge, or the explanations of the intimate structure of matter furnished by Bohr's theory require modification. T. H. POPE.

Coloration of alkaline-earth sulphides under the influence of pressure. J. STALONY-DOBRZANSKI (Rocz. Chem., 1926, 6, 633—640).—The colours observed in compressed alkaline-earth sulphides correspond with those given by the respective element in the Bunsen flame, with the difference that the absorption bands are more diffuse. Absolutely pure sulphides prepared by reduction of sulphates also become coloured under pressure, showing that the presence of an activator is not essential for this phenomenon. If very great pressure is used, the sulphides are less intensely coloured than with lower pressures; this is shown to be due to the greater homogeneity of these specimens, so that the light passing through suffers less internal reflexion, and consequently travels through the mass by a shorter path. R. TRUSZKOWSKI.

Infra-red absorption of coloured glasses and salt solutions. T. DREISCH (Z. Physik, 1927, 40, 714—724).—The infra-red absorption spectra of the following metal glasses and metallic solutions have been examined in the range 0·75—2·0 μ: green and greyish-violet ferrous oxide glasses, ferrous sulphate, ferrous ammonium sulphate, and ferric chloride solutions; green and blue copper glasses, cupric sulphate, and cupric chloride solutions; yellowish-green chromium glass and chromic sulphate solution; blue cobalt glass and cobalt chloride solution; violet and yellowish-brown nickel glass and nickel chloride solution; uranium glass and uranyl nitrate solution. Marked similarities are to be found between the absorption of these metal salts in aqueous and vitreous solution, so that the compound to which the colour of a glass is due may be identified from the absorption spectrum of the glass. R. W. LUNT.

Infra-red absorption spectra. II. Chloroacetic acids. W. H. BENNETT and F. DANIELS (J. Amer. Chem. Soc., 1927, 49, 50—57).—The predicted shift of a band in the near infra-red absorption spectrum of acetic acid with increased substitution of chlorine has been observed for the band at 5·9 μ (corresponding with the ·CO_2H band), which moves about 0·05 μ towards shorter wave-lengths for each chlorine atom substituted in the methyl group (cf. Daniels, A., 1926, 108). The absorption spectra of methyl acetate and acetic anhydride were also determined. Improvements in technique are described, notably a micrometer absorption cell, the use of which permits the rapid and accurate determination of the spectra of a liquid at different thicknesses. With its aid, Lambert's law is tested for chloroform; the law is valid when the transmission is high, but the calculated transmission becomes too high as the thickness of the liquid is increased beyond 2 or 3 mm. The deviations, which are most pronounced for the band at 3·32 μ, may be due to imperfections in the spectrometer, which lead to scattered radiation. S. K. TWEEDY.

Absorption spectrum of solid benzene at −180°. P. PRINGSHEIM (Physikal. Z., 1926, 27, 856—859).—Riemann has shown that the relatively diffuse bands observed in the fluorescence spectrum of benzene are partly resolved at −180°, and the spectrum shows a close resemblance to that of the vapour. The absorption spectrum of benzene has now been investigated at −180°. Films 10 μ in thickness were frozen between quartz plates immersed in liquid air.

Intense bands between 230 and 270 μμ are shown by liquid air, so that this material must not occur in the path of the light. A hydrogen discharge-tube with a quartz window served as a source of light with a continuous spectrum. Solid benzene at 0° gives an absorption curve not differing appreciably from the curve for liquid benzene due to Henri; eight approximately equidistant broad bands are shown in such a curve. The vapour spectrum shows the bands resolved into a complicated fine structure, whilst for solid benzene at −180° a roughly intermediate degree of resolution is attained.

The results for benzene at −180° may be expressed by $\nu=\nu_0+an-bp$ (n and p are integers 0, 1, 2 . . ., $\nu_0=37{,}000$, $a=920$, $b=80$ cm.$^{-1}$). In Henri's scheme of levels, b is connected with the unexcited and a with the excited state. The difference between a and b is regarded as too great to harmonise with this view, and for the above and other reasons a somewhat different scheme is adopted for systematising the observed constant frequency differences (cf. Marsh, A., 1925, ii, 625). R. A. MORTON.

Ultra-violet absorption spectra of some substances with two benzene nuclei. A. CASTILLE (Bull. Acad. roy. Belg., 1926, [v], 12, 498—519).—The substances were examined in hexane solution and also when possible in the state of vapour, curves being plotted between the logarithm of the coefficient of molecular absorption and the wave-length and frequency, respectively. With diphenylmethane and *s*-diphenylethane, where the nuclei are connected by a grouping which is saturated, the same bands occur, although somewhat more diffuse, as with benzene, showing that the two nuclei interfere only very slightly. Where the nuclei are connected by an unsaturated grouping which is moreover not a chromophore (diphenyl, stilbene, diphenylbutadiene, diphenylamine, and *as*-diphenylethylene), the spectrum contains one large band common to all the substances and resulting from the fusion of corresponding narrow bands in benzene. These facts are explained by Henri's theory ("Structure des molecules," 1925), according to which the two nuclei have opposite polarities, and when connected by a saturated grouping, only the electronic vibrations are neutralised, each nucleus thus retaining its characteristic vibration; but when connected by an unsaturated grouping, the opposite charges of the nuclei are completely neutralised and a band results. As the length of the

connecting chain increases, the bands are displaced increasingly towards the red, since the energy required to raise the molecule from one level to another will be less, and the frequency therefore also less, as the nuclei become farther apart. The coefficient of absorption increases with the number of ethylenic linkings, and since diphenylamine has the greatest coefficient of the substances examined, it is inferred that the :NH group is unsaturated. The case of nuclei connected by a grouping which contains a chromophore is also considered. S. J. GREGG.

Polarisation of fluorescence light. Mean period of activated molecules. F. PERRIN (J. Phys. Radium, 1926, [vi], **7**, 390—401).—The light emitted from fluorescent solutions is usually partly polarised. Accepting fluorescence as due to the return from an activated state of period τ to the normal state, a quantitative formulation of the relations existing between τ, viscosity of solvent, and polarisation of the light emitted is advanced. This leads for glycerol–water solutions of fluorescein to a value for τ of $0{\cdot}43 \times 10^{-8}$ sec. R. A. MORTON.

Two problems in the extinction of iodine fluorescence. G. RAMSAUER (Z. Physik, 1927, **40**, 675—685).—The sensitivity of the various resonance series of iodine to the effect of collisions between excited iodine molecules and oxygen molecules has been examined, and data are given for the relative extinction produced by frequencies characteristic of sodium, cadmium, and carbon arcs between the limits 5153 and 6295 Å. R. W. LUNT.

Correlation of the fluorescence and absorption spectra of iodine. F. W. LOOMIS (Physical Rev., 1927, [ii], **29**, 112—134).—The lines near Hg 5460 Å. in Wood's fluorescence spectrum of iodine excited by the quartz mercury arc are identified with definite lines in the absorption spectrum, whereby new values of the constants of the iodine spectrum are obtained. The calculation of absolute rotation quantum numbers furnishes direct evidence for the hypothesis of half-quantum numbers. Three new series of fluorescence doublets were observed. The fluorescence spectrum confirms Lenz's theory to account for the simple fundamental series of doublets excited by the narrow green mercury line. A. A. ELDRIDGE.

Spectrum of luminescence of cæsium in electrodeless discharge. G. BALASSE and O. GOCHE (Bull. Acad. roy. Belg., 1926, [v], **12**, 621—630).—Wave-lengths between 2300 and 7000 Å. in the spectrum produced by the action of the electrodeless discharge on cæsium at 170° are recorded. They are in general agreement with Sommer's spark-spectrum figures (A., 1925, ii, 4). R. CUTHILL.

Decay of phosphorescence of zinc sulphide. H. A. TAYLOR (J. Physical Chem., 1927, **31**, 115—123).—The effect of temperature on the rate of decay of phosphorescence over the range 25—110° has been investigated by measuring the time taken by a sample of zinc sulphide, saturated with the exciting radiation, at a given temperature, to decay to a fixed photometric standard. The temperature coefficient in the case of five different samples of sulphide is 1·20/10° in the neighbourhood of 70°, corresponding, on the basis of the radiation theory, with $\lambda = 6{\cdot}65\,\mu$, in contradistinction to the value $1\,\mu$ given by Perrin (A., 1922, ii, 628). The values of the temperature coefficient tend to increase with increasing temperature, in harmony with Lenard's view that different processes of short, medium, and long duration are involved. Further, the smallness of the value suggests that phosphorescence is a photochemical rather than a thermal process. The abnormal decaying effect of radiation on zinc sulphide phosphorescence is not confined to any particular frequency or region of the spectrum, but all frequencies incapable of causing phosphorescence accelerate decay. The line of demarcation is quite sharp. The contradictory nature of previous data is pointed out.

L. S. THEOBALD.

Validity of Stokes' law for phosphors. F. SCHMIDT and W. ZIMMERMANN (Ann. Physik, 1927, [iv], **82**, 191—200).—According to Stokes' law, the light emitted by a phosphor must be of longer wave-length than the exciting light. Monochromatic light was obtained by the use of filters and a quartz mercury-vapour lamp. For the isolation of the line at $435\,\mu\mu$, the filtering system consisted of dilute cuprammonium solution, blue glass, copper sulphate solution, and dilute æsculin solution, whereas, for the $492\,\mu\mu$ line, dark green gelatin was substituted for blue glass. The following phosphors were used in the investigation of the momentary luminescence (fluorescence): ZnS–Cuα, CaS–Cuα, SrS–Biα. In each case, illumination with radiation down to $365\,\mu\mu$ caused the appearance of the entire emission band, but the use of monochromatic radiation of $492\,\mu\mu$ brought about the excitation of only the portions on the long-wave side of the line. Stokes' law thus holds rigidly for the momentary or true fluorescence effect. When, however, the phosphorescence or luminescence of longer duration is considered for the phosphors CaS–Biα, SrS–Biα, excited by the $435\,\mu\mu$ line, light of wave-lengths shorter than $435\,\mu\mu$ is emitted. Stokes' law is therefore not valid for this process. It is concluded that the energy emitted in the fluorescence effect springs from the absorbed light energy, whereas the emission centres must supply energy at the expense of the heat content, in the phosphorescence effect of longer duration. R. A. MORTON.

Activation of hydrogen in the electric discharge. G. A. ELLIOTT (Trans. Faraday Soc., Jan., 1927, advance proof).—The formation of monatomic hydrogen is investigated quantitatively. The activated hydrogen produced by submitting pure hydrogen to an electric discharge in a Siemens ozoniser is measured by its reducing action on sulphur and is found to vary inversely as the rate of flow of the gas through the apparatus. The yield also varies with the pressure, and shows no linear relation to the voltage used, being negligible above 7 cm. and below 3000 volts.

The results are considered in the light of the expressions deduced (Elliott, Joshi, and Lunt, this vol., 212) for the velocity of a chemical reaction in the silent electric discharge. A. S. CORBET.

Activation of molecular hydrogen by electron impact. G. GLOCKLER, W. P. BAXTER, and R. H.

DALTON (J. Amer. Chem. Soc., 1927, 49, 58—65).—The activation of hydrogen molecules commences with electrons of energy 11·4 volts, indicating that the first stage in the activation process at low voltages is the formation of a resonated hydrogen molecule (cf. Witmer, A., 1926, 552). There was no evidence that electrons of energy 3—5 volts dissociate hydrogen molecules. S. K. TWEEDY.

Ionisation phenomena in active nitrogen. P. A. CONSTANTINIDES (Nature, 1927, 119, 163).—Differences in the ionisation effects according to the gases mixed with the nitrogen are held to indicate that active nitrogen may be due to a metastable state of the nitrogen molecule with energy between 9·4 and 10·4 volts. A. A. ELDRIDGE.

[Ionisation phenoma in active nitrogen.] (LORD) RAYLEIGH (Nature, 1927, 119, 163).—A brief reply to Constantinides (preceding abstract). A. A. ELDRIDGE.

Ionisation in hydrogen chloride vapour. H. A. BARTON (Nature, 1927, 119, 197—198).—The ions previously observed have been identified as : $(Cl^{35})^+$, $(HCl^{35})^+$, $(Cl^{37})^+$, $(HCl^{37})^+$, $(Cl^{35})^-$, and $(Cl^{37})^-$. The isotopic ratios were equal to that computed from the at. wt. of chlorine. The only ion produced by an impact of an electron of between 4 and 75 volts' energy on a hydrogen chloride molecule is $(HCl)^+$, corresponding with an ionisation potential of 13·8 volts. Reasons are given for discrediting the assumption that the primary process consists of the formation of H^+ and Cl^- ions. A. A. ELDRIDGE.

Meaning of the time-effect in the formation of hydrogen bromide from its elements. A. SKRABAL (Ann. Physik, 1927, [iv], 82, 138—142; cf. Bodenstein and others, A., 1925, ii, 218; 1926, 680; Rideal, *ibid.*, 484; Herzfeld, *ibid.*, 1919, ii, 503).—A new mechanism for the reaction is advanced which leads to an equation identical with that based on the experiments of Bodenstein and Lind. R. A. MORTON.

Electricity in flames. J. A. J. BENNETT (Phil. Mag., 1927, [vii], 3, 127—146).—The electrical conductivity of a Bunsen flame containing the spray of very dilute solutions of rubidium chloride and of cæsium chloride has been measured at different temperatures between 1920° and 1570° Abs. The conductivity of the salt-free flame is several times less than that of the flame containing the spray. The conductivity of the flame increases with the temperature and with the concentration of the solution used for the spray. The ionisation equilibrium constant for rubidium chloride has been calculated from the flame conductivities, and the values are in good agreement with those calculated from Saha's thermodynamical theory of temperature ionisation. There is better agreement between the values, obtained by the two methods, at the higher than at the lower temperatures, indicating that Saha's theory holds good only at high temperatures. From the conductivity measurements, the velocities of electrons in the Bunsen flame have been calculated. The results show that the velocities change from 2700 cm./sec. at 1920° Abs. to 1800 cm./sec. at 1570° Abs. A. E. MITCHELL.

Pressure dependence of dielectric constant of gases and vapours at low pressures. K. WOLF (Physikal. Z., 1926, 27, 830; cf. A., 1926, 1081).—An addendum. R. A. MORTON.

Dielectric constant and diamagnetism of hydrogen and helium in the new quantum mechanics. J. H. VAN VLECK (Proc. Nat. Acad. Sci., 1926, 12, 662—670).—Theoretical. The new Heisenberg–Schrödinger quantum mechanics is applied to the calculation of dielectric constants and diamagnetic susceptibilities of hydrogenic atoms. The values so calculated are usually in much closer agreement with available experimental data than are those calculated on the basis of the older quantum theory. The dielectric constant calculated for monatomic hydrogen is 1·000229, Langer's experimentally determined value (this vol., 93) being 1·000136. In view, however, of the experimental difficulties, it is possible that the error introduced into this determination is greater than the tentative estimate, $\pm 0{\cdot}000034$. Langer's theoretical value (*loc. cit.*), 1·000338, is held to be erroneous. J. S. CARTER.

Influence of a magnetic field on the dielectric constant of a diatomic dipole gas. L. PAULING (Physical Rev., 1927, [ii], 29, 145—160).—The dielectric constant of a diatomic dipole gas in a magnetic field is calculated according to both the old quantum theory and the new quantum mechanics. The latter treatment, which predicts no effect in a magnetic field, is in accord with the experimental result of Mott-Smith and Daily (this vol., 92) for hydrogen chloride and nitric oxide. A. A. ELDRIDGE.

Molecular and atomic volumes. XII. Volume of ammonia in some ammoniates of cuprous, silver, and aurous halides. W. BILTZ [with H. HERZER] (Z. anorg. Chem., 1926, 159, 96—102).—The value of the volume of a molecule of ammonia in the ammoniates of cuprous, silver, and aurous halides lies between 19 and 25, the mean being 21·5 c.c. This value approximates to the zero-point value for ammonia, *i.e.*, 18—20 c.c., and it is only slightly greater than the value determined for ammonia from other ammoniates. The volume of the ammonia molecule appears to depend to a certain extent on the anion. With increasing numbers of ammonia molecules in the compounds, the value for the volume of a single molecule is smaller; moreover, the densities of the original halides vary with their previous treatment. M. CARLTON.

Optical anomalies of calcite under pressure. S. NISHIO (Proc. Imp. Acad. Tokyo, 1926, 2, 395—397).—From a knowledge of the optical anomalies shown by a specimen of calcite, it is possible to discuss its geological history. R. W. LUNT.

Thickness of the optical transition layer in liquid surfaces. C. V. RAMAN and L. A. RAMDAS (Phil. Mag., 1927, [vii], 3, 220—223).—The coefficient of ellipticity of light reflected from pure water and from a number of organic liquids has been measured. In all cases, the coefficient is positive, irrespective of the value of the refractive index of the bulk of the liquid, and there is no definite correlation between

the refractive index of the liquid and the magnitude of the ellipticity. From these results, it follows that the surface layer is optically less dense than the body of the liquid. Hence it is suggested that there is no orientation of the molecules of the surface of a pure liquid. With the aid of Drude's formula, it is shown that the thickness of the transition layer is of the same order as the linear dimensions of the molecules forming the liquid. Examination of the ellipticity of light reflected from films of oleic and palmitic acids spread on water shows that the film is unimolecular.

A. E. MITCHELL.

Ionic refractivity and the scattering of light by gases. T. H. HAVELOCK (Phil. Mag., 1927, [vii], **3**, 158—176).—From a consideration of the constituents of a molecule as isotropic resonators in fixed relative positions in the molecule, formulæ for the refractivity of gases have been derived for both straight-line and triangular configurations. The formulæ have been applied to an examination of the refractivities of hydrogen chloride, hydrogen bromide, hydrogen sulphide, steam, carbon dioxide, and carbon disulphide. From experimentally-determined values of the refractivity and of the polarisation of the scattered light with the aid of the distance between nuclei inferred from infra-red measurements, the refractivities of the hydrogen and chlorine constituents of the hydrogen chloride molecule have been deduced. The value of the hydrogen refractivity has been combined with other data for the examination of the other gases. The molecular refractivities of the ions obtained by this method are $H^+=0{\cdot}13$, $Cl^-=6{\cdot}14$, $Br^-=8{\cdot}62$, $O^{--}=2{\cdot}58$, $S^{--}=8{\cdot}19$, and $C^{++}=0{\cdot}045$. These values are discussed in relation to those obtained from other sources.

A. E. MITCHELL.

Preparation, refractive index, and dielectric constant of red crystalline selenium. S. KYROPOULOS (Z. Physik, 1926, **40**, 618—620).—Crystals were obtained about 2 mm. long by means of a circulating convection stream of selenium in carbon disulphide; they are ruby red by transmitted light and have a blue metallic lustre by reflected light. The index of refraction for polarised light of wave-length 620 was 2·8 for vibrations parallel to the (100) surface and 2·3 perpendicular thereto. The dielectric constant at 2·7° was 7·39, agreeing with the Maxwell relation and indicating no special absorption frequency in the infra-red.

E. B. LUDLAM.

Molecular refraction and the parachor. W. HERZ (Z. anorg. Chem., 1927, **159**, 316—318).—Calculations are made of the molecular refraction and of the parachor for 51 organic liquids, using values previously published, and it is shown that the quotient of the parachor divided by the molecular refraction is a constant, independent of the liquid. Abnormal values were obtained for liquefied gases. A close relation between refractive index and surface energy is indicated.

E. S. HEDGES.

Determination of refractive indices from reflexion measurements in the infra-red. A. KREBS (Ann. Physik, 1927, [iv], **82**, 113—137).—The relation between angle of incidence and reflexion has been studied for the residual rays from calcium carbonate, silica, and fluorite. The Fresnel formulæ fit the reflexion data for the transparent substances selenium, sodium chloride, potassium chloride, potassium bromide, and calcium fluoride. Brewster's law affords a means of calculating refractive indices from the angle of polarisation corresponding with the reflexion data. By combining the Fresnel formulæ, a simpler method can be used. The reflexion of residual rays from various commercial glasses has enabled their refractive indices to be determined experimentally.

R. A. MORTON.

Theory of mixed substances and the logarithmic mixture rule. K. LICHTENECKER (Physikal. Z., 1926, **27**, 833—837).—Various mixture rules are discussed and compared with experiment. The logarithmic mixture law is applied to two- and three-dimensional aggregates, and a correction curve is utilised. The electrical conductivity of artificial gold–silver particles, the heat conductivity of tin–zinc alloys, and the dielectric constant of carbon tetrachloride–chloroform mixtures all obey the logarithmic mixture rule after certain simple corrections have been made. The rule has been applied to lead metasilicates as a means of arriving at the refractive index of a molten liquid containing a definite lead oxide–silica ratio. The logarithmic mixture rule, corrected for three-dimensional aggregates, reproduces quantitatively the refractive index of common salt solutions over the range 0—25% by weight of salt.

R. A. MORTON.

Stereochemistry of platinous salts. H. REIHLEN and K. T. NESTLE (Z. anorg. Chem., 1927, **159**, 343—348).—A reply to Grünberg (this vol., 34; cf. Reihlen and Nestle, A., 1926, 699).

E. S. HEDGES.

Model for the molecules of methane and other compounds of the type XY_4. I and II. J. H. DE BOER and A. E. VAN ARKEL (Z. Physik, 1927, **41**, 27—37, 38—47).—I. A calculation of the energy of ionisation of compounds of the type CX_4 and SiX_4 is made on the assumption that the X atoms behave as negative ions (A., 1926, 888). By means of a cyclic process, the ionisation energy is calculated for the silicon compounds from experimentally-determined constants. The agreement in value between the calculated energy of ionisation and that experimentally determined is good.

II. The dipole moment and energy of ionisation of chloroform and methyl chloride are calculated on the assumption that the hydrogen exists as negative ions in these two compounds. The calculated energies of ionisation are in good agreement with the values obtained from experimentally-determined constants by means of a cyclic process.

W. E. DOWNEY.

Polarisation of a medium and its molecular structure. Benzene and *cyclo*hexane. J. ERRERA (Bull. Acad. roy Belg., 1926, [v], **12**, 327—339).—Measurements of the specific inductive capacity of benzene and *cyclo*hexane in the liquid and solid states at and near the m. p. indicate the absence of molecular doublets. The polarisation due to atomic vibrations is 1·48 for benzene and 0·74 for *cyclo*hexane.

H. F. GILLBE.

Molecular diameter of unassociated liquids at their b. p. N. DE KOLOSSOVSKI (Z. Elektrochem., 1927, **33**, 11).—An equation derived by Schuster

(A., 1926, 670) connecting the molecular diameter, surface tension, and internal pressure of an unassociated liquid at its b. p. is compared with relations developed by Walden (A., 1909, ii, 119, 547).

H. J. T. ELLINGHAM.

Element of atomic number 61: florentium [illinium]. III. L. ROLLA and L. FERNANDES (Gazzetta, 1926, **56**, 862—864; Atti R. Accad. Lincei, 1926, [vi], **4**, 498—499; cf. A., 1926, 1083; this vol., 9, 31).—The authors give the text of a paper which was deposited under seal with the Reale Accademia dei Lincei in June 1924 and announces the discovery of the element of atomic number 61. They claim that the name florentium then given to this element should be retained. T. H. POPE.

Existence of the element of atomic weight 61. R. BRUNETTI (Atti R. Accad. Lincei, 1926, [vi], **4**, 515—518).—This note, deposited under seal with the Accademia on June 21, 1924, gives the results of investigation of the *K*-absorption spectra of rare earths supplied by Rolla (cf. preceding abstract). An absorption band observed in the spectral region between samarium and neodymium has a wave-length agreeing closely with that calculated for the previously unknown element of atomic number 61.

T. H. POPE.

Identification of the element of atomic number 61. R. BRUNETTI (Atti R. Accad. Lincei, 1926, [vi], **4**, 518—521; cf. preceding abstracts).—The results previously obtained are confirmed, the samarium fraction obtained by Rolla and Fernandes containing a small proportion of the element of atomic number 61. T. H. POPE.

Concentration and identification of the element of atomic number 61. J. M. CORK, C. JAMES, and H. C. FOGG (Proc. Nat. Acad. Sci., 1926, **12**, 696—699).—Since an examination of the *X*-ray *K* emission lines of certain specimens of samarium and neodymium suggested the presence of small amounts of the element of atomic number 61 as impurity, attempts have been made to increase its concentration. The small amount of neodymium which accompanied the yttrium earths derived from a large quantity of Brazilian monazite sand was concentrated by fractional crystallisation of the bromates and magnesium double nitrates. The resulting sample, containing about 1% of element 61, was submitted to *X*-ray examination. Seven *L*-series lines were obtained, viz., α_1, α_2, β_1, β_2, β_3, γ_1, γ_2 (Siegbahn's notation), the wave-lengths being 2·279, 2·289, 2·078, 1·952, 2·038, 1·799, and 1·725, respectively. J. S. CARTER.

Crystal structure of nickel oxide, cobalt oxide, and lead sulphide. F. M. BRAVO (Anal. Fis. Quím., 1926, **24**, 611—646).—Measurements made by the Debye-Scherrer *X*-ray method show that nickel oxide, cobalt oxide, and lead sulphide have lattices of the sodium chloride type. The mean values obtained for the length of side of the lattice cube are 4·244, 4·32, 5·96 A. for nickel oxide, cobalt oxide, and lead sulphide, respectively. G. W. ROBINSON.

Crystal structure of magnesium dizincide. J. B. FRIAUF (Physical Rev., 1927, [ii], **29**, 34—40).—The crystal has hexagonal axes, with a 5·15, c 8·48 Å.; the unit cell contains four molecules. The atoms have the positions: zinc: $u, u, \frac{1}{4}$; $2u, u, \frac{1}{4}$; $u, 2u, \frac{1}{4}$; $u, u, \frac{3}{4}$; $2u, u, \frac{3}{4}$; $u, 2u, \frac{3}{4}$; 0, 0, 0; 0, 0, $\frac{1}{2}$; magnesium: $\frac{2}{3}, v$; $\frac{1}{3}, \frac{2}{3}, \frac{1}{2} - v$; $\frac{2}{3}, \frac{1}{3}, \frac{1}{2} + v$; $\frac{2}{3}, \frac{1}{3}, v$, where $u = 0{\cdot}830$ and $v = 0{\cdot}062$. The least distance between two magnesium atoms is 3·15 Å., between two zinc atoms 2·52 Å., and between a magnesium and a zinc atom 3·02 Å. A. A. ELDRIDGE.

Space-lattice of "permalloy." R. FORSTER (Physikal. Z., 1926, **27**, 829—830).—"Permalloy" (78% nickel, 22% iron) shows a face-centred cubic lattice of side 3·56 Å. The lattice constant increases with increasing iron content, since the value 3·54 is obtained for pure nickel and 3·63 for γ-iron (corrected to the ordinary temperature). McKeehan's result of 3·60 Å. for the alloy 30% nickel, 70% iron confirms the additivity of the lattice constant. The lattice is independent of magnetic properties.

R. A. MORTON.

Crystalline structure of zircon. W. BINKS (Min. Mag., 1926, **21**, 176—187).—Zircon (d 4·67) examined by the spectrometer and powder *X*-ray methods shows a structure corresponding with the space-group D_4^{19}. The unit cell containing eight molecules of $ZrSiO_4$ has dimensions $a = 9{\cdot}30$, $c = 5{\cdot}93$ Å. The silicon and zirconium atoms form two interpenetrating face-centred lattices, and the oxygen atoms are arranged tetrahedrally around the silicon atoms. L. J. SPENCER.

***X*-Ray examination of aramayoite.** (MISS) K. YARDLEY (Min. Mag., 1926, **21**, 163—168).—Laue photographs through the perfect basal cleavage of aramayoite show an absence of symmetry. Spectrometer and powder data show that the mineral is triclinic with $a = 5{\cdot}672$, $b = 5{\cdot}688$, $c = 5{\cdot}623$ Å., $\alpha = 86° 55'$, $\beta = 90° 53'$, $\gamma = 93° 18'$. The structure is pseudo-tetragonal with two molecules of $Ag(Sb,Bi)S_2$ in the minimum cell. L. J. SPENCER.

Structure of baddeleyite and of prepared zirconia. (MISS) K. YARDLEY (Min. Mag., 1926, **21**, 169—175).—Spectrometer measurements made on a crystal of baddeleyite (d 5·82) from Ceylon give for the unit monoclinic cell containing four molecules of ZrO_2 the dimensions $a = 5{\cdot}21$, $b = 5{\cdot}26$, $c = 5{\cdot}37$ Å., $\beta = 80° 32'$. A better agreement in the calculated spacings is obtained when the mol. wt. is taken as slightly higher (viz., 128), probably due to the presence of some hafnia in the mineral. Baddeleyite crystals from Brazil gave similar results. Powder photographs of the nodular fibrous zirconia from Serra de Caldas, Brazil (A., 1903, ii, 554), prove the identity of this material with baddeleyite. Similar results were also obtained with artificially prepared zirconia (which has previously been described as tetragonal and as cubic).

L. J. SPENCER.

Crystal structure of some oxalates. J. F. WOOD (Proc. Univ. Durham Phil. Soc., 1925—1926, **7**, 111—116).—Using the Bragg ionisation spectrometer and the rhodium $K\alpha_2$ line (0·616 Å.) as the *X*-radiation, the dimensions of the unit cell, assuming the latter to contain two molecules in each case, have been determined for oxalic acid, for which $a = 6{\cdot}10$, $b = 3{\cdot}61$, $c = 12{\cdot}05$ Å., $\beta = 106° 12'$; ammonium oxalate, $a = 8{\cdot}06$, $b = 10{\cdot}34$, $c = 3{\cdot}82$ Å.; and methyl oxalate, $a = 3{\cdot}93$, $b = 11{\cdot}84$, $c = 6{\cdot}17$ Å., $\beta = 103° 22'$.

The orientation of the molecules in the cell is discussed. M. S. BURR.

Polymorphism of fatty acids. J. THIBAUD (Compt. rend., 1927, **184**, 96—98).—*X*-Ray measurements of the crystal-spacings of fatty acids show that these are a function of the number of carbon atoms in the molecule. For the various crystalline forms of certain acids (*e.g.*, stearic), different values are obtained according to their number (cf. this vol., 98). It is suggested that the variations are due to the different projections of the carbon chains on the base of the molecule, the spacings of the chains themselves being identical. Apart from slight variations due to the positions of the terminal groups, this is in agreement with the observed and calculated crystal-spacings. For stearic acid, the values obtained are 1·41, 1·22, and 1·0 Å., where 1·41 is the true distance between the consecutive carbon atoms. There is a tendency for the acids to crystallise preferentially in one particular form according to their structures. J. GRANT.

Crystallography of phenyl α-naphthyl ketone. T. J. WOYNI (Rocz. Chem., 1926, **6**, 653—660).—The crystallographic and optical constants of crystals of phenyl α-naphthyl ketone were determined by the theodolite method. R. TRUSZKOWSKI.

Electron distribution in the atoms of crystals. Sodium chloride and lithium, sodium, and calcium fluorides. R. J. HAVIGHURST (Physical Rev., 1927, [ii], **29**, 1—19).—With certain assumptions, Fourier analysis is applied to the determination of electron density. Curves show the variation of electron density along the cube edges of the unit cells of sodium chloride, lithium fluoride, and sodium fluoride, and along the cube diagonal of calcium fluoride; radial electron distribution curves are plotted for the various ions. It appears to be definitely proved that the lattice points of the crystals are occupied by ions. The sum of the computed radii of the ions is in every case very slightly less than the distance of closest approach as determined by ordinary *X*-ray analysis. Thus the unit cell of a crystal appears to contain a number of spherical electron systems practically in contact with each other and distributed regularly over the lattice points, each system having a dense electron atmosphere near its centre, which becomes extremely rarefied at its outer limit. The atomic radii correspond closely with those of Wasastjerna (A., 1923, ii, 593; Bragg, *ibid.*, 1926, 780). The electron distribution of an atom may be modified by the external forces which act on it in a crystal; the sodium ion possesses different electron distributions in the chloride and fluoride, whilst those of the fluorine ion are the same in the lithium, sodium, and calcium compounds. The radial distribution curve for the chlorine ion is not in agreement with that of Compton, and the curve for fluorine contains an unexplained hump. Further, spherical symmetry of the electron distribution has been assumed. A. A. ELDRIDGE.

Measurements and interpretation of the intensity of *X*-rays reflected from sodium chloride and aluminium. J. A. BEARDEN (Physical Rev., 1927, [ii], **29**, 20—33).—Measurements of the intensity of *X*-rays reflected from sodium chloride and aluminium have been made, and electron distribution curves plotted for sodium, chlorine, and aluminium. There is no evidence of any failure of the classical electrodynamics as applied to calculations of the intensity of *X*-ray reflexion. A. A. ELDRIDGE.

Reflecting power of the carbon atom for high-frequency rays. M. PONTE (Phil. Mag., 1927, [vii], **3**, 195—209).—In an examination of the intensity of *X*-ray reflexion from crystals, diamond powder has been investigated by the ionisation chamber method. The structure factor for the amplitude has been found to be $1/\sqrt{2}$, and the law of variation of the reflecting power with the angle of reflexion has been found to be the same for several wave-lengths. For diamond, $f_{C(111)}$ has been found to be 2·75 to about 10% accuracy. Examination, by the same method, of naphthalene and anthracene gives for the reflecting power of these molecules 16·5 and 20·2, respectively. These results lead to values of f_C of 5·7 and 5·9, respectively. The reflecting power of graphite on the cleavage plane led to the value $f_C = 3·4$. A. E. MITCHELL.

Crystallisation of metals. C. H. DESCH (Proc. Univ. Durham Phil. Soc., 1925—1926, **7**, 107—110).—An investigation of the influence of surface tension on the process of crystallisation in metals is being conducted. M. S. BURR.

Effect of working on the physical properties of tungsten. J. W. AVERY and C. J. SMITHELLS.—See B., 1927, 113.

Formation of twin metallic crystals. L. W. MCKEEHAN (Nature, 1927, **119**, 120—121).—A criticism of conclusions of Carpenter and Tamura (this vol., 10). A. A. ELDRIDGE.

[Formation of twin metallic crystals.] H. C. H. CARPENTER and S. TAMURA (Nature, 1927, **119**, 121).—A reply to McKeehan (preceding abstract). A. A. ELDRIDGE.

State of ionisation of the atoms in the space-lattice of beryllium oxide. W. ZACHARIASEN (Z. Physik, 1926, **40**, 637—641).—The observed interference patterns can be interpreted as due either to ions or to uncharged atoms. E. B. LUDLAM.

Ionic sizes and their relationship to crystal structure type, solid solution, and double salt formation and the stabilities of hydrates and ammoniates. E. J. CUY (J. Amer. Chem. Soc., 1927, **49**, 201—215).—If ions all behaved as point charges, uni-univalent and bi-bivalent salts would be expected to crystallise in the body-centred cubic lattice (cæsium chloride type), this being the structure in which each ion is surrounded by the maximum number of ions of opposite sign. That other lattices occur is attributed to the influence of the relative sizes of ions. On the assumption that the sphere of influence is tangential to the spheres of influence of the surrounding negative ions, a maximum value for the ratio of the radii of the two ions, r'/r'', is computed for the structure types possessed by compounds of the forms AB and AB_2. For uni-univalent and bi-bivalent salts, the sequence of structure types: cæsium chloride, sodium chloride, zinc sulphide, and

zinc oxide parallels the order of r'/r''. For salts of the type AB_2, the calcium fluoride structure is to be preferred, except for large ratios of r'/r''. With some additional assumptions, it is shown that the greater this ratio is the greater is the tendency for the salts to form hydrates and ammoniates and the greater the stability of these substances when formed. A parallelism is shown to hold between r_1/r_2 and the four possible types of binary temperature–composition diagrams for salts with a common ion, r_1 and r_2 being the radii of the uncommon ions. Critical footnotes by M. L. Huggins are appended. S. K. Tweedy.

Non-magnetic films of iron, nickel, and cobalt. J. D. Hanawalt and L. R. Ingersoll (Nature, 1927, 119, 234—235).—Non-magnetic films of nickel may be produced by cathodic sputtering in hydrogen or argon, and of cobalt and iron in helium. The films become ferro-magnetic when heated in a vacuum at 350°. The non-magnetic film has in general the same crystal structure as after heating, but with a larger lattice spacing. The distension may be due to the occlusion by the metal of large amounts of the residual gas. The constancy of the amount of distension suggests that there may be a chemical or quasi-chemical union of the metal and the gas. It is not believed possible that the metals could sputter as non-magnetic oxides. A. A. Eldridge.

Principal magnetic susceptibilities of crystals. I. I. Rabi (Physical Rev., 1927, [ii], 29, 174—185).—The principal magnetic susceptibilities are tabulated for the following crystals: (*a*) sulphates of the form $MSO_4,R_2SO_4,6H_2O$: copper ammonium, copper potassium, copper rubidium, nickel ammonium, nickel potassium, nickel rubidium, cobalt ammonium, cobalt potassium, cobalt rubidium, ferrous potassium, manganous ammonium, which are paramagnetic, the values depending almost entirely on the paramagnetic ion, (*b*) sodium nitrate, calcite, aragonite, potassium nitrate, and strontium nitrate, which are diamagnetic. A. A. Eldridge.

Molecular theory of solidity and solidification. A. Smekal (Physikal. Z., 1926, 27, 837—844).—In actual crystals, a not inconsiderable fraction of the lattice cells which make up the entire crystal show deviations from the theoretical structure. Apparently, the outer electrons of the atoms making up these anomalous aggregates are not arranged in the ordinary way. On this basis, the phenomena of "inner" photo-electric sensitivity, electrical conduction, phosphorescent materials (Lenard's phosphors), and the coloration of materials like sodium chloride by *X*-ray bombardment, all receive a rational explanation connected with deviations from the normal lattice. Defective cohesion appears to be related to the existence of gliding planes in actual crystals, which owe their properties primarily to defects in the lattice. R. A. Morton.

Polishing of surfaces. N. K. Adam (Nature, 1927, 119, 162—163).—It appears unnecessary to suppose that actual liquefaction occurs, an amorphous layer indistinguishable from a supercooled liquid being formed by any mechanism which rearranges the surface molecules at random. Moreover, the resolidification of a liquefied surface layer might result in crystallisation (cf. Macaulay, A., 1926, 998; Preston, this vol., 100). A. A. Eldridge.

Diamagnetism of mesomorphic substances; orientation of smectic substances by the magnetic field. G. Foex (Compt. rend., 1927, 184, 147—149).—The decrease in diamagnetism produced when a substance passes from the isotropic to the oriented nematic state is due to the corresponding change of the electronic orbits responsible for diamagnetism from a haphazard to an ordered orientation parallel to the field. In general, orientation is not produced unless the substance is cooled in the magnetic field, so that the latter acts during the passage from the isotropic to the smetic phase. The diamagnetism then decreases continuously with increase in the field-intensity, and it is shown that orientation is still incomplete in fields having intensities above 12,600 gauss. The coefficient of magnetisation is almost independent of temperature. When passing from the oriented to the isotropic state, nematic substances show no discontinuity on the curve of the variation of diamagnetism. Ethyl azoxybenzoate, however, shows a marked discontinuity when passing from the smetic to the isotropic state. Smetic substances tend to approach a crystalline state more readily than nematic substances. J. Grant.

Relative resistivity of metals at temperatures of liquid helium. W. Tuyn and H. K. Onnes (Arch. Neerland., 1927, III A, 10, 5—41).—The ratio of the resistivity at temperatures in the range 2—20° Abs. to the normal resistivity has been determined for tin, lead, radioactive lead (radium-Ω), cadmium, zinc, germanium, aluminium, platinum, copper, and alloys of lead with tin. It is concluded that the phenomena of superconductivity are confined to the metals mercury, thallium, lead, indium, and tin. R. W. Lunt.

Electrical conductivity of technical aluminium. G. Masing and C. Haase.—See B., 1927, 112.

Electrostatic charge on glass floats in very dry liquids. H. V. A. Briscoe, P. L. Robinson, and H. C. Smith (Phil. Mag., 1927, [vii], 3, 63—64).—When glass floats were placed in very dry liquid silicon tetrachloride, any slight movement or vibration of the liquid was sufficient to cause them to acquire a charge of positive electricity. The effect was so great as to make the floats adhere firmly to the walls of the containing glass tubes and to render impossible measurements of the flotation temperatures of calibrated glass floats. When the liquid was left undisturbed for a considerable period after being distilled, the floats lost the greater part of their charge, and it became possible to make the measurements with the desired precision. The loss of charge points to a progressive increase in the conductivity of the glass, and it is suggested that this is due to a reaction between the liquid and the glass. Similar results were obtained in very pure boron trichloride. The floats were again positively charged, but the magnitude of the effect was not sufficient to interfere with the precision of measurement. The charges were completely lost after a period of one day, whilst with silicon tetrachloride slight charges remained even after four months. A. E. Mitchell.

Specific heat of gaseous nitrogen tetroxide. E. D. McCollum (J. Amer. Chem. Soc., 1927, 49, 28—38).—The specific heat, C_p, of gaseous nitrogen tetroxide was determined in an improved constant-flow calorimeter between the temperatures 33° and 98°. The apparent heat capacity is large, and attains a maximum at 62°; on subtraction of the heat of dissociation, the true heat capacity is obtained, which increases with rise of temperature. Calculation indicates that C_p is slightly greater for nitrogen tetroxide than for nitrogen dioxide. S. K. Tweedy.

M.-p. curve of helium. G. Tammann (Ann. Physik, 1927, [iv], 82, 240—243).—Keesom (A., 1926, 893) has shown that the vapour pressure and m.-p. curves of helium between 1·13° and 4·21° Abs. do not intersect, and that a triple point in which solid, liquid, and vapour are in equilibrium does not occur. The expression $T - 1 = \log(p - 24{\cdot}0)$ fits the observations over the range $T = 1{\cdot}13$—$2{\cdot}50°$. At higher temperatures, the temperature increases more rapidly than is given by $\log(p - 24)$. For $T = 0$ dT/dp equals 4·3° per atmosphere, and $R_p/T = 0{\cdot}23\Delta v$ cm./kg. Thus dT/dp is large, but not infinite, and R_p/T is small, but not zero, as would be expected from Nernst's theory. R. A. Morton.

Latent heats of fusion of metals and specific heats at high temperatures. S. Umino (Sci. Rep. Tohoku Imp. Univ., 1926, 15, 597—617).—The specific heats of the metals detailed below were determined at high temperatures by the method of mixture, and the latent heats of fusion obtained by extending the heat content curves in the liquid and solid phases to the m. p. With the ferromagnetic metals iron, cast iron, cobalt, and nickel, the heat content–temperature curves are complex below the m. p., owing to the numerous transformations, and are linear above the m. p. Their mean specific heat increases more rapidly than linearly in the ferromagnetic range, and then linearly to the m. p., at which it increases abruptly, and may then either remain constant or decrease. With the non-magnetic metals, the mean specific heat below the m. p. increases slowly and almost linearly with rise of temperature, increases abruptly at the m. p., and then gradually decreases. The true specific heats of non-magnetic metals below the m. p. increase linearly or more rapidly than linearly, and decrease abruptly at the m. p., except with antimony and zinc, which, like the ferromagnetic metals, show an increase. The true specific heats of all metals do not change above the m. p. With the ferromagnetic metals and alloys, the true specific heats show abnormal changes in the ferromagnetic range. The following new values are found for the latent heats of fusion and m.p. Tin 14·20, bismuth 14·10, cadmium 12·90, lead 5·50, zinc 23·60, antimony 40·75, aluminium 79·64, silver 24·90, gold 15·73, copper 49·95, nickel (1450°) 70·40, cobalt (1489°) 67·00, chromium (1600°) 70·05, iron (0·04% C, m. p. 1520°) 69·20, iron (4·22% C, m. p. 1169°) 47·00. When the latent heats of fusion are plotted against the at. wts., a periodic type of curve is obtained. W. Hume-Rothery.

Latent heat of vaporisation and density. W. Herz (Z. anorg. Chem., 1927, 159, 304—306).—The quotient $L_t/(d_t - d_c)$, where, at the temperature t, L is the latent heat of vaporisation, d_t the density of the liquid, and d_c the critical density, is independent of the temperature for each of the non-associated liquids examined, and also for certain associated liquids. The value of the constant is characteristic for each liquid. Results are shown over a wide temperature range for the liquids octane, stannic chloride, methyl alcohol, and ammonia, using previously-recorded values of the terms. The quotient is not constant for propyl alcohol, ammonia, or acetic acid. In the last case, the variation of the latent heat of vaporisation with temperature is known to be abnormal. E. S. Hedges.

Latent heats of vaporisation. M. de Heptinne (Bull. Acad. roy. Belg., 1926, [v], 12, 296—308).—An experimental verification of Prud'homme's formula connecting latent heat of vaporisation and b. p. (A., 1925, ii, 188). Good agreement is obtained for water, ammonia, pentane, hexane, heptane, octane, carbon tetrachloride, chlorobenzene, and benzene. For methyl and ethyl acetates and methyl alcohol, the agreement is less satisfactory. The formula is inapplicable to acetic acid, on account of the maximum in its specific heat–temperature curve. H. F. Gillbe.

Heat of formation of surface layer at the bounding surface of solutions. P. Rehbinder (Physikal. Z., 1926, 27, 825—829).—For dilute solutions and an extended surface, the author's expression $Q = RT(1 - T/G \cdot dG/dT)$ (G is surface activity) can be deduced from well-known thermodynamic equations without special assumptions. On this basis and using earlier measurements, the heats of adsorption for solutions of surface active materials (aliphatic acids) have been calculated. The expression $Q = 1/\Gamma(\Delta\sigma - T \cdot d\Delta\sigma/dT)$ is a special case of the author's formula above if $-d\sigma/dc - G - (\sigma_0 - \sigma)/c$ (cf. A., 1924, ii, 662; 1926, 674). R. A. Morton.

Heats of combustion of proposed secondary standard substances and of position and optical isomerides. L. J. P. Keffler and F. C. Guthrie (J. Physical Chem., 1927, 31, 58—68).—There is described an adiabatic calorimeter of the submarine type which gives results of an accuracy sufficient for use in the determination of the heats of combustion of standard substances. Increased accuracy results from selecting for all combustions the same initial and final temperatures on the Beckmann scale. The heats of combustion found, in g.-cal.[15] per g. (air, v=constant), are, for naphthalene 9614·2, for salicylic acid 5243·1 (cf. Verkade and Coops, A., 1926, 785; Berner, *ibid.*, 116), and for *m*- and *p*-hydroxybenzoic acids, 5244·2 and 5237·8, respectively (cf. Stohmann, *ibid.*, 1889, 1096), the maximum deviation from the mean value being approximately 2 g.-cal. Naphthalene, and especially salicylic acid, on account of its lower volatility, are very suitable secondary standards for bomb calorimetry. From the results obtained with the hydroxybenzoic acids, it is concluded that the energy contents of the *o*- and *m*-isomerides are the same, whilst that of the *p*-isomeride shows a slight difference. The two optically active forms of borneol gave practically the same values for their heats of combustion. L. S. Theobald.

Reconciliation of values obtained for thermochemical constants of organic compounds. W. SWIENTOSLAWSKI (Rocz. Chem., 1926, 6, 578—602).—Values obtained for the heats of combustion of various organic compounds by different authors are compared and correction coefficients determined for them. R. TRUSZKOWSKI.

Friction, heat conductivity, and diffusion in gaseous mixtures. I. M. TRAUTZ (Ann. Physik, 1927, [iv], 82, 227—239).—A new conception of the theoretical treatment of friction, heat conductivity, and diffusion in gaseous mixtures is outlined with special reference to friction in pure gases and in mixtures. The theory of collisions between like and unlike molecules forms the basis of the work. The experimental evidence will shortly be published. R. A. MORTON.

Allotropy of tin. A. TRAVERS and HUOT (Compt. rend., 1927, 184, 152—155).—Tin exists in three allotropic forms, rhombohedric, quadratic, and grey tin, with densities of 6·55, 7·28, and 5·8, respectively. The transformation from one type to another has been followed by density, dilatometric, and calorimetric measurements, anomalous results having been previously obtained. It is now shown that the results are dependent on the previous thermal treatment of the metal, irrespective of its purity. Thus samples heated at 350° for some minutes showed no discontinuities on the calorimetric curve, whilst heating at 500° for 2 hrs. produced a sharp break at 170—171°, this being accentuated by an increase in the time or temperature. Solid samples showed no break even after 52 hrs. at 190°. The transformations denoted by the breaks are accompanied by characteristic decrepitations. J. GRANT.

Association of liquids and a relation between the capillary constant and the heat of vaporisation. P. WALDEN (Z. anorg. Chem., 1926, 158, 244—248).—The relation, $E=0{\cdot}000095MT$, for the molecular elevation of the b. p., in which T is the b. p. of a solvent of mol. wt. M, deduced by de Kolosovski (A., 1926, 1008), is not new, having been previously advanced by Beckmann (*ibid.*, 1896, ii, 236). The author claims priority for the conclusion reached by de Kolosovski, that the ratio of the heat of vaporisation of a liquid to its capillary constant is independent of temperature for a non-associated liquid (*ibid.*, 1909, ii, 119). A. S. CORBET.

Density, compressibility, and at. wt. of nitrogen. G. P. BAXTER and H. W. STARKWEATHER (Proc. Nat. Acad. Sci., 1926, 12, 703—707).—The average values for the densities of nitrogen at 0° and 253·33, 506·67, and 760 mm. at sea-level, latitude 45°, are 0·41667, 0·83348, and 1·25036, respectively. If the value of PV at 1 atm. be assumed to be 1, the values at $\frac{2}{3}$ and $\frac{1}{3}$ atm. are 1·00011 and 1·00028, respectively, the average value of the coefficient of deviation from Boyle's law between 0 and 1 atm. being −0·00045, a value in agreement with existing data. These results lead to the value 14·007 for the at. wt. of nitrogen. J. S. CARTER.

Density of oxygen and its compressibility below one atmosphere. II. G. P. BAXTER and H. W. STARKWEATHER (Proc. Nat. Acad. Sci., 1926, 12, 699—703; cf. A., 1925, ii, 188).—If the most recent value for the gravitational constant be used, the densities of oxygen at 0° and at 190, 380, 570, and 760 mm. at sea-level, latitude 45°, are 0·35699, 0·71415, 1·07149, and 1·42897, respectively. If the value of PV be assumed to be 1 at a pressure of 1 atm., the values of PV at 0·75, 0·50, and 0·25 atm. are 1·00022, 1·00047, and 1·00071, respectively, whence the coefficient of deviation from Boyle's law per atm. is −0·00092, a value very near to the mean value, −0·00094, calculated by Pickering (A., 1926, 569). J. S. CARTER.

Ten years' work on gases. E. MOLES (Gazzetta, 1926, 56, 915—947).—A review, containing also an account of unpublished work on the density of atmospheric air. Tables and graphs show the variation of the weight of a normal litre of air with the atmospheric pressure at Madrid (mean weight 1·29315) and Barcelona (mean 1·29285). The results are in agreement with the Loomis–Morley–Guye law, that all minima of atmospheric (reduced) density correspond with maxima of pressure; most density maxima correspond also with pressure maxima. As the maximum variation in the normal density of air at any one place may be as great as 0·1%, the use of air as a standard of gas density should be abandoned. E. W. WIGNALL.

Method of measuring vapour pressure by air bubbling. H. I. DOWNES and E. P. PERMAN (Trans. Faraday Soc., Jan., 1927, advance proof).—The apparatus previously devised by Perman (Proc. Roy. Soc., 1903, 72, 72) for measuring vapour pressure by air bubbling has been considerably improved to give accurate results over a large temperature range. The vapour pressures and densities of aqueous sucrose solutions have been determined between 40° and 80°, and the values of the osmotic pressures of such solutions, calculated by three methods from the vapour-pressure values, are concordant and in agreement with those obtained by other workers. A. S. CORBET.

Vapour pressure and resistance thermometers in the region of liquid nitrogen and liquid hydrogen. F. HENNING (Z. Physik, 1927, 40, 775—785).—By means of a constant-volume helium gas thermometer, the vapour pressure of liquid and solid nitrogen was determined between 60° and 80° Abs., and of hydrogen between its normal b. p., 20·4° Abs., and its triple point, 14·04° Abs. The change of resistance of pure platinum was determined over the same range. The triple point of nitrogen is 63·12° Abs., at which temperature the vapour pressure is 92·89 mm. The vapour pressure of hydrogen at 14·04° Abs. is 54·86 mm. E. B. LUDLAM.

Critical constants of various gases. S. F. PICKERING (U.S. Bur. Standards Sci. Paper 541, 1926, 21, 597—629).—From a review of the available data for the more common gases and the inert gases the most trustworthy values have been tabulated. The constant RT_cd_c/MP_c seems to vary from 3·0 for krypton to 4·12 for ammonia. The critical data for krypton appear to be inaccurate. In ammonia, the high values are due to the abnormality of the substance. The equations of van der Waals and of Dieterici require values of 2·67 and 3·70, respect-

ively, for RT_cd_c/MP_c, as against $3{\cdot}52_3$, the mean of the values available. R. A. MORTON.

Pressure-temperature formula for vapours. A. BATSCHINSKI (Nature, 1927, **119**, 198).—A satisfactory formula is $t+c=k[p^{1/4}-10^{\alpha-(\beta/\log p_k-\log p)}]$, where p_k is the critical pressure and c, k, α, β are constants, different for different substances. At sufficiently high pressures (*e.g.*, 1—3 atm. to the critical pressure), the formula becomes $t+c=kp^{1/4}$. A. A. ELDRIDGE.

Sublimation pressures of substituted quinones and quinols. A. S. COOLIDGE and (MISS) M. S. COOLIDGE (J. Amer. Chem. Soc., 1927, **49**, 100—104).—The sublimation pressures, p, of twelve substituted quinones and quinols are recorded for various temperatures. In each case log p is a linear function of $1/T$. S. K. TWEEDY.

Influence of centrifugal force on rate of evaporation. E. MACK, jun. (J. Amer. Chem. Soc., 1927, **49**, 135—142).—The rate of sublimation of iodine as observed in a small high-speed centrifuge is directly proportional to the centrifugal force up to values of the latter equal to 250 times gravity and probably higher, always provided that an adsorbent at the end of the diffusion space absorbs the iodine vapour as fast as it arrives. The somewhat amorphous solid iodine surface probably loses molecular aggregates and loosely-held molecules under the influence of the force. When the iodine vapour diffuses against centrifugal force, the rate of evaporation is the same as that found when normal diffusion occurs in the centrifuge at rest. S. K. TWEEDY.

Transformation phenomena of low-melting alloys (Rose's metal). R. FLEISCHMANN (Z. Physik, 1927, **41**, 8—17).—Rose's metal (1Sn, 1Pb, 2Bi) is shown, by dilatometric and resistance measurements, to exist in three different modifications, named σ, α, and β. The σ-form is obtained in the just-solidified metal. The α-form is stable below, and the β-form above, 76°. Below the m. p., only the following transformations are possible: $\sigma\rightarrow\alpha$, $\alpha\rightarrow\beta$, α. Thermo-electric experiments on the alloy confirm these results. W. E. DOWNEY.

The characteristic equation of gases. K. SHIBA (Proc. Imp. Acad. Tokyo, 1926, **2**, 398—400).—A discussion of the equation of state advanced by the author (Nippon Sugaku-Buturigakkwai Kizi, 1926, [iii], **8**, 31), in which it is concluded that the equation of Clausius cannot be considered as a corrected form of that of van der Waals. The limitations of Goebel's equation are discussed (A., 1904, ii, 311, 706); and the law of intermolecular force is deduced to be of the inverse 8th or 9th power for carbon dioxide, in approximate agreement with Debye's theory (*ibid.*, 1919, ii, 211). R. W. LUNT.

Relation between surface tension and temperature. J. E. VERSCHAFFELT (Bull. Acad. roy. Belg., 1926, [v], **12**, 566—572).—The effect of the temperature T, on the surface tension, γ, can be expressed by the empirical formula $\gamma=A(T_c-T)^B$, where T_c is the critical temperature, and $B=1{\cdot}2$, approximately, for "normal" liquids. A similar expression can be deduced from van der Waals' theory of capillarity, but B then has the value 1·5. This is probably because the theory admits of the equation of state being continuous in the neighbourhood of the critical point, which seems to conflict with the experimental evidence (cf. A., 1923, ii, 533). On the assumption of discontinuity, a value is obtained for B which agrees satisfactorily with that found by experiment. R. CUTHILL.

Simple lecture experiment on the viscosity of gases. K. PRZIBRAM (Physikal. Z., 1926, **27**, 830).—A small hollow brass cube is fitted with glass windows on opposite sides. A movable stiff wire traverses the cube in a horizontal direction. A cloud of ammonium chloride falls slowly in the cube, and when this is placed in the beam from a projection lantern, the viscosity of air can be demonstrated by deflexion of the falling cloud as the wire is moved to and fro. R. A. MORTON.

Laws of viscosity of fluids. J. DUBIEF (J. Phys. Radium, 1926, [vi], **7**, 402—413).—No law is yet known which expresses viscosity in terms of density or pressure for the entire fluid state. Maxwell's law ($\eta_0=mu/3\pi\rho^2\sqrt{2}$) is applicable only to perfect gases, since for actual fluids it fails as Boyle's law fails. On the basis of the kinetic theory, $\eta=\eta_0 v/(v-b)$ (η being viscosity of a fluid of volume v, η_0 that of a perfect gas at the same temperature, b the co-volume of van der Waals). The unusual form of this expression leads to a consideration of the following expression for the equation of state: $pv=(1-\gamma\phi(T)/v)\,.\,\eta RT/\eta_0-\pi$, $-$ being a linear function of the density. The latter function appears to be discontinuous, but the argument may be vitiated by experimental errors, and existing compressibilities may be subject to systematic errors. R. A. MORTON.

Viscosity [of copper, brass, and bronze] at high temperatures. J. COURNOT and R. PAGES.—See B., 1927, 112.

Passage of hydrogen through metals. G. BORELIUS and S. LINDBLOM (Ann. Physik, 1927, [iv], **82**, 201—226).—The passage of hydrogen through the walls of tubes of iron, nickel, monel metal, and a palladium–platinum alloy (80% palladium, 20% platinum) has been investigated at pressures below 1 atm. and at temperatures up to 700°. For iron, the investigation was extended to high pressures over the temperature range 25—700°, and also to the diffusion of hydrogen into the tube during electrolysis. The tube was immersed in an electrolyte and used as an electrode, and the quantity of gas entering was investigated for different current densities and temperatures between the ordinary temperature and 100°. The diffusion showed a normal relation with the dimensions of the tube. At constant pressure, the temperature effect is a function of $e^{-b'/T}$, where b is a constant and T is temperature Abs. The diffusion of hydrogen through iron when electrolysis is carried out at a constant current density shows the same temperature relationship as the constant pressure–high temperature diffusion. In each case b is the same.

At constant temperature, the measurements indicate an approximate proportionality to $\sqrt{p}$, where p

is the gaseous pressure. More exact proportionality is given by $\sqrt{p}-\sqrt{p_t}$ for $p>p_t$, where p_t is a threshold value for the pressure. For iron at different temperatures, p_t decreases with increasing temperature. Bodenstein has recorded that at constant temperature the effect varies as $\sqrt{I}$, where I is current density. Over the range 0·005—0·05 amp./cm.^{2}, the proportionality follows the relation $\sqrt{I}-\sqrt{I_t}$, where $I>I_t$ and I_t is a threshold value for current density. The electrolysis and the gaseous diffusion are thus strictly analogous, and current densities can be equated with pressures. Thus 1 amp./cm.^{2} is equivalent to 1700 atm. for iron and 2% sodium hydroxide solution. At moderate temperatures, hydrogen molecules are adsorbed from a gas, and either at the surface or in the metal suffer dissociation, but recombination must occur before the gas can be set free in either the electrolytic or the gaseous process. R. A. Morton.

Density of binary liquid mixtures at 25°. R. M. Woodman (Chem. News, 1927, **134**, 36).—Values of d_4^{25} are recorded for binary mixtures of water with acetic acid, pyridine, and phenol, of benzene with phenol and acetic acid, and of acetic acid with toluene. R. Cuthill.

Theory and properties of binary mixtures. F. Schuster (Z. anorg. Chem., 1927, **159**, 307—315).—A theoretical paper, in which it is shown that Dolezalek's theory (A., 1909, ii, 22; 1910, ii, 184) cannot be regarded as a general law. From the properties of negative vapour-pressure curves, it is deduced that the saturation of residual valencies, to which molecular-compound formation is due, does not follow stoicheiometrical rules, as in the solid state, but is controlled by a strengthened attraction between the molecules. E. S. Hedges.

Principles of the analysis of rectification of liquid mixtures. C. Grabowski (Rocz. Chem., 1926, **6**, 815—823).—The application of various theoretical considerations to the fractionation of liquids is illustrated and certain graphical methods used in distilleries are explained.
R. Truszkowski.

Rate of crystallisation of binary and ternary mixtures from which the pure components separate. G. Tammann and A. A. Botschwar (Z. anorg. Chem., 1926, **157**, 27—40).—The crystallisation of supercooled fused mixtures of acetanilide and 2 : 4-dinitrophenol and of azobenzene and benzil, respectively, has been studied by observing the rate of growth of the crystals. For each system there is a range of mixtures for which the eutectic crystallisation occurs more rapidly than the primary crystallisation. The velocity of the former is a minimum for the mixture of the composition of the eutectic. With increase in the rate of crystallisation and the degree of supercooling, the size of the crystals formed diminishes. Observations have also been made on the ternary system acetanilide–2 : 4-dinitrophenol–benzil.
R. Cuthill.

Thermal conductivity and conductivity-relation of alloys in relation to constitution. A. Schulze (Z. anorg. Chem., 1927, **159**, 325—341).—The constitution of alloys is investigated from the curves obtained by plotting values of thermal conductivity, λ, electrical conductivity, K, and conductivity-ratio, λ/K, against the composition. A pair of completely miscible metals (silver and gold) give curves for λ and K having a pronounced minimum, showing that the conductivity of either pure metal is lowered considerably by slight amounts of the other; the λ/K curve exhibits a corresponding maximum, which is more pronounced at 100° than at 0°. With heterogeneous alloys (tin and zinc), points on the λ and K curves lie on a nearly straight line connecting the extreme values; the conductivity-ratio is here a constant. Alloys of partly miscible metals (lead and bismuth) represent combinations of the two preceding examples, and the curves are compounded of the two forms. With pairs of metals which form chemical compounds, sharp peaks occur in all three curves, indicating their composition. In this case, the type of curve varies according to whether the compound is immiscible with the pure metals (antimony and cadmium) or is completely miscible with the pure metals (antimony and bismuth), or forms more than one compound (copper and palladium). E. S. Hedges.

Colour of copper–nickel alloys. J. A. M. van Liempt (Rec. trav. chim., 1927, **46**, 8—10).—Copper–nickel alloys of varying composition were annealed at 900°, and their colours determined by comparison with a revolving circular disc of copper the surface of which could be partly or completely covered with sectors of nickel, the colour being measured by the relative areas of the disc covered by each metal. The colour is not an additive effect. Alloys containing more than 25 vol.-% of nickel are indistinguishable from pure nickel, whilst between 0 and 25 vol.-% of nickel the graph connecting the colour and volume composition is a curve and not a straight line. This indicates that the electron shells of the copper and nickel atoms are deformed by their close proximity in the solid solution. W. Hume-Rothery.

Transformations in homogeneous, anisotropic phases without crystallisation. G. Tammann and O. Heusler (Z. anorg. Chem., 1926, **158**, 349—358).—It is suggested that the β-transformation in copper–zinc alloys containing 51—55% Cu at 453—470° (cf. Haughton and Griffiths, A., 1925, ii, 973) represents a new type of change which may be due to molecular dissociation. An explanation is given based on the lattice structure of the Cu–Zn compound, and the degree of dissociation is then defined as the ratio of the number of unbound atoms to the total number present. The difference between the β-brass transformation and that of the copper–gold alloy containing 0·25 mol. Au (cf. Johansson and Linde, *ibid.*, 1926, 112) lies in the tendency of the latter to supercool and may depend on a slow suspension of the dissociation equilibrium in the Cu_3Au alloy. The loss of ferromagnetism is analogous to the β-brass transformation. A. S. Corbet.

Limits of resistance of tungsten–molybdenum mixed crystals. II. J. A. M. van Liempt (Rec. trav. chim., 1927, **46**, 11—17; cf. A., 1926, 896).—The action of various mixtures of water and one or more acids on tungsten–molybdenum alloys of vary-

ing composition has been investigated at different temperatures. In some cases, corrosion starts rapidly at a particular composition, whilst in others the corrosion increases continuously with increase in the percentage of molybdenum. Where a sharp corrosion limit is shown, it is not a constant, but depends on the nature of the reagent, the temperature, and usually also on the time of reaction. The positions of the resistance limits do not agree with the $N/8$ molecular content demanded by Tammann's theory, and the author's previous criticisms of this theory (*loc. cit.*) are confirmed. W. HUME-ROTHERY.

Thermo-electric properties of certain metallic solid solutions. A. L. NORBURY (Phil. Mag., 1926, [vii], **2**, 1188—1198).—The *E.M.F.* set up at temperatures between −191° and 500° by a series of copper α-solid solutions, containing aluminium, manganese, nickel, zinc, silver, and tin, when coupled against pure copper, have been determined. Except with manganese alloys, which give complicated results, the results are normal and simple in nature. When the effects on the thermo-electric properties of copper, of equal atomic proportions of the different solute elements except manganese are compared, the order of magnitude of the atomic effects is that in which the elements appear in the periodic table. A similar result is obtained from an analysis of the results of other observers for different types of solid solutions. It is shown that the temperature–*E.M.F.* relationship of the platinum–platinum rhodium (rhodium 10%) thermocouple is most accurately represented by a formula of the type $E.M.F. = -a + bT + c \cdot 10^{-dT}$, where T is the absolute temperature of the hot junction and a, b, c, and d are constants dependent on the thermocouple and the cold junction temperature. A. E. MITCHELL.

Thermo-electric force of alloys. E. VAN AUBEL (Bull. Acad. roy. Belg., 1926, [v], **12**, 559—566).—The thermoelectric *E.M.F.* referred to copper of alloys of bismuth and thallium, antimony and tin, and antimony and silver have been measured. The *E.M.F.*–composition curves show points of inflexion or minima corresponding with alloys of the composition Ag_3Sb, SbSn, and Bi_5Tl_3, respectively. R. CUTHILL.

What are mixed crystals ? E. HALPERN (Rocz. Chem., 1926, **6**, 661—678).—Data for the solubility of mixed crystals of zinc and copper ammonium sulphates at 6·8° and of nickel and copper ammonium sulphates at 0° and 8·5° are recorded. The results are in agreement with Retgers' (A., 1889, 931) and Thiel's laws (*ibid.*, 1903, ii, 531). Nernst's distribution law is, however, only approximately satisfied, applying more closely when the solubilities of the constituent salts of a mixed crystal are close to one another. R. TRUSZKOWSKI.

Additive qualities of mixed crystals. D. OSTERSETZER (Rocz. Chem., 1926, **6**, 679—688).—The solubilities of mixed crystals of ferrous and zinc ammonium sulphates at 7° and of copper and nickel ammonium sulphates at 0° and 8° have been determined. Temperature differences do not appear to affect the relative solubilities of the constituent salts in the latter case. The results confirm the conclusions of Halpern (cf. preceding abstract). R. TRUSZKOWSKI.

Nature of mixed crystals. A. PLOIN (Rocz. Chem., 1926, **6**, 690—699).—The solubilities of mixed crystals of copper and cobalt potassium sulphates at 0° and 7·8° and of copper and zinc potassium sulphates at 6·8° are recorded. The results confirm the conclusions of Halpern (cf. *supra*). R. TRUSZKOWSKI.

Relation between composition and solubility of mixed crystals. B. HABER-CHUWIS (Rocz. Chem., 1926, **6**, 700—704).—Data representing the solubility of mixed crystals of copper and ferrous ammonium sulphates at 0° and at 8·2° and of ferrous and zinc potassium sulphates at 6·8° are recorded. Thiel's law (cf. Halpern, *supra*) is followed in both cases. Nernst's distribution law is, however, true only for the former pair of salts, where the solubilities of the constituent salts are low and close to one another, but not for the second pair, where the solubility difference is greater. R. TRUSZKOWSKI.

Solubility of mixed crystals. B. BERTISCH (Rocz. Chem., 1926, **6**, 705—710).—The solubilities of mixed crystals of copper and cobalt ammonium sulphates at 0° and at 8° and of copper and manganese ammonium sulphates at 7° confirm the conclusions of Halpern (cf. preceding abstracts). R. TRUSZKOWSKI.

Solubility of pure and atmospheric nitrogen in distilled- and sea-water. J. H. COSTE (J. Physical Chem., 1927, **31**, 81—87; cf. A., 1923, ii, 852).—A theoretical paper in which the data of previous investigators are discussed. After due allowance has been made for the effect of argon on the solubility of atmospheric nitrogen, considerable uncertainty still exists as to the absorption coefficient of this mixed gas and of pure nitrogen in both distilled- and sea-water. The probable causes of such uncertainty are considered, chief among which is the difficulty of completely removing the gases of the air from water (cf. Leduc, A., 1906, ii, 155). Congelation appears to be the best means of effecting such removal. L. S. THEOBALD.

Solubilities of rare-earth salts. II. C. JAMES, H. C. FOGG, B. W. MCINTIRE, R. H. EVANS, and J. E. DONOVAN (J. Amer. Chem. Soc., 1927, **49**, 132—135).—The solubilities in water of the bromates $M(BrO_3)_3,9H_2O$, where M represents lanthanum, praseodymium, neodymium, samarium, gadolinium, or terbium, are recorded for 5° intervals between 0° and 45°. The solubility curves for the salts of the cerium group are of a similar type. S. K. TWEEDY.

Capillarity and displacement. K. SCHULTZE (Kolloid-Z., 1927, **41**, 6—11; cf. A., 1926, 1094).—Experiments are described on the behaviour of pairs of non-miscible liquids in capillary spaces. When light petroleum is contained in a capillary tube, and water, coloured with ammoniacal cupric oxide, is drawn up into the tube, the water begins to spread from the meniscus separating the two liquid phases, and along the sides of the glass tube, displacing therefrom the petroleum. Finally, the petroleum–glass

interface becomes entirely a water-glass interface, irrespective of which liquid is placed on top.

E. S. HEDGES.

Solubility of strong, simple electrolytes in water. G. ÅKERLOF (J. Physical Chem., 1926, 30, 1585—1596; cf. McAulay, A., 1926, 1089).—It is suggested that the solubility of strong electrolytes in water is dependent on the ability of the ions of the electrolyte to change the dielectric capacity (*D.C.*) of the solvent. Each ion influences the solubility, which is a function of the algebraic sum of the individual changes of the ions on the *D.C.* of the solvent, the ion with the greatest effect on the state of the solvent being the most soluble. When the total influence on the *D.C.* is zero, the solubility is zero, and as the change produced in the *D.C.* of the medium increases, the solubility always increases. In general, a fair agreement has been found between the calculated changes in *D.C.* and the observed solubilities of electrolytes (cf. Harned and Åkerlof, A., 1926, 796; Åkerlof, *ibid.*, 688). L. S. THEOBALD.

Solubility of solids at low temperatures. W. JACEK (Rocz. Chem., 1926, 6, 501—509).—The solubility of iodine in pentane, *iso*pentane, and carbon tetrachloride is very small at temperatures of about −100° (0·018% in pentane at −71°, 0·017% in *iso*pentane at −79°, and 0·148% in carbon tetrachloride at −24°). At these low temperatures, the iodine solutions are colourless, probably owing to the formation of an unstable compound between iodine and the solvent. The solubility of sulphur in carbon tetrachloride and in toluene was also determined. In all cases, the solubility s agrees with $d \log s = \theta dt$, where θ is a constant for the given solvent and solute.

R. TRUSZKOWSKI.

Adsorption by carbon in viscous media. G. WEISSENBERGER and S. FRANKEL (Kolloid-Z., 1927, 41, 14—27).—The amount of iodine adsorbed by various charcoals from glycerol solutions was determined by titration after equilibrium was attained. Measurements of the viscosity of the solutions were also made. Experiments were also carried out on the adsorption of iodine from aqueous solution by carbon, kaolin, and reddle. The results show that the formula of Lockemann and Paucke (A., 1911, ii, 720) holds in highly viscous solutions, and that the relation between total adsorption and the viscosity of the medium is given by the formula $m_r = \Gamma \cdot \eta^{l/r}$, where Γ and l/r are constants. The formula $m_r = K \cdot \gamma^p$, where γ is the initial concentration and K and p are constants, was found to hold in the cases examined, but is of only empirical significance. It is shown that colouring matters can be determined in boiling solution containing strong sulphuric acid by means of permanganate titration. The maximum error observed was ±1·2%. E. S. HEDGES.

Active charcoal. Charcoal activated by mineral substances. M. SWIDEREK (Rocz. Chem., 1926, 6, 603—632).—Charcoal activated by carbonisation in presence of mineral substances such as zinc chloride or asbestos owes its activity to the extension of its surface by the fine division of the charred mass on the mineral basis. Its adsorptive power is determined by the dimensions of the pores, and this, again, depends on the rapidity of carbonisation. Such charcoal-covered granules adsorb gases and decolorise liquids at about the same rate as ordinary charcoal. The activity of such activated charcoal varies with the proportion of the charcoal in the preparation.

R. TRUSZKOWSKI.

Adsorption of gases by metallised silica gels. L. H. REYERSON and L. E. SWEARINGEN (J. Physical Chem., 1927, 31, 88—101; cf. this vol., 16).—The adsorption of various gases by silica gels metallised with silver, copper, platinum, and palladium by the method of Latshaw and Reyerson (A., 1925, ii, 412) has been measured at 0°, 64·5°, 100°, 138°, and 218°. Hydrogen is appreciably adsorbed by the copper, platinum, and palladium gels, carbon monoxide by all the gels except that of copper, whilst ethylene is absorbed more strongly than by silica gel alone. Oxygen is specifically absorbed by all the gels, especially by the copperised gel. Methane shows no specific effect, neither does carbon monoxide, except possibly in the case of copper. Rise of temperature rapidly reduces adsorption. Successive metallisations of the gel by platinum have no great effect except in the case of carbon monoxide, where a steady increase in the amount adsorbed occurs up to four metallisations. With silica gel alone, the amounts of the above-mentioned gases adsorbed at 0° and 760 mm. increase with the b. p. of the gas, except in the case of carbon monoxide. For all gels, metallised or not, the Freundlich equation holds whenever considerable adsorption takes place. The adsorption isotherms, together with comparative data for the different gases, and for helium and nitrogen on silica gel at 0°, are given.

L. S. THEOBALD.

Adsorption of benzene vapour on the plane surfaces of glass, fused quartz, and platinum. Isosteric heat of adsorption of benzene on platinum. S. LENHER (J.C.S., 1927, 272—281).—The adsorption of benzene on different surfaces at pressures above 90% of the equilibrium pressure has been measured by a method previously described (McHaffie and Lenher, A., 1925, ii, 854; Lenher, *ibid.*, 1926, 898). The adsorption is expressed in terms of the number of molecular layers. The equilibrium film on glass which will just exert the saturated vapour pressure of benzene remains of practically constant thickness, approximately 20 mols. over the temperature range considered, viz., about 294—303° Abs. The free energy decrease on undergoing adsorption is very low, indicating that there is very little affinity between benzene vapour and a glass surface. Since the amount of adsorption decreases as pressure and temperature are increased, the temperature coefficient of desorption must be greater than the pressure coefficient of adsorption. The adsorption values on silica are very similar. On platinum, the adsorption is from five to seven times as great as that on glass or silica. From 295° to 300° Abs., the amount of benzene vapour adsorbed on a platinum surface at saturation pressure increases with increasing temperature and pressure, but from 300° to 305° Abs. it decreases rapidly. The isosteric heats of adsorption on platinum at constant pressure of benzene vapour are found to be of practically the same magnitude as the latent heat of con-

densation to liquid at the same temperature. Data are also given of the thickness of films of both benzene and water exerting the saturated equilibrium pressure at different temperatures. The adsorption of vapours on solid surfaces over a wide range of pressure is briefly discussed. M. S. BURR.

Absorption of water by rubber. H. H. LOWRY and G. T. KOHMAN (J. Physical Chem., 1927, **31**, 23—57; cf. van Rossem, Koll.-Chem. Beih., 1918, **10**, 43; Boggs and Blake, B., 1926, 374).—The mechanism of the absorption of water by simple rubber–sulphur compounds has been investigated by studying the various factors which influence the amount and the rate of absorption. The vapour pressure–absorption curves at 25° show that for vapour pressures below 16 mm. the solubility of water is directly proportional to the pressure, and thus indicates the formation of a true solution. The time–absorption curves support this view by showing that soluble impurities in rubber do not affect the amount of water absorbed at low pressures, although at pressures above 16 mm. they have a noticeable effect. Above this pressure, the solubility of water in rubber is greater than Henry's law predicts. Removal of soluble impurities reduces the amount of water absorbed. Measurements at 0°, 15°, 25°, and 40° showed that the rate of absorption increases with increasing temperature, but the amount absorbed is not greatly influenced. A hydrostatic pressure of 10,000 lb./sq. in. reduced the rate, but had no effect on the amount absorbed at equilibrium (cf. Schulze, Gummi-Ztg., 1898, **12**, 118). A slow ageing process occurring in rubber compounds immersed in solution from which air is not excluded increases the amount absorbed. This ageing takes place to the greatest extent on the surface of rubber compounds containing approximately 7% of combined sulphur.

It is inferred that the most important factor determining the amount of water absorbed is the vapour pressure of the water with which a given sample of rubber is in equilibrium, and that absorption consists of (i) a true solution of water in rubber and (ii) the formation of solutions internal to the rubber of water-soluble constituents which can be removed by washing. Finally, the amount of water absorbed decreases greatly with increased rigidity of the rubber compound. L. S. THEOBALD.

Derivation of adsorption isotherms. II. B. TAMAMUSHI (Bull. Chem. Soc. Japan, 1926, **1**, 257—260; cf. A., 1926, 1201).—Theoretical. A further adsorption isotherm is deduced, involving Gibbs' adsorption formula and Volmer's surface correction, and resembles Freundlich's general parabolic equation. The expression is applied to data for the adsorption of acetic acid from solution by animal charcoal.

A. S. CORBET.

Do substances in solution retain any of the properties characteristic of them in the solid state? C. MONTEMARTINI and L. LOSANA (Notiz. chim.-ind., 1926, **1**, 205—207).—The density–temperature curves for dissolved substances have been compared with those for the substances in the solid state. The curve for sulphur (9%) in nitrobenzene changes direction at about 90° and shows an arrest at 115°; those for 3 and 20% acetamide show arrests at 42° and 65°, respectively. Naphthalene (3·5 and 30%) in xylene shows arrests at 58° and 80°; at concentrations of 2, 4, 10, and 20% in toluene it shows arrests at 48°, 58°, 63°, and 67°. The curves for solutions of *p*-toluidine in xylene (5 and 10%), toluene (10%), and benzene (10%) show arrests at 30°, 41°, 36°, and 33°, respectively. Aqueous (25%) nickel sulphate hexahydrate has an arrest at 42—50°; ammonium nitrate (5, 15, and 25% and solution saturated at 15°) changes direction without arrest at 28°, 30°, 31°, and 32°, respectively. Aqueous (10%) hydrazine sulphate changes direction at 35° and shows an arrest at 55°; 20% aqueous lithium ammonium sulphate shows an arrest at 45°, and 15% aqueous sodium magnesium sulphate tetrahydrate an arrest at 22—23°. In general, but more particularly in the case of concentrated solutions, characteristic breaks are found which are not far removed from the temperatures at which changes occur in the solid state.

CHEMICAL ABSTRACTS.

Rhythmical precipitation of calcium hydroxide. W. M. FISCHER and A. SCHMIDT (Rocz. Chem., 1926, **6**, 404—414).—Periodic variation in light intensity may cause rhythmical precipitation of calcium hydroxide. True rhythmical precipitation, due to chemical factors alone, may be observed when calcium chloride solution diffuses into a sodium hydroxide solution, under a cover-glass. The calcium hydroxide which is at first precipitated soon disappears, being replaced by an unstable hydrate, $2Ca(OH)_2,H_2O$, which then rapidly changes back to the stable normal hydroxide. The optical and crystallographic constants of these two hydroxides are determined and compared. R. TRUSZKOWSKI.

Liesegang rings. D. NAMASIVAYAM (J. Proc. Asiatic Soc. Bengal, 1924, **20**, 367—369).—Experiments on the formation of rings in capillary tubes are described in which ammonia solution diffused into a copper–agar-agar sol gave alternate bands, pale green and dark blue in colour. In every case, the central band in the tube was pale green. An explanation of ring formation on the basis of the movements of electrically-charged colloidal particles is advanced. CHEMICAL ABSTRACTS.

Liesegang phenomenon and stratification. M. COPISAROW (J.C.S., 1927, 222—234; cf. *ibid.*, 1923, **123**, 785).—It has been shown that, in the formation of Liesegang rings, the two salt or salt–acid systems may be substituted by (1) one basic salt, *e.g.*, sodium carbonate, sodium hydroxide, barium hydroxide, etc., and (2) a gas or its aqueous solution, hydrochloric acid, formaldehyde, ammonia, etc. Liesegang rings may also be formed in an aqueous medium, *e.g.*, when a solution of sodium carbonate is carefully run over a solution of calcium chloride. Another phenomenon may also be observed in this case, viz., the formation of trees or streamers. Both this phenomenon and ring formation are greatly influenced by temperature, and the former is inhibited by the presence of gelatin or agar-agar. Light has a directive action on tree formation and also on the formation of rings. It is considered that Liesegang rings are due to a primary and a secondary cause.

The primary cause is the periodic deformation or coagulation of the fibrillar structure of the colloid under the influence of the electrolyte. The secondary cause, which really contributes to the viscosity and thickness of the rings rather than to their formation, is the salting out or deposition of the electrolyte on the coagulated membrane. The action of formaldehyde or hydrochloric acid, for example, on gelatin shows that the secondary cause may be eliminated without interfering with the periodic effect. When the initial substances taking part in the Liesegang formation are neutral in character, the formation of acidic or basic substances by hydrolysis often precedes ring formation. These facts, together with the phenomena observed in aqueous solutions, show that no single theory hitherto put forward affords a sufficient explanation. The influence of the presence of hydroxy-compounds such as glycerol, and also of gelatin, on the formation of colloidal calcium carbonate has been studied. These and previous results (*loc. cit.*) show that it is only hydration to pentahydrate which is absolutely necessary for the stratification of calcium carbonate, but that the presence of colloids and salts, and experimental conditions such as temperature and pressure, which influence hydration, have an important effect on the nature of the product. M. S. BURR.

Theory of periodic precipitation. N. R. DHAR and A. C. CHATTERJI (Z. anorg. Chem., 1926, **159**, 129—144).—Conductivity and diffusion experiments show that silver chromate in gelatin is present as a colloid and not as a supersaturated solution. The same applies to lead chromate, iodide, chloride, etc. in agar and to other substances present in different gels. The theories of Bradford, Wilhelm Ostwald, Wo. Ostwald, and Fischer on the formation of periodic precipitation are discussed and shown to be inadequate.

If silver chromate were present in gelatin as a supersaturated solution, inoculation by some crystals of the solid must suffice to destroy the supersaturation. Experiment shows that a large amount of silver chromate is necessary to cause coagulation.

The most important points of the theory of periodic precipitation are that periodic precipitations are formed by the coagulation of a peptised sol and that the coagulated masses in their formation and after their precipitation absorb and completely or partly coagulate the sol of the same material in the neighbouring layer. M. CARLTON.

Anomalous osmosis through collodion membranes. P. J. JURISIĆ (Physikal. Z., 1926, **27**, 774—778).—When a collodion membrane of the same size and shape as a large test-tube is fitted with a capillary, filled with a salt solution, and immersed in distilled water, it is claimed (Loeb, A., 1919, ii, 399; 1920, ii, 94, 358, 476) that the capillary rise is anomalous. Observations with sodium sulphate have shown that for many of the membranes used, the capillary rise increases with the concentration in a continuous manner. The anomalies are in no case so well marked as in the work of Loeb (*loc. cit.*) and of Preuner. The results are, however, anomalous in the sense that the osmotic values are much higher than those which would correspond with isotonic dextrose solutions. Anomalous osmosis is thus not a general property of collodion membranes in the sense indicated by Loeb and by Preuner. The anomalous results depend on other factors, such as perhaps the size of the pores in the membrane. Preuner's claim that a parallelism exists between diffusion *P.D.* values on the two sides of the membrane and the capillary rise in the anomalous osmotic concentration range is not confirmed. R. A. MORTON.

Spheroidal state of liquids on heated metallic surfaces. I. MÓSCICKI and J. BRODER (Rocz. Chem., 1926, **6**, 321—354).—Apparatus is described for the concentration of nitric acid in iron vessels, corrosion being avoided by heating the iron to such a temperature that no wetting of the surface takes place. Experiments were made to determine the limiting temperatures at which the wetting of wires immersed in various liquids comes to an end. The conception of " adsorption pressure " is introduced, this being the pressure exerted on the metal surface by the molecules of the layer of liquid wetting it; the actual pressure exceeds this by the pressure of the atmosphere. Hence the b. p. of this layer is higher than that of the rest of the liquid, and is identical with the limiting temperature at which wetting ceases. It is shown that this temperature is a constant for a given liquid and metal, invariably higher than the b. p. of the former, and independent of its temperature. The limiting wetting temperature for aqueous solutions of non-electrolytes at a platinum surface is higher than for pure water (130°), pointing to a greater concentration of solute in the surface layer. It increases according to the series Pt, Fe, Ag, Ni, Cu, Pb. R. TRUSZKOWSKI.

True and colloidal viscosity. J. SAMESHIMA (Bull. Chem. Soc. Japan, 1926, **1**, 255—257).—True and colloidal viscosity may be distinguished by electrical conductivity measurements. The conductivity of solutions of the same relative viscosity and containing 0·1*N*-potassium chloride was markedly depressed by the presence of alcohol, glycerol, or sugars (true viscosity), but was almost normal in presence of gum-arabic, soluble starch, or gelatin (colloidal viscosity). A. S. CORBET.

Viscosity measurements of certain sols in presence of electrolytes. D. N. CHAKRAVARTI and N. R. DHAR (J. Physical Chem., 1926, **30**, 1646—1659).—Viscosity measurements at 23·1° and 25° have been made on sols of chromium hydroxide, gum dammar, gamboge, ferric arsenate, stannic hydroxide, Congo-red, Nile-blue, and thioflavin, in presence and absence of suitable electrolytes. In every case, there is first a decrease in viscosity on addition of small amounts of the electrolyte, followed by an increase in viscosity with increasing amounts of the latter. This decrease is attributed to the increase in the charge and the consequent dehydration of the particles of the sol (cf. A., 1926, 123). Sols of vanadium pentoxide and ceric hydroxide become more viscous as dialysis proceeds, and this is explained on the view that the less the charge on the sol the greater is its viscosity. The surface tension of sols in relation to viscosity is discussed. L. S. THEOBALD.

Graphical method for the construction of the viscosity–shear gradient curve. E. HATSCHEK (Kolloid-Z., 1927, **41**, 11—14).—A purely graphical method of constructing tho viscosity–shear gradient curve is developed from an equation derived in a previous paper (A., 1926, 1003). E. S. HEDGES.

Viscosimetry by variation in velocity of flow, and a new viscosimeter. WO. OSTWALD and R. AUERBACH (Kolloid-Z., 1927, **41**, 56—62).—Existing forms of viscosimeter are described and critically discussed. A new type of viscosimeter (the "overflow" viscosimeter) is described. In this form, the liquid is contained in a vertical, graduated tube, falls through hydrostatic pressure through a capillary tube, and overflows by means of a U-tube into a receptacle. The methods of measurement and calculation of results are demonstrated.

E. S. HEDGES.

Visible and latent differentiated zones in macroscopic homogeneous suspensions. A. STEIGMANN (Kolloid-Z., 1927, **41**, 18; cf. A., 1921, ii, 46, 147).—A description is given of the differentiated zones formed by colloidally-precipitated silver salts. These have in some cases a cellular structure and resemble anatomical preparations. The differentiation is more apparent when the system is exposed to bright daylight than in diffused light. E. S. HEDGES.

Formation of layers in clay suspensions. E. UNGERER (Kolloid-Z., 1927, **41**, 51—54).—The frequent formation of parallel layers observed in suspensions of clay which are left undisturbed (A., 1921, ii, 96) is not a coagulation phenomenon. Observations were made of the particle-density of the layers and of their movement in an electric field. The layers are due solely to the size and weight of particles falling in accordance with Stokes' law. The layer formation takes place also in electrolyte-free clays.

E. S. HEDGES.

Anisotropic copper, silver, and gold. S. BERKMAN, J. BOHM, and H. ZOCHER (Z. physikal. Chem., 1926, **124**, 83—95).—The dichroism and double refraction of finely-divided copper, silver, and gold impregnated in ramie threads and of streaming colloidal solutions of silver and gold have been investigated with results in accordance with Zocher's rule (Naturwiss., 1925, **13**, 1015). *X*-Ray examination of the silver and gold threads shows that the metallic crystals are irregularly disposed; it is inferred that rod-anisotropy is exhibited by such preparations.

L. F. GILBERT.

Reactions of colloidal gold with electrodialysed serum-albumin. R. WERNICKE and F. MODERN (Anal. Asoc. Quim. Argentina, 1926, **14**, 270—287).—See A., 1926, 1005.

Colloid chemistry of "viscose" solutions. I. Velocity function of viscosity. T. MUKOYAMA (Kolloid-Z., 1927, **41**, 62—71).—Measurements of the viscosity of glycerol made with the Ostwald–Auerbach viscosimeter (cf. *supra*) showed the Hagen–Poiseuille formula to hold. Measurements were also made of the viscosity of "viscose" solutions of varying age. These all showed "structure-viscosity," and the older solutions exhibited "structure-turbulence" (A., 1926, 240). The absolute value of the critical velocity corresponding with this structure-turbulence decreases with increasing age of solution. E. S. HEDGES.

Preparation of different-coloured gold sols by means of biological fluids. S. UTZINO (Kolloid-Z., 1927, **41**, 28—35).—The biological fluids examined were saliva, serum, cerebrospinal fluid, and urine, all obtained from man. In the general case, the liquid was diluted with a large volume of distilled water and boiled, and a measured quantity of a solution of gold chloride added to the boiling liquid. The boiling was continued for several hours, the progress of formation of the colloidal solution being observed meanwhile. The results obtained were as follows: dialysed saliva gave gold sols of a bright red colour, whilst the dialysate produced blue or green sols; serum gave a bright red and cerebrospinal fluid a dark red sol, although the latter produced a blue sol in presence of potassium carbonate; light red gold sols were obtained from dialysed urine, whilst the dialysate gave violet sols; with undialysed urine, violet sols were formed in presence of a small amount of potassium carbonate, but red sols with larger amounts. All the sols were characterised by considerable stability.

E. S. HEDGES.

Colouring of starch grains. R. HALLER (Kolloid-Z., 1927, **41**, 81—87).—The colouring of starch grains with indigo, Prussian-blue, methyl-violet, methylene-blue, fuchsin, purple of Cassius, and iodine was studied. After colouring, the grains were allowed to swell in a suitable liquid, causing the outer skin to burst and the contents of the cell to exude. Examination of this process under the microscope showed that in all cases only the outer cuticle was concerned with the colouring, the contents of the cell remaining colourless. The effect of different swelling agents was studied, and a concentrated solution of calcium nitrate proved to be the most suitable. Further evidence was obtained that the blue substance formed between starch and iodine is an adsorption compound. This system shows a close analogy to the colouring of cotton. E. S. HEDGES.

Condition of silver chromate in gelatin from electric conductivity and diffusion experiments. A. C. CHATTERJI and N. R. DHAR (Trans. Faraday Soc., 1927, **23**, 23—30).—See A., 1926, 1203.

Birefringence of cellulosic gels. O. FAUST (Kolloid-Z., 1927, **41**, 54—55).—When "viscose" is allowed to flow from a fine opening into a hot concentrated ammonium chloride solution, a thread-like structure, consisting of the xanthate, is formed. This does not exhibit birefringence, nor does the hydrated cellulose regenerated when the product is treated with a mineral acid, but the substance is doubly refractive when stretched. The birefringence of artificial silk is due to this state of tension, and not to crystalline form. *X*-Ray examination of cellulose esters fails to reveal a crystalline structure.

E. S. HEDGES.

Effect of chemically active rays on gelatin. H. BRINTZINGER and K. MAURER (Kolloid-Z., 1927, **41**, 46—50).—Gelatin subjected to the rays from a quartz lamp was altered so that its tendency to swell in water was lessened, the effect being proportional

to the duration of illumination. Further, the solubility of the swollen gelatin in water was reduced, prolonged boiling being necessary to effect dissolution. Elementary analysis failed to detect a difference, but the irradiated specimen was found to reduce ammoniacal silver nitrate solution. The same effect was observed when the gelatin was irradiated in an oxygen-free atmosphere, but was considerably reduced by rigorous purification of the gelatin. The effect of light is dependent on the presence of an iron catalyst normally found in the ash of gelatin.

E. S. Hedges.

Flocculation of mastic suspensions. A. Boutaric (J. Chim. phys., 1926, 23, 850—870).—The flocculation of mastic suspensions in dilute alcohol has been determined under a large number of conditions by measuring the opacity of such solutions with a Féry spectrophotometer for the light of wavelength 5900 Å. Aqueous solutions of sulphuric acid, potassium chloride, and barium chloride increase the velocity of flocculation for grains of constant size; with increasing grain size the velocity diminishes. The influence of temperature is specific to the coagulating electrolyte. No difference could be observed in the velocity when the coagulation was carried out in the dark, in red, and in blue light. The influence of the addition of stable organic colloids and of protective electrolytes has also been examined.

R. W. Lunt.

Mechanical and electrical coagulation. Wo. Ostwald (Kolloid-Z., 1927, 41, 71—80).—The effect observed by Freundlich and Kroch (this vol., 18) that certain colloid systems are coagulated by mechanical stirring is discussed, and their conclusions are criticised. It is considered more likely that the coagulation is due to electric charges set up by differences of potential between the stirrer and the colloid system. It is shown that the observations of Freundlich and Kroch can be explained quantitatively on this basis.

E. S. Hedges.

Equilibrium in colloid systems. II. Coagulation. O. K. Rice (J. Physical Chem., 1926, 30, 1660—1668).—A theoretical paper in which the conclusions of a previous paper (A., 1926, 352) are revised and extended. On the assumption that surface tension and other properties of colloid particles do not vary with particle size when this is large, the disperse state is shown to be stable when the surface tension of the particles is negative, and unstable when the surface tension is positive. Coagulation occurs at certain definite concentrations and potentials of the particles corresponding with $\gamma=0$.

L. S. Theobald.

Influence of alcohols on the coagulation of dispersoid solutions. A. Janek and B. Jirgensons (Kolloid-Z., 1927, 41, 40—46).—A study was made of the effect of methyl, ethyl, propyl, and *iso*-butyl alcohols on the coagulation of dialysed sols of ferric hydroxide, silver, and arsenious sulphide by electrolytes. When coagulation was carried out by means of sodium chloride, small amounts of the alcohols sensitised the sols (*i.e.*, rendered coagulation easier), the effect increasing with increasing mol. wt. of the alcohol. Higher concentrations of alcohols stabilised the sols. This effect, although not very noticeable with ferric hydroxide, was easily recognisable with silver sol and quite pronounced with arsenious sulphide. In the case of arsenious sulphide, a maximum stabilising concentration was reached, further increase of alcohol causing sensitisation again. In this case, also, methyl alcohol differed from the others in sensitising throughout. The best stabilising effect was found in the coagulation of arsenious sulphide by barium chloride, with small quantities of alcohol. In this case also, methyl alcohol exerted a sensitising effect, and at higher concentrations ethyl alcohol did likewise.

E. S. Hedges.

Lyotropic properties of the fluorine ion. H. Freundlich and M. Aschenbrenner (Kolloid-Z., 1927, 41, 35—40).—The fluorine ion is regarded as the extreme end of the Hofmeister series. The experimental data on which this conclusion rests are the following effects, due to the presence of fluorine ions: (1) the lowering of the solubility of highly soluble substances, (2) the large increase of surface tension at a water–air interface, (3) the change in the electropotential at a water–air interface, (4) the favourable influence on the sol–gel transformation of a gelatin solution. Fluorine ions have a strong coagulative effect on the weakly hydrophilic colloid, ferric hydroxide, but a weaker effect than the chlorine ion on the hydrophobic cupric oxide sol.

E. S. Hedges.

Influence of hydrophilic colloids on the colour change of indicators. A. Gutbier and H. Brintzinger (Kolloid-Z., 1927, 41, 1—6).—The effect of hydrophilic colloids on the end-point, as shown by various indicators, was determined by direct titration of 0·1*N*-hydrochloric acid with 0·1*N*-sodium hydroxide and *vice versa*. In the cases where a difference was noticed, the amount of deviation increased progressively with increasing amounts of colloid, and the result depended on whether the neutral point was approached from the acid or alkaline side. The colloids studied were gelatin, gum arabic, and dextrin, and the results obtained with the indicators were as follows: azolitmin and neutral-red underwent the colour change at the normal value of p_H; phenolphthalein and rosolic acid behaved normally in the titration of acid, but the end-point was premature in the titration of alkali; alizarin behaved normally in the titration of acid, but the end-point was delayed in the titration of alkali; Congo-red and methyl-orange gave a premature end-point in the titration of acid and a delayed end-point in the titration of alkali. The use of indicators in such cases is thus very limited. Parallel experiments, following the course of the titration electrometrically, showed that the presence of the colloid depresses the concentration of hydrogen ions in acid and of hydroxyl ions in alkaline solutions. The electrometric titration curve of hydrochloric acid and sodium hydroxide in presence of 3% of gelatin or gum arabic resembles that of a weak acid and a weak base. In addition to the buffering effect of the colloid, it is considered that the degree of dispersion of the indicator partly accounts for the effect. Excepting solutions of methyl-orange and alkaline solutions of phenolphthalein, rosolic

acid, and Congo-red, the indicators were found to be colloidally dispersed. E. S. HEDGES.

Relations of phenol to proteins and other colloids. Disinfectant action. E. A. COOPER and E. SANDERS (J. Physical Chem., 1927, **31**, 1—22; cf. Cooper and Woodhouse, B., 1923, 1094A).—The nature of the change produced in various proteins by phenol and the mechanism of disinfection have been studied. Precipitation commences when the concentration of phenol reaches 1% for serum-albumin, 0·5% for euglobulin, and 0·001% for pseudoglobulin, and is complete at 1·8, 1·5, and 2·0%, respectively. Experiments with dialysers of "viscose" give a partition coefficient of 11 between phenol and serum-albumin, and the absorption of phenol in this case is a reversible process. Comparison with egg-albumin shows that the precipitating action of phenol is not primarily determined by the absolute amount present. With pseudoglobulin, the values 6·6 and 12 were obtained for the partition coefficient, but absorption here is not strictly reversible. Myosinogen and paramyosinogen are completely precipitated at concentrations of 1·2% and 0·8% of phenol, respectively, and this suggests a similarity with the action of heat, myosinogen being coagulated at a higher temperature.

The distribution ratio between phenol and edestin, as in the case of casein (Cooper, A., 1912, ii, 1199), increases with increasing concentration of phenol. The distribution of phenol between gliadin and water, gliadin and 70% alcohol, and between gliadin and absolute alcohol was also investigated.

In order to test the hypothesis that the precipitation of protein by phenol is due to chemical action, the distribution ratios of gelatin derivatives were measured. The substitution of the methylene group, the quinone nucleus, and bromine in the amino-groups increases the solubility of phenol, although treatment of the gelatin is without effect on the partition coefficient. In general, phenol is distributed between water and proteins in the emulsoid state according to the partition law, but at a certain concentration the protein is precipitated, and this is accompanied by an increased absorption of the former. With certain precipitated proteins, viz., casein, edestin, gliadin, gelatin and its derivatives, the coefficient continues to increase with the concentration of the phenol, in agreement with the view that phenol is associated when dissolved in precipitated proteins. The behaviour of gelatin is anomalous. With resorcinol as the precipitant, the partition coefficient does not increase with increasing concentration.

The bactericidal action of the phenols is not determined merely by their solubility in proteins, but is apparently due to a subsequent action on the colloidal structure of the bacterial cell.

L. S. THEOBALD.

Imbibition of colloids. P. BARY (Rev. gén. Colloid., 1926, **4**, 322—327).—A theoretical paper in which the failure of the Noyes and Whitney expression for the velocity of imbibition (J. Amer. Chem. Soc., 1897, **19**, 930) is discussed on the hypothesis that a colloid is a homogeneous solvent into which the liquid diffuses. It is shown that the discrepancies cannot be traced to a non-uniform distribution of liquid through the solid colloid; and they are explained by suggesting that imbibition is accompanied by the depolymerisation of the solid, and that the liquid must in some way combine with the solid.

R. W. LUNT.

Physico-chemical structure of the collagenic substance. I. Spiral arrangement and hygroscopic torsion of collagenic bundles of tendons. G. C. HERINGA and (MISS) H. A. LOHR (Proc. K. Akad. Wetensch. Amsterdam, 1926, **29**, 1081—1086).—Dark-field observation of longitudinal and transverse sections of various tendons shows that they consist of collagenic bundles intertwined in a spiral form, and a similar condition was found in microscopic preparations of skin and loose connective-tissue. Further evidence was obtained from experiments on the swelling and desiccation of tendons and of isolated bundles of collagen fibres. Torsion occurs in both swelling and desiccation, but in opposite senses. The conclusions were strengthened by the results of an *X*-ray spectrographic examination.

E. S. HEDGES.

Physico-chemical structure of the collagenic substance. II. An optical phenomenon. G. C. HERINGA and M. MINNAERT (Proc. K. Akad. Wetensch. Amsterdam, 1926, **29**, 1087—1091).—A description is given of a peculiar diffraction figure obtained when longitudinal sections of a cow's tendon (enclosed in a lævulose–gelatin mixture) are held in front of a source of light. The phenomenon is shown not to be due to a periodic ridging of the surface, or to a periodic variation in the ordinary refractive index, but is believed to indicate a periodic change in double refraction throughout the fibre. Microscopical examination also indicated an undulatory structure, and direct measurement of the period of a group of clearly-defined wavelets gave a wave-length of 40 μ. The bundles of fibre behave like uniaxial crystals the axes of which are disposed in a spiral form. E. S. HEDGES.

Physico-chemical structure of the collagenic substance. III. *X*-Ray investigation. G. C. HERINGA and N. H. KOLKMEIJER (Proc. K. Akad. Wetensch. Amsterdam, 1926, **29**, 1092—1094).—A rough analysis was made of *X*-ray spectrographs obtained from the tendon of a mouse-tail. The striations which appeared are believed to be due to the occurrence of a linear succession of equal elements in the long axis of the fibres. E. S. HEDGES.

Fibrillous coagulation *in vitro* of collagen dissolved in a dilute acid. J. NAGEOTTE (Compt. rend., 1927, **184**, 115—117).—Collagen from the tendons of the tail of a rat swells up and partly dissolves in acetic acid solution (1 in 25,000), but is reprecipitated as a clot after some days. The fibrils of the coagulum are cylinders with pointed ends, usually long, and of thicknesses varying from 1 μ downwards. Under the ultramicroscope, needle-shaped crystals like those of tyrosine can be seen. The fibrils, but not the crystals, give the tinctorial reactions characteristic of collagen. Their great sensitiveness to dilute acids and bases is suppressed

by the action of fixing agents. The structure is definitely colloidal and independent of the medium. J. GRANT.

Equilibrium constant [K_c] of the esterification reaction in the gaseous phase. W. SWIENTOSLAWSKI and S. POZNANSKI (Compt. rend., 1927, 184, 92—94; cf. A., 1924, ii, 601).—The value K_c has been redetermined with an improved apparatus for a series of mixtures of alcohol, acetic acid, water, and ester in a state of equilibrium. A mean value of 58 was obtained, the mean experimental error being ±10%. J. GRANT.

Methane equilibrium. R. C. CANTELO (J. Physical Chem., 1927, **31**, 124—130; cf. this vol., 20).—Calculations of the equilibrium constants for the ten possible reactions involved in the thermal decomposition of methane, ethane, or ethylene indicate that above 400° the final system consists of methane, carbon, and hydrogen, whatever the initial hydrocarbon might be. This conclusion agrees with the experimental results of previous investigators on the decomposition of ethylene or ethane by heat, alone and in presence of catalysts (cf. Bone and Coward, J.C.S., 1908, **93**, 1197). L. S. THEOBALD.

Theory of perfect solutions. W. DANIEWSKI (Rocz. Chem., 1926, **6**, 556—568).—Theoretical. R. TRUSZKOWSKI.

Conductivity and mol. wt. of halogen acids in dry and moist nitrobenzene. M. HLASKO and E. MICHALSKI (Rocz. Chem., 1926, **6**, 534—555).—The conductivities of hydrogen chloride and bromide in dry nitrobenzene and nitromethane are, in spite of the high dielectric constants of the latter solvents, very small. Thus for dry nitrobenzene, α is $4{\cdot}0\times10^{-4}$ for 0·6*N*-hydrogen chloride, and $6{\cdot}7\times10^{-4}$ for 0·6*N*-hydrogen bromide, whilst in nitromethane α is $9{\cdot}4\times10^{-4}$ for 8·7*N*-hydrogen chloride. The presence of 0·1% of moisture increases the conductivity tenfold. Hydrogen bromide is in all cases more dissociated than the chloride. Cryoscopic measurements show that water, hydrogen bromide, and hydrogen chloride, dissolved in nitrobenzene or in formic acid, are present as simple molecules, but that the addition of hydrogen bromide or chloride to wet nitrobenzene produces little depression of f. p., owing to the formation of hydrates of the type HCl,H_2O, provided that it is added in quantities not greater than the water content. It follows that conclusions relative to the association of dissolved substances in the above solvents are not valid unless precautions are taken to eliminate water, and for this reason the results of Zanninovich-Tessarin (A., 1896, ii, 352) and of Beckmann and Lockemann (*ibid.*, 1907, ii, 845), which indicated polymerisation of hydrogen halides in the above solvents, are not acceptable. R. TRUSZKOWSKI.

Soret effect. C. C. TANNER (Trans. Faraday Soc., Jan., 1927, advance proof).—The concentration difference set up in a solution by a temperature gradient has been studied by an optical method involving measurements of the change of refractive index. Solutions of acids, bases, and metal halides, nitrates, and sulphates of varying normality have been thus examined for temperature differences of 14° and 20°. The fractional change per degree of the normality of the solution passes through a maximum for hydrochloric and sulphuric acids, whilst the low values for lithium and magnesium salts and the large values for alkali hydroxides are in substantial agreement with the results obtained by Chipman (A., 1926, 1206). A. S. CORBET.

Dilution law for strong electrolytes. B. SZYSZKOWSKI (Rocz. Chem., 1926, **6**, 510—534).—The equivalent conductivities of strong electrolytes (univalent anion and cation) satisfy the following law from 0·0001 to 0·1*M*-solutions: $1-\lambda/\lambda_0=0{\cdot}5\beta C^{1/2}-\gamma c+1{\cdot}5\delta C^{3/2}$, where β, γ, and δ are constants. This expression agrees fairly well with Kohlrausch's experimental values and affords a confirmation of Debye and Hückel's theory for solutions of completely dissociated electrolytes. R. TRUSZKOWSKI.

Dissociation constant of carbonic acid. A. KLEMENC and M. HERZOG (Monatsh., 1927, **47**, 405—413).—The conductivity of sodium hydrogen carbonate in aqueous solution at 0° and 12·5° and of carbonic acid at 12·5° has been determined, the method of Walker and Cormack (J.C.S., 1900, **77**, 5) being employed. Extrapolation of the equivalent conductivity values for sodium hydrogen carbonate by means of the Noyes equation $1/\lambda=1/\lambda_\infty+K(C\lambda)^{n-1}$, where $n=1{\cdot}5$, gives the values 49·8 and 73·1 for λ_∞ at 0° and 12·5°, respectively. The degree of hydrolysis of sodium hydrogen carbonate solution is discussed, and the authors confirm the conclusion of Auerbach and Pick (A., 1911, ii, 1078) that the hydrolysis is independent of the concentration. Calculations of the mobility of the HCO_3 ion and of the limiting conductivity of carbonic acid from the new data give values in good agreement with those of Kendall (*ibid.*, 1916, ii, 512). The value of the apparent first ionisation constant of carbonic acid $[H'][HCO_3]/[CO_2+H_2CO_3]$ obtained from the conductivity measurements is $2{\cdot}65\ (\pm0{\cdot}04)\times10^{-7}$ at 12·5°. The values of the true dissociation constant and the apparent second ionisation constant of carbonic acid obtained by previous authors (cf. Thiel, *ibid.*, 1917, ii, 134, and references there quoted; and McCoy, *ibid.*, 1903, ii, 413) are examined in the light of the new data, and suggest that carbonic acid H_2CO_3 is completely ionised. J. W. BAKER.

Dissociation constant of nitroamide. J. N. BRONSTED and C. V. KING (J. Amer. Chem. Soc., 1927, **49**, 193—200; cf. A., 1925, ii, 982).—Nitroamide decomposes in pure water at 15° 10% faster than in acid solution. The conductivities of aqueous nitroamide solutions were determined between unplatinised electrodes; the (acid) dissociation constant is $2{\cdot}55\times10^{-7}$ at 15°. The conductivities of the sodium salt were also determined. S. K. TWEEDY.

Determination of the dissociation constants of phenol and of the hydroxyl group of tyrosine by means of absorption measurements in the ultra-violet. W. STENSTROM and N. GOLDSMITH (J. Physical Chem., 1926, **30**, 1683—1687; cf. Stenstrom and Reinhard, A., 1926, 10).—The dissociation constant is calculated from the expression

$D=[H](\varepsilon-a)/(b-\varepsilon)$, where a is the extinction coefficient for molecules not ionised at the hydroxyl group, b that for molecules which are so ionised, and ε that for a mixture of ions and molecules. A suitable value for ε lying between a and b is determined graphically for a certain p_H value, at a chosen wave-length. Between 18° and 24°, two aqueous solutions of phenol ($N/1570$) gave $D=1{\cdot}38\times10^{-10}$ and $1{\cdot}21\times10^{-10}$, respectively, when $\lambda=2825$ Å.; $N/1550$ tyrosine solutions gave $D=1{\cdot}24\times10^{-10}$ and $1{\cdot}33\times10^{-10}$ at $\lambda=2840$ Å. L. S. THEOBALD.

Cupriammonia ion and its stability. P. JOB (Compt. rend., 1927, **184**, 204—206).—The coefficients of absorption of various mixtures of solutions of cupric and ammonium salts have been measured with a Féry spectrophotometer. The molecular concentrations of the copper and ammonia, respectively, varied from 0·2 to 0·01 and 1·0 to 0·1, the salts being dissolved in a concentrated solution of ammonium nitrate to prevent the formation of cupric hydroxide by retarding the electrolytic dissociation of the ammonia. Curves connecting the absorption as a function of the composition showed marked maxima, corresponding in the case of equimolecular mixtures with the formula $Cu(NH_3)_4$. For the non-equimolecular solutions, the dissociation constant was calculated, and was found to agree with the results obtained from the absorption data. A value of 5×10^{-10} was found at 16°. The tetra-ammonia ion, therefore, is probably the only cupriammonia ion stable at the ordinary temperature. The affinity of ammonia for the cupric ion is 12,400 g.-cal. J. GRANT.

Rotatory power of organic compounds as a function of the p_H; malic acid. E. VELLINGER (Compt. rend., 1927, **184**, 94—96).—The curves obtained for the dispersion and rotatory power of malic acid as functions of its p_H value resemble those given by tartaric acid. The rotation curve is expressed by the same formula, the two ends, however, being depressed to a greater extent, whilst the position of the point of inflexion indicates that the greatest variations in the rotatory power are determined by the first stage dissociation. When plotted according to the method of Darmois, the dispersion lines do not all converge to the same points, as in the case of tartaric acid (A., 1926, 1201). This may be accounted for by an experimental error of 3—5%.

J. GRANT.

Solvation and complex formation as causes of colour change in cobaltous halides. A. HANTZSCH (Z. anorg. Chem., 1927, **159**, 273—303).—Previous work on the subject is reviewed, and it is shown that the colour change cannot be due to the formation of ions of the type CoX_4''. Consideration of the colour of solid compounds of the type CoX_2A_2 (blue or violet), CoX_2A_4 (red), and CoX_2A_6 (rose), where X is a halogen atom and A is a molecule capable of addition (*e.g.*, H_2O, NH_3, etc.), indicates that solvation is a primary cause. The constitutions of the first and third types are, respectively, $\left|\begin{matrix}A\\A\end{matrix}\right>Co<\begin{matrix}X\\X\end{matrix}\Big|$ and $[CoA_6]X_2$, whilst that of the second type is doubtful. Since *cis-trans* isomerism is possible with the first type, this explains the existence of a blue and a violet form. The change of the red forms to blue when heated or on concentration of the solution is in agreement with the solvation theory. The absorption spectra of a large number of representatives of this type were examined in various solvents. In general, a large optical difference was found between the salts CoX_2A_2 and CoX_2A_6, but, in each of these groups, the nature of the halogen atom and of the combined group A made little difference. The absorption was strengthened slightly in the order Cl<Br<SCN. Experiments on the dehydration of cobalt chloride hexahydrate did not indicate the existence of the hydrates $CoCl_2,4H_2O$ and $CoCl_2,1{\cdot}5H_2O$ described in the literature. The cobalt thiocyanate tetrahydrate described by Grossmann and Hünseler (A., 1906, i, 7) appears to be a trihydrate, but the existence of the hemihydrate described by Rosenheim and Cohn (*ibid.*, 1901, i, 455) was confirmed. Methods of preparation of the following new *compounds* are described: the dimethyl-alcoholates of cobalt bromide and of cobalt thiocyanate, $Co(CH_3{\cdot}OH)_2X_2$; the hexamethyl-alcoholates of cobalt bromide and of cobalt chloride, $Co(CH_3{\cdot}OH)_6X_2$; the corresponding thiocyanate could not be isolated; the tetrabenzyl-alcoholates of cobalt chloride and of cobalt bromide, $Co(C_6H_5{\cdot}CH_2{\cdot}OH)_4X_2$; diacetonitrile cobalt bromide, $Co(CH_3{\cdot}CN)_2Br_2$; dipyridine cobalt sulphate, $CoSO_4,2C_5H_5N$; dipyridine cobalt oxalate, $CoC_2O_4,2C_5H_5N$. E. S. HEDGES.

Molecular structure in solution. I. Densities and viscosities of aqueous solutions of cobalt chloride and hydrochloric acid. O. R. HOWELL (J.C.S., 1927, 158—170).—The change from red to blue when hydrochloric acid is added to a solution of cobaltous chloride is probably due to a change from six to four in the number of groups or atoms with which an atom of cobalt is associated, as already shown by *X*-ray examination for red and blue cobalt pigments (Hill and Howell, A., 1924, ii, 817). In the aqueous solution, the cobalt is probably present as hydrated ions $Co(H_2O)_6''$, which, as the concentration of hydrochloric acid is increased, are progressively converted into $CoCl_4''$ ions. The densities and viscosities of a series of aqueous solutions containing a constant amount of cobalt chloride, but increasing amounts of hydrochloric acid, have been determined and compared with a similar series of values for hydrochloric acid alone. Differences in viscosity and density for corresponding solutions have been plotted against concentration of acid. At the same concentration of acid, there is, in the density difference curve, a point of inflexion, and in the viscosity difference curve a well-defined maximum. These points are considered to mark the concentration at which equal numbers of the two different kinds of ions are present. This point does not mark the maximum colour change, because the blue colour is much more intense then the red. M. S. BURR.

Complex formation amongst the nitrates. I. Ternary system copper nitrate–cobalt nitrate–water. K. W. WILCOX and C. R. BAILEY (J.C.S., 1927, 150—153).—The system copper nitrate–cobalt nitrate–water has been examined at 14°, 20°, and 30°. The so-called trihydrate of copper nitrate has the com-

position $Cu(NO_3)_2,2\frac{1}{2}H_2O$, and its transition point to the hexahydrate is 25·4°. A double salt of the probable composition $6Cu(NO_3)_2,Co(NO_3)_2,(42\pm1)H_2O$ has been isolated. It is smoke-blue in colour, crystallising from a purple solution, is very deliquescent, melts at about 17°, and is decomposed by water.

M. S. Burr.

Revision of some activities in water–alcohol mixtures. G. Scatchard (J. Amer. Chem. Soc., 1927, **49**, 217—218).—The activity coefficients of hydrogen chloride in aqueous alcohol are revised, an error in the calculations of the previous paper being corrected (A., 1925, ii, 971). The theoretical calculations are improved by utilising the vapour-pressure measurements of Dobson (J.C.S., 1925, **127**, 2866). The revised results do not preclude the combination of 1 mol. of hydrogen chloride with 2 mols. of water, although this is considered to be unlikely. The ionic size of lithium chloride calculated from the results of Drucker and Schingnitz (A., 1926, 911) agrees much better with the effect of lithium chloride on the activity of non-electrolytes than the results of Pearce and Hart (*ibid.*, 1923, ii, 7).

S. K. Tweedy.

Activity coefficients, ionic concentrations, and kinetic salt effects of formic acid in neutral salt solutions. H. S. Harned (J. Amer. Chem. Soc., 1927, **49**, 1—9).—The ionisation constant, K, of a weak acid is affected by the addition of neutral salt, and this interferes with the calculation of velocity constants from the rate of hydrolysis of esters in neutral salt solutions (cf. Manning, J.C.S., 1921, **119**, 2079). The activity coefficient products of formic acid in various halide and sulphate solutions are calculated from Manning's results, on the assumption that K varies on the addition of neutral salts, but is constant during a reaction in a medium of practically constant ionic strength. The concentration hypothesis yields more reasonable values for the products than the activity theory. The activity coefficient products are higher the lower the activity coefficient of the neutral salt. This effect is considered to be due to a distortion of the readily-deformed, unsymmetrical anions of these substances by the electrical field produced by the neutral salt.

S. K. Tweedy.

Activity coefficients of the ions in certain phosphate solutions. Theory of buffer action. E. J. Cohn (J. Amer. Chem. Soc., 1927, **49**, 173—193).—The p_H values for concentrated solutions containing both potassium dihydrogen phosphate and dipotassium hydrogen phosphate are recorded. The graph of the concentration of the latter salt against p_H shows that the more concentrated the solution the more acid is the reaction and the greater is the deviation of the curve from that required by the mass law. This divergence is greater in concentrated acid than in concentrated alkaline solutions. The activities of the ions in the solutions are calculated and equations representing p_H are deduced with the aid of the Debye–Hückel theory, the results being discussed in the light of the theory of buffer action. Tables and graphs are given facilitating the preparation of buffer solutions of the same ionic strength and varying p_H and *vice versa*. S. K. Tweedy.

Relation between pseudobinary lines and solid solutions in metallic ternary systems. R. A. Morgen (J. Amer. Chem. Soc., 1927, **49**, 39—43).—Mixtures corresponding with the pseudobinary line of the ternary metallic system A–B–C (*i.e.*, the line joining A with the point representing BC, the compound existing in the solid phase) do not behave like ordinary binary systems. Since BC dissociates in the liquid phase, a consideration of the f.-p. diagram for the system A–BC shows that the above mixtures are represented by a two-dimensional point distribution on the surface of a ternary diagram, solid solution occurring at the expense of the compound BC if the latter is "weak." Experiment supports these conclusions. S. K. Tweedy.

Mass unit of chemical potential. W. D. Bancroft (J. Physical Chem., 1927, **31**, 69—80).—Selected passages from the work of Gibbs ("The Collected Papers of J. W. Gibbs") are quoted and explained. Chemical potentials may be referred to any mass units, but general relations are more clearly shown if the appropriate units are employed. For reactions which involve the pressure of gases, or the osmotic pressures of solutions, the mol. wt. of the reacting substance or ion is the appropriate unit, as is the electrochemical equivalent for electrochemical reactions. The appropriate mass units in the case of electrical endosmose or of frictional electricity have yet to be worked out. With organic compounds, there are as many chemical potentials as there are linkings to be broken or activated. Equations for velocity of reaction have still to be deduced from relations between potentials. L. S. Theobald.

Vapour pressures of mixtures of (*a*) methyl acetate and water, (*b*) methyl acetate, sucrose, and water. A. McKeown and F. P. Stowell (J.C.S., 1927, 97—103).—Total vapour pressures at 25° and 35° of methyl acetate–water mixtures, up to concentrations of ester of about $2N$, and also of solutions containing a constant concentration of ester of $0{\cdot}2542N$ along with sucrose of concentration varying up to 600 g. per litre of solution, have been determined by a static method (cf. Morton, A., 1919, ii, 448). The partial vapour pressures of ester and water have been determined by a dynamical method. The ratio of the partial pressures of ester at 35° and 25° decreases as the concentration of ester increases. The same result is obtained if, with a constant concentration of ester, its molar fraction is artificially increased by addition of sucrose. This behaviour suggests the possibility of compound formation between water and methyl acetate in aqueous solution of the ester. M. S. Burr.

Vapour pressure of water over sulphuric acid–water mixtures at 25°. I. R. McHaffie (J.C.S., 1927, 112—116).—The vapour pressure of water over sulphuric acid–water mixtures, of concentration varying from 65·9 to 83·5% of acid, has been determined by a method previously described (A., 1926, 700) for the measurement of small amounts of water vapour in permanent gases. The results are in agreement with those obtained by a number of other investigators, and thus confirm the accuracy of the method of measurement. M. S. Burr.

Vapour pressures of potassium nitrate solutions. J. C. W. Frazer, B. F. Lovelace, and R. K. Taylor (J. Physical Chem., 1926, 30, 1669—1677).—The vapour pressures of 0·1—2·9*N*-solutions of potassium nitrate have been measured at 19·94°, and show this salt to be a more nearly ideal solute than other electrolytes which have been examined. A comparison of these results with f.-p. and b.-p. data shows that von Babo's law is not obeyed, except in the case of very dilute solutions when the heat of dilution is small. Certain changes in technique (cf. Frazer, Lovelace, and Sease, A., 1921, ii, 239) are described. L. S. Theobald.

System sodium nitrate–sodium chloride–water. F. Holzl and H. Crotogino (Z. anorg. Chem., 1926, **159**, 78—86).—The isotherms of the system sodium nitrate–sodium chloride–water were determined at 0°, 15°, 25°, 50°, 83°, and 103° for solutions saturated with only one component at a time. They approximate to straight lines as the temperature rises. The investigation covers the ice region and the limit of the b. p. of the system and indicates a moderate tendency to hydration in the case of sodium nitrate. M. Carlton.

Vapour pressure and heat of dilution of aqueous solutions. II. and III. W. R. Harrison and E. P. Perman (Trans. Faraday Soc., 1927, **23**, 1—22).—Vapour-pressure and density measurements of calcium and potassium chloride solutions, at concentrations up to saturation, and at temperatures from 40° to 80°, have been made by a statical method which is a modification of that used by Perman and Saunders (A., 1923, ii, 737). The heats of dilution of these solutions have also been determined, over the same temperature range, by an electrical method, which is independent of the sign of the heat change. Calcium chloride has thus been found to have a large negative heat of dilution increasing with temperature, and the values obtained experimentally are in fairly good agreement with those calculated from the vapour pressure. Potassium chloride has a small positive heat of dilution below 70°, but in the neighbourhood of this temperature it becomes negative. In this case also, there is agreement between calculated and experimental values. By taking into account the heat of dilution, a more reasonable value for the mol. wt. of calcium chloride in solution is obtained. M. S. Burr.

Concentration of water vapour in compressed hydrogen, nitrogen, and a mixture of these gases in the presence of condensed water. E. P. Bartlett (J. Amer. Chem. Soc., 1927, **49**, 65—78).—The water-vapour content of compressed hydrogen and compressed nitrogen in contact with liquid water at 50° and at pressures up to 1000 atm., and of mixtures of these gases (3 : 1 by volume) at 25°, 37·5°, and 50°, was investigated. It depends on the nature of the gas, the differences for the two gases not being explained by differences in free space. Poynting's law is not obeyed (Phil. Mag., 1881, [iv], **12**, 32). In the case of the mixture, the effect of compression is greater at 50° than at 25°. The proportional effect at 37·5° is not the mean of the effects at 25° (at which it is greatest) and 50°. The Leduc rule of additive volumes at constant temperature and pressure holds for the mixture at 50° and probably also at the other temperatures. No quantitative expression of the results has been obtained; qualitatively, the compressed gas appears to act as a solvent for the water vapour. S. K. Tweedy.

Temperatures of magnetic transformations in the system iron–iron sesquioxide. J. Huggett and G. Chaudron (Compt. rend., 1927, **184**, 199—201; cf. this vol., 11).—Mixtures of iron and iron sesquioxide obtained by partial reduction of the latter were analysed by complete reduction in hydrogen, and the temperatures at which anomalies occurred in the temperature–magnetisation curves plotted as a function of the ratio of the oxygen removed by reduction to the total oxygen present in the mixture. The points representing the true points of magnetic transformation were also plotted, the anomalies being due to decomposition of the proto-oxide into iron and magnetic oxide, and to the reverse reaction. In the system iron sesquioxide–magnetic oxide, reversible transformations were observed at 570° and 650°, corresponding with Fe_3O_4 and a saturated solid solution of Fe_3O_4 in Fe_2O_3, respectively. The systems Fe_3O_4–FeO and FeO–Fe showed transformation points at 570° (due to Fe_3O_4) and 765°, respectively. The graphs also show the point of decomposition of FeO, the resulting transformation point of Fe_3O_4, and the recombination of iron and the magnetic oxide. J. Grant.

Properties [thermal decomposition] of diaspore and bauxite. Y. Yamaguchi and T. Takebe (Bull. Chem. Soc. Japan, 1926, **1**, 240—244).—Air was passed over the heated sample, and from the weight of water formed, its dissociation pressure p was calculated. In agreement with the Clausius–Clapeyron equation, $\log p$ was found to vary linearly with $1/T$, but with bauxite two curves were obtained, one covering the range 200—340° and the other the range 350—450°. The calculated heats of decomposition are: diaspore, $Al_2O_3,H_2O = Al_2O_3 + H_2O - 42{,}300$ g.-cal.; bauxite, $Al_2O_3,2H_2O = Al_2O_3,H_2O + H_2O - 10{,}100$ g.-cal.; $Al_2O_3,H_2O = Al_2O_3 + H_2O - 8100$ g.-cal. S. J. Gregg.

Nernst's heat theorem and the impossibility of absolute zero. A. Schidlof (J. Chim. phys., 1926, **23**, 814—820).—From statistical considerations, it appears highly probable that the absolute zero of temperature and infinitesimal absolute temperatures have no physical significance. If this is so, it can be shown that Nernst's heat theorem is a direct consequence, and that at 0° Abs. the coefficient of expansion and specific heat at constant volume of all substances would be zero. R. Cuthill.

Heats of adsorption of several gases and vapours on charcoal. F. G. Keyes and M. J. Marshall (J. Amer. Chem. Soc., 1927, **49**, 156—173).—The heats of adsorption, q, of oxygen, chlorine, carbon dioxide, ammonia, ether, chloropicrin, and water at 0° on ash-free charcoal are very large initially and fall rapidly to an apparently constant value as the concentration increases. In the case of water, there is a tendency for q to rise with increasing

concentration. The empirical relation $q=ac^b$ appears to hold fairly well, except for oxygen. The final energies of adsorption are proportional to the potential energies of the molecules from a state of contact to infinity, a magnitude which is calculated from the constants A and β in the Keyes equation of state; in the case of molecules of the non-permanent electrical moment type, the energy of adsorption is proportional to the electrical polarisation of the molecule as calculated from dielectric constant data. It is suggested that the adsorbed material is in a condition in which only the first layer is under the direct influence of the adsorbent. Each succeeding layer constitutes a fresh adsorbing surface, but the peculiarities of the first layer are progressively lost, until a layer is eventually reached in which the molecular state is practically a molecular "contact" arrangement. S. K. TWEEDY.

Partial molal heat capacity of the constituents and the specific heat of aqueous solutions of sodium and hydrogen chlorides. M. RANDALL and W. D. RAMAGE (J. Amer. Chem. Soc., 1927, 49, 93—100).—The partial molal heat capacities, c, of the two constituents and the specific heats of the above dilute solutions at 25° have been determined directly in a twin calorimeter (cf. Randall and Bisson, A., 1920, ii, 289). The following values were obtained (m is the molality; c_1 refers to the solvent and c_2 to the solute): sodium chloride, $c_1=17{\cdot}98-0{\cdot}1082m^{1{\cdot}5}$, and $c_2=-21+18m^{0{\cdot}5}$; hydrogen chloride, $c_1=17{\cdot}98-0{\cdot}0842m^{1{\cdot}5}$, and $c_2=-41+14m^{0{\cdot}5}$. S. K. TWEEDY.

Conductivity and velocity measurements in *iso*butyl alcohol. H. GOLDSCHMIDT [with V. K. LUND, A. THUESEN, E. MATHIESEN, and L. THOMAS] (Z. physikal. Chem., 1926, **124**, 23—40).—The electrical conductivities of solutions of hydrogen chloride, bromide, and iodide, of piperidine hydrochloride and picric acid in *iso*butyl alcohol, and of hydrogen chloride and picric acid in aqueous *iso*butyl alcohol have been determined. The conductivities of the hydrogen halides are less in the *iso*- than in the *n*-alcohol. On addition of water to the hydrochloric acid solutions, the conductivity is depressed, passing through a minimum and subsequently rising with increasing concentration of water. With picric acid, there is no initial fall on the addition of water. The rates of esterification of twelve different organic acids in *iso*butyl alcohol, with hydrogen chloride as catalyst, were measured. Water formed in these reactions reduces the rate in accordance with a formula previously advanced (A., 1925, ii, 976); this, however, does not hold for larger (added) quantities of water. An approximate direct proportionality obtains between the velocity coefficient and the concentration of hydrochloric acid. The ratio of the coefficients for phenylacetic acid in *iso*butyl alcohol with two different concentrations of picric acid as catalyst is roughly equal to the ratio of the conductivities of the picric acid. When picric acid is the catalyst, addition of aniline picrate lowers the rate of esterification, but the addition of aniline hydrochloride when hydrogen chloride is the catalyst has little influence. Hydrogen bromide and hydrogen iodide are more efficient catalysts than is the chloride, as in the case of *n*-butyl alcohol (cf. *ibid.*, 1926, 686). The results are generally similar to those observed with other alcohols. L. F. GILBERT.

Flow potentials. H. LACHS and J. KRONMAN (Rocz. Chem., 1926, **6**, 641—652).—Glass and quartz tubes acquire a negative charge if water is run through them. This charge is reduced by the addition of various electrolytes; at certain concentrations of aluminium or thorium ions, it may even be reversed in sign. The maximum potential attainable under similar conditions with the same apparatus cannot be reproduced with an accuracy greater than 14%. This is due to the flow potential not being constant; at the beginning of the experiment it rises to a maximum value, after which it falls. This variation is probably the result of physico-chemical changes at the boundary of the liquid, which lead to variations in the thickness of the layer of liquid in contact with the tube. Thus all results obtained for the flow potentials of such systems must be considered to be merely qualitative. R. TRUSZKOWSKI.

Behaviour of the quinhydrone electrode in solutions of neutral copper sulphate. J. B. O'SULLIVAN (Trans. Faraday Soc., 1927, **23**, 52—56).—An attempt has been made to determine the cause of the gradual change in potential of the quinhydrone electrode in a solution of neutral copper sulphate (cf. A., 1925, ii, 822). Experiment has shown that the effect is not due to autoxidation of quinol nor to the formation of complexes between copper ions and the organic matter. A precipitate containing copper is, however, gradually formed from a mixture of copper sulphate and quinol or quinhydrone in solution, the amount of copper increasing with the reducing power of the mixture. It seems probable, therefore, that the potential change and gradual production of a precipitate are due to the formation and slow hydrolysis of cuprous sulphate. M. S. BURR.

Diffusion oxygen electrode. S. VON NARAY-SZABÓ (Z. Elektrochem., 1927, **33**, 15—20).—Diffusion oxygen electrodes (cf. diffusion hydrogen electrodes, Schmid, A., 1924, ii, 324) of various types have been prepared and their behaviour has been examined at the ordinary temperature. By passing oxygen under a few mm. excess pressure into a porous carbon tube closed at the other end and dipping into an aqueous electrolyte solution, an oxygen electrode was obtained, the potential (ε_h) of which eventually reached the following approximately constant values: +0·83 volt in 2N-sulphuric acid, +0·38 in 27% ammonium chloride solution, +0·20 in 15% sodium hydroxide solution. The electrodes were easily polarised even by small current densities, but recovered completely afterwards. Oxygen electrodes in which Pasteur–Chamberland filter candles coated externally with a very thin film of sputtered platinum were used as diffusion tubes gave more positive equilibrium potentials than the above, but were much more readily polarised. The best results were obtained by using a carbon tube coated with a sputtered platinum film (1·7 μ thick); its potentials in the above-mentioned solutions were, respectively, +0·96,

0·43, 0·22 volt. With a current density of 0·4 amp./dm.^{2} these values became +0·22, +0·01, −0·09; and with 2 amp./dm.^{2} −0·11, −0·36, −0·38 volt. Up to 4—5 amp. could be obtained from the cells of the type: oxygen (platinised carbon)| electrolyte|zinc. Diffusion oxygen electrodes prepared from carbon rods made by the firm Le Carbone could also be used at high current densities, but did not behave as well as the above platinised carbon tubes. The mechanism of the behaviour of oxygen electrodes is discussed. When carbon is the intermediary, a surface compound of the type C_xO, where x is probably about 3, is regarded as the electromotively active substance. At platinised carbon, however, this oxide is assumed to react rapidly with platinum, yielding the hypothetical platinum "Primaroxyd," which is regarded as the electromotively active substance at oxygen–platinum electrodes. It is concluded that stable diffusion oxygen electrodes can be prepared, giving high power yield per unit area, which are undamaged by short-circuiting.

H. J. T. Ellingham.

Electrode equilibrium in the Weston standard cell. W. C. Vosburgh (J. Amer. Chem. Soc., 1927, 49, 78—92).—The high initial *E.M.F.* of Weston cells, the subsequent lack of constancy, hysteresis (cf. Vosburgh and Eppley, A., 1924, ii, 149), and the abnormal values obtained in rotation experiments (Hulett, Physical Rev., 1907, 25, 16), are attributed to the presence of the mercuric ion in the cathode system at a concentration in excess of that required for equilibrium. Cells prepared with mercurous sulphate free from mercuric salt can be duplicated with respect to their *E.M.F.* after a month or so. High initial values resulted when basic mercuric sulphate was added. The presence of 0·02*M*-sulphuric acid increases the solubility of the basic sulphate and prevents the high initial values. The cathode of an acid cell is in stable equilibrium; such cells are more trustworthy than neutral cells, in which the *E.M.F.* tends to decrease indefinitely. The continual decrease observed in some (neutral) cells (Smith, Trans. Roy. Soc., 1908, 207, 407) is possibly due to mercurous sulphate, prepared in acid solution, tending to change slowly into a more stable state (*e.g.*, solid solution) in presence of neutral saturated cadmium sulphate solution. The maintenance of a low hydrogen-ion concentration is essential for the change, which, however, is stopped by 0·01*M*-acid. Hysteresis is caused by a change in the equilibrium between mercury, mercurous, and mercuric ions with temperature, which leaves an excess of mercuric ion in the cell after a decrease in temperature. The presence of sulphuric acid makes the two electrode systems univariant (pressure and temperature constant), but they become practically invariant if the acid concentration is kept low enough; 0·01 mol./litre is recommended (cf. A., 1925, ii, 1164).

S. K. Tweedy.

Mechanism of oxidation–reduction potential. M. Dixon (Proc. Roy. Soc., 1927, B, 101, 57—70; cf. Wieland, A., 1913, i, 1304).—If it is assumed that the hydrogen atoms on the surface of platinum-black immersed in a solution of, say, quinol, are in equilibrium, not only with hydrogen molecules and hydrogen ions, but also with the quinol and quinone in the solution, the ordinary equation for oxidation–reduction potential follows at once. This theory, which postulates the direct transfer of hydrogen atoms as such from the solution to the electrode, necessarily leads to the same result as the thermodynamically equivalent theory of Clark (U.S. Pub. Health Rep., 1923, No. 826; 1925, No. 1017), according to which the doubly-charged anions produced by the ionisation of the quinol first give up to the electrode their pairs of electrons, thus rendering it more negative, so that it then withdraws hydrogen ions from the solution. It is not yet possible to say which theory is correct. There will always be a slight diffusion of hydrogen from the electrode into the solution, but usually this effect will be small. With the sulphydryl compounds examined by Dixon and Quastel (J.C.S., 1923, 123, 2943), however, the reduction process is irreversible, so that considerable diffusion must occur, or the hydrogen pressure at the electrode would increase indefinitely. These authors' results can, in fact, be accounted for quantitatively on the assumption that the irreversible transfer of hydrogen to the electrode is compensated for by diffusion. In such cases as this, the observed reduction potential will not, in general, be a measure of the real reducing power of the solution, and will be the more negative the slower the diffusion from the electrode, *i.e.*, the higher the overvoltage of the electrode. This is borne out by experiment.

R. Cuthill.

Normal oxidation–reduction potential of mercury. S. R. Carter and R. Robinson (J.C.S., 1927, 267—272).—The oxidation–reduction potentials of solutions containing varying proportions of mercuric and mercurous perchlorates have been measured at 18°. Correction has been made for hydrolysis of the salts, and also for the degree of ionisation on the assumption that it is the same as that of barium perchlorate of the same concentration. The normal potential deduced for $2Hg^{\cdot\cdot} \longrightarrow Hg_2^{\cdot\cdot}$ is then found to be 1·1902 volts, with an average error of ±0·0008 volt, referred to the calomel electrode as 0·560 volt, or 0·913 volt referred to hydrogen. The effect of varying concentration of perchloric acid on the potential has been determined, and is satisfactorily explained as due to decrease in the degree of ionisation of the perchlorates, and not to complex ion formation.

M. S. Burr.

Reaction between bromine and chloride ion in hydrochloric acid. Bromine monochloride. G. S. Forbes and R. M. Fuoss (J. Amer. Chem. Soc., 1927, 49, 142—156; cf. A., 1926, 128).—The graph representing the oxidation potential of a hydrochloric acid solution of chlorine containing a bromide as a function of the bromide concentration reveals two steeply-descending linear portions, the "bromine monochloride point" and the "bromine point." These two points are investigated (at 25°) with the aid of cells of the type $Pt(H_2)|HCl|HCl|HCl+Cl_2+BrCl+Br_2+Br'|PtIr$. The molal potential of bromine monochloride in 6*N*-hydrochloric acid is 1·1548+0·0005 volts referred to a hydrogen electrode in the same acid; in 4*N*-acid, the value is 1·221

0·001 volts. Tho dissociation constant of bromine monochloride is $3·2 \pm 0·2 \times 10^{-4}$ in either 6*N*- or 4*N*-acid, the main reaction being assumed to be $Br_2 + Cl_2 \rightleftharpoons 2BrCl$. The constant $K = [Br']^2[Cl_2]/[Br_2][Cl']^2$ is $3·0 \times 10^{-12}$ in 6*N*-acid and $5·6 \times 10^{-12}$ in 4*N*-acid; the ratio of these values of K may be calculated from the activity coefficients of hydrobromic and hydrochloric acids. The amount of bromine which reacts in hydrochloric acid to give bromide ion and bromine monochloride appears to increase as the bromine concentration diminishes. A general mathematical analysis of electrometric titration curves is given. S. K. TWEEDY.

Decomposition potentials and metal overvoltages in liquid ammonia and in water. A. A. GROENING [with H. P. CADY] (J. Physical Chem., 1926, 30, 1597—1615).—"Dynamic" decomposition voltages and metal overvoltages have been determined by the direct method for many salts in liquid ammonia and in water. Rapid rotation of the electrodes was employed. The straight portions of the current–voltage curves were extrapolated to the voltage axis to give the "dynamic" decomposition voltages. Similarly, the current–cathode overvoltage curves gave the metal overvoltage at zero current density. Measurements were made for solutions of silver, nickel, cadmium, mercuric, lead, zinc, copper, and ferric nitrates in ammonia and in water, of cadmium and zinc iodides and silver nitrite in ammonia and in water, of silver and mercuric iodides and mercuric chloride in ammonia, as well as of ammonium nitrate, chloride, bromide, and iodide in the same solvent. The dynamic decomposition voltages of nitrates and chlorides are lower in ammonia than in water, but the metal overvoltages are generally higher. Traces of water in liquid ammonia and traces of ammonia in water have marked effects on the decomposition voltages and the overvoltages of copper nitrate. Ammonium salts have the same dynamic decomposition voltage of 2·1 volts in dry liquid ammonia. The bromide and the nitrate show several breaks in the current-voltage curve. Temperature has little effect on the dynamic decomposition voltage in liquid ammonia. L. S. THEOBALD.

Electromotive behaviour of aluminium. A. DADIEU (Monatsh., 1927, 47, 497—510).—The potentials of aluminium and its amalgam in a molten mixture of aluminium and potassium bromides and in a solution of aluminium bromide in ethyl bromide have been derived from the *E.M.F.* of cells fitted with a standard electrode and from the decomposition potentials, using both platinum and mercury cathodes. The values obtained in the molten solution are −0·372 volt ±0·0040 for aluminium, and −0·370 volt ±0·0027 for the amalgam, the corresponding values obtained in solutions in ethyl bromide being −0·372 ±0·0037 and −0·368 ±0·0056 volt, respectively. Thus in each case the values obtained for aluminium and for its amalgam are the same. The metal in these solutions thus shows normal electromotive behaviour, and there is no evidence of the activation by mercury found by Smits (cf. Smits and Gerding, A., 1925, ii, 794). The author considers that the abnormal reactions observed in aqueous solutions are due to interaction of the metal and the solvent, and considers that the oxide film theory of the passivity of aluminium (cf. Günther-Schulze, A., 1921, ii, 535) best explains the facts. J. W. BAKER.

Effect of neutral salts on the potentials of glycine solutions as compared with the hydrogen electrode. S. KAWAI (J. Biochem. Japan, 1926, 6, 101—115).—Various cations have the effect of diminishing the p_H and thus increasing the acid dissociation constant of glycine and decreasing the basic dissociation constant. This effect of the neutral salts on an ampholyte substance is therefore essentially the same as was found for very dilute acids or alkalis. CHEMICAL ABSTRACTS.

Electrostatic capacity of aluminium and tantalum anode films. N. A. DE BRUYNE and R. W. W. SANDERSON (Trans. Faraday Soc., 1927, 23, 42—51).—By a bridge method, the capacity of an aluminium or tantalum rectifier has been determined for different audio-frequencies. Assuming that an electrolytic condenser is the equivalent of a network of simple and calculable form, it may be shown that the values of the constituent parts are not independent of frequency. No simple network can be found, however, which is an exact equivalent of the condenser, so that no exact physical significance can be attached to any values of capacity which may be obtained. The reciprocals of the capacity at successive intervals of time after the application of different formation voltages, for the frequencies 1945 and 1170 cycles per second, have been plotted against time. The curves are only approximately logarithmic. The results, however, are in agreement with the law that film thickness is proportional to formation voltage. M. S. BURR.

Anodic overvoltage measurements with the cathode-ray oscillograph. E. NEWBERY (Proc. Roy. Soc., 1927, A, 114, 103—110; cf. A., 1925, ii, 405).—By means of a rotating commutator and a cathode-ray oscillograph, measurements have been made of the overvoltage of the following metallic anodes in *N*-sulphuric acid solution: platinum, gold, lead (unattackable electrodes); nickel, iron, chromium (electrodes showing passivity); antimony, bismuth, tantalum (electrodes showing valve action). The apparatus was identical with that previously described (*loc. cit.*). The phenomena of overvoltage and transfer resistance shown by unattackable electrodes and by passive electrodes in the passive state are similar in every way to those observed during cathodic treatment. It is very probable that a lead anode in dilute sulphuric acid must be classed as a passive metal, and that, as with nickel and iron, the cause of passivity is the formation of an insoluble, electrically conducting coating of an overvoltage compound which may, or may not, form a solid solution in the electrode surface. The fact that lead gives a visible coating of appreciable thickness, as compared with the invisible coating on iron and nickel, is due to the porosity of the lead dioxide, which permits deeper action on the electrode surface. Chromium is to be regarded as a metal which is easily passivated with respect to the formation of tervalent ions, but which cannot be passivated with respect

to the formation of sexavalent ions. Valve action is due to the formation of an insoluble, electrically insulating coating of oxide or other compound, which forms the dielectric of a condenser made up of the electrode as one plate and the electrolyte as the other. From the data available from the curves, the capacity of such a condenser is roughly calculated as being of the order of a microfarad per sq. cm.; the thickness of the film of oxide, in the case of antimony, is calculated as being of the order of 4×10^{-5} mm., and in the case of tantalum, of the order of 10^{-6} mm. It is suggested tentatively that the action of an electrolytic rectifier may be due partly to condenser action, and partly to the oxide film acting as a semi-permeable membrane, permeable only to hydrogen ions.

L. L. Bircumshaw.

Electrolysis of water. J. E. Verschaffelt (Natuurwetensch. Tijdschr., 1926, 8, 121—130).—A theoretical discussion of the mechanism of electrolysis of water, and of solutions of salts, strong acids, and strong bases. The ions produced by dissociation of the solutes play only a passive part, raising the conductivity of the liquid, but not being liberated at the electrodes; hydrogen is liberated at the cathode directly from the water, and oxygen at the anode by dissociation of the hydroxyl ions of the water. The term electrolysis should be reserved for cases of actual chemical decomposition; the residual current, for example, is due only to simple transport of electricity by the ions of the electrodes or by hydrogen ions occluded by them. S. I. Levy.

Magnetic chemical effect. A. N. Schukarev (J. Russ. Phys. Chem. Soc., 1926, 57, 426—427).—The author, in abandoning work on this subject (cf. A., 1914, ii, 618; 1916, ii, 172), describes his final experiments. When a chloride is electrolysed in a strong magnetic field, dissolved in 10% potassium chloride solution containing a little potassium iodide and starch solution, a coloured ring is formed, which is at first symmetrically disposed about a central electrode. In some cases (*e.g.*, barium chloride, potassium chloride solution), the ring moves in the direction of the positive field; in others (calcium chloride, potassium chloride solution), it moves in the opposite direction. Photographs have been taken and are offered to anyone investigating this problem.

E. Rothstein.

Velocity of chemical reactions. J. J. Boguski (Rocz. Chem., 1926, 6, 291—320).—A reprint of an earlier paper (Ber., 1876, 9, 1646).

R. Truszkowski.

Supposed law of flame speeds. W. Payman and R. V. Wheeler (Nature, 1927, 119, 238).—Importance is not attached to the mixtures mentioned by White (this vol., 115) from the point of view of flame speeds, since they exhibit the peculiar phenomena of the "cool flame." A. A. Eldridge.

Movement of flames in closed vessels. Correlation with development of pressure. O. C. de C. Ellis and R. V. Wheeler (J.C.S., 1927, 153—158).—The direct synchronisation of the rate of development of pressure and the rate of spread of flame in an explosive mixture is effected by simultaneous photographic registration on a rapidly-revolving drum. The explosive mixtures were carbon monoxide and air saturated with water vapour at 19°. In spherical vessels, the moment of maximum pressure coincides with the arrival of the flame front at the boundary of the vessel. With a cubical vessel, the pressure develops after the flame front has touched the wall of the cube, but the point of maximum pressure is antecedent to the moment of complete inflammation.

W. Thomas.

"Uniform movement" of flame in mixtures of hydrogen and air. E. H. M. Georgeson and F. J. Hartwell (J.C.S., 1927, 265—267).—The propagation of flame from the open end of a tube towards the closed end in mixtures of hydrogen and air over a considerable portion of the range of inflammability has been analysed by a photographic method, using a quartz explosion tube and a quartz lens. Photographs representing propagation over a distance of 80 cm. from ignition show after a gradual retardation a movement which, although marked by small undulations, is sensibly uniform; this is recorded as the speed of "uniform movement." W. Thomas.

Combustion of carbon monoxide. C. F. R. Harrison and J. P. Baxter (Phil. Mag., 1927, [vii], 3, 31—50).—A method for the investigation of flame velocities at constant volume in a sphere is described and is extended to obtain an insight into the chemical reactions involved and into the variations of temperature at any point in an explosion chamber. The method has been applied to the investigation of the explosion of carbon monoxide and oxygen at an initial pressure of 105 cm. Carbon monoxide may be oxidised with air either in the dry state or in the presence of water vapour. In the second case, the ignition is easier and the flame velocity much higher. In all ordinary cases, both normal oxidation and oxidation through the water-gas reaction occur simultaneously. When the nitrogen diluent is replaced by oxygen or carbon monoxide, the velocity of combustion and of flame propagation is accelerated. Carbon monoxide has a much greater accelerating effect than has oxygen. The presence of small traces only of hydrogen in the mixture produces effects in no way proportional to the amount of hydrogen present. The hydrogen appears to be the chief intermediary for the propagation of the flame.

A. E. Mitchell.

Propagation of flame in mixtures of methane and air. V. Movement of the medium in which the flame travels. W. R. Chapman and R. V. Wheeler (J.C.S., 1927, 38—46).—It is assumed that in the propagation of flame in a tube there is a movement of the unburnt mixture ahead of the flame (cf. B., 1926, 970). When a tube open at both ends was restricted at the end at which the mixture was ignited, the speed of the flame was increased. If, in addition, restrictions were introduced in the path of the flame, the resistance offered thereby to the movement of the medium caused a retardation of the flame; greatly enhanced speeds of flame were obtained after passing the restriction. The effect of restricting the far end of the tube decreases considerably the speed of the flame. Closing the ignition end of the tube had no influence, but closing the far end of the

tube resulted in a very slow speed of the flame, which was not greatly affected by restrictions, except locally. Increased speed of the flame in wide tubes is assumed to be due to an increased facility for the movement of the mixture. A simple relationship has been found connecting the diameter of the tube and the speed of uniform movement of the flame along it. W. THOMAS.

Inflammability of hydrogen. III. Influence of ethyl selenide and of hydrogen selenide on the limits of inflammability of hydrogen–air mixtures. Y. TANAKA and Y. NAGAI (Proc. Imp. Acad. Tokyo, 1926, 2, 494—497).—The limits of inflammability of hydrogen–air mixtures containing (*a*) 0·0—3·0 mol.-% of ethyl selenide and (*b*) 0·0—6·0 mol.-% of hydrogen selenide have been examined by a simple spark-ignition method. In each series, the upper limit of inflammability is lowered and the lower limit raised, and the results are thought to indicate that the temperature of activation of the two diluents is 1750°. R. W. LUNT.

Velocity of chemical reaction in the silent electric discharge. G. A. ELLIOTT, S. S. JOSHI, and R. W. LUNT (Trans. Faraday Soc., Jan., 1927, advance proof).—An hypothesis is advanced that the velocity of a chemical reaction produced by electric discharge through a gas is connected with the number of collisions between ions and gas molecules in which the energy of the ions is not less than a definite value, termed the critical activation energy. With certain assumptions, expressions are derived relating the velocity of the reaction and the critical activation potential to the gas pressure, the mean free paths of the ions producing activation, and the electrical factors determining the discharge. A. S. CORBET.

Rate of unimolecular reactions. (SIR) J. J. THOMSON (Phil. Mag., 1927, [vii], **3**, 241—257).—Hirst and Rideal (A., 1926, 32) have established the result that the rate of the unimolecular reaction $2N_2O_5=2N_2O_4+O_2$ is independent of the pressure when that is above about 0·27 mm. The rate increases as the pressure is diminished below this value. Their analysis of the reaction velocity, taking into consideration both collisions and radiation, gives results of the same form as, but of different magnitudes from, their observed values. An alternative method by which the decomposition may be effected is discussed. It is suggested that even in the absence of collisions and radiation the energy content of a molecule does not remain constant. It is shown that if the forces inside a molecule are intermittent instead of being perfectly continuous, then even if in the initial stages the energy contents of a large number of molecules are the same, they will change so that the energy is distributed among them according to Maxwell's law of distribution. The principle of the conservation of energy does not hold for a single molecule, but holds on the average for a large number, and since the distribution of energy is represented by Maxwell's law, the theory is similar to the classical except for the numerical values, as the rate of reaction is not fixed by the number of molecules which at any time possess enough energy to be active, but is measured by the number which receive this energy in unit time. If N be the number of molecules having, in a steady state, a particular amount of energy, the number passing out of that state in time δt is $N\delta t/T$, where T is a time constant and N/T will measure the rate of reaction. If the energy is conveyed to the molecules by collision, T is the average interval between collisions, and if the energy is conveyed by radiation, T becomes the average interval between collisions of a molecule with light quanta. If, however, the surging of the energy is due to the intermittence of the force, T will depend on the average interval between two impacts and may compare with the interval between collisions either between molecules or between molecules and light quanta. The smaller value of T would thus make the rate due to this cause much more rapid than that due to radiation, or to collisions at low pressures. Numerical results are in fair agreement with the observations of Hirst and Rideal. A. E. MITCHELL.

Quasi-unimolecular reactions. Decomposition of ethyl ether in the gaseous state. C. N. HINSHELWOOD (Proc. Roy. Soc., 1927, **A**, **114**, 84—97).—The author's previous work on chemical kinetics in gaseous systems is briefly reviewed. If the idea of the energy of activation of a molecule is extended to energy of all kinds in every possible distribution in a large number of degrees of freedom, the only condition being that the total energy should exceed E (the " energy of activation "), then the last term in the equation for a homogeneous bimolecular reaction, viz., number of molecules reacting=number entering into collision $\times e^{-E/RT}$, should be replaced by $e^{-E/RT}(E/RT)^{\frac{1}{2}n-1}/\frac{1}{2}n-1$. The discrepancies between the observed and calculated rates of decomposition in certain cases (*e.g.*, the decomposition of acetone) now tend to disappear. The decomposition of ethyl ether ($Et_2O=CO+2CH_4+0{\cdot}5C_2H_4$) was investigated by measuring the increase of pressure developed, and it is shown that this is a true unimolecular reaction above a pressure of 200 mm., below which the velocity coefficient falls. The reaction is predominantly homogeneous, and the addition of sufficient hydrogen completely prevents the decrease of the coefficient below 200 mm. From the temperature coefficient, the heat of activation is found to be 53,000 g.-cal., and values of k calculated from the formula $\log_e k=26{\cdot}47-(53{,}000/RT)$ agree with those determined experimentally. Calculations on the above basis for the condition of a pressure of 0·2 atm., where k begins to fall, shows that the participation of about eight degrees of freedom conforms with activation by Lindemann's mechanism. A table is given showing the relation between the complexity of a molecule and the type of mechanism by which it decomposes. Simple molecules usually decompose bimolecularly, more complex ones in a quasi-unimolecular way, as would be expected on theoretical grounds. L. L. BIRCUMSHAW.

Rate of racemisation of pinene. A first-order homogeneous gas reaction. D. F. SMITH (J. Amer. Chem. Soc., 1927, 49, 43—50).—The racemisation of *d*-pinene between 184° and 237° is a unimolecular reaction. The rate is practically the same in both the gas and liquid phases and in solution; in

the latter case, it is independent of the concentration and the solvent. Dushman's "activation" equation (A., 1921, ii, 315) is obeyed to the same order of agreement as in the case of nitrogen pentoxide (Tolman, *ibid.*, 248), from which it is concluded either that the life of activated molecules of the dissimilar substances nitrogen pentoxide and pinene is nearly the same, or that the rate of reaction is determined by the rate of activation. S. K. TWEEDY.

Velocity of decomposition of potassium persulphate in aqueous solution. A. KAILAN and L. OLBRICH (Monatsh., 1927, 47, 449—484).—The velocity of decomposition of potassium persulphate, either alone or with the addition of sulphuric acid as a catalyst at 25°, and both alone and with the addition of potassium sulphate, sulphuric, nitric, and phosphoric acids at 99·4°, has been studied in detail by the method of Green and Masson (J.C.S., 1910, 97, 2083). Measurements at both temperatures confirm the conclusion previously reached by Levi and Migliorini (A., 1907, ii, 81) and by Green and Masson (*loc. cit.*) that both in absence and presence of catalysts the decomposition approximates closely to a unimolecular reaction, and the value of the coefficient obtained agrees within the experimental error with that extrapolated from the measurements of the latter authors. For numerical data, the original must be consulted, but the main conclusions reached are as follows: with the same original concentration of potassium persulphate the value of the unimolecular coefficient increases with increasing concentration of added sulphuric acid much more slowly than direct proportionality would require, but for equal sulphuric acid concentrations it decreases with increasing concentration of the persulphate. The velocity of decomposition is considerably increased by the addition of strong acids and is the greater the stronger the acid, but this is not merely a hydrogen-ion effect, since nitric acid has a greater accelerating influence than equivalent quantities of sulphuric or phosphoric acid. Hence acid anions must also affect the reaction velocity, the nitrate ion having an accelerating influence. The non-increase in the unimolecular coefficient during the course of the reaction, in spite of the fact that it is increased by lowering the initial concentration of persulphate, can be explained only on the assumption that the potassium ion exerts a retarding influence on the decomposition. The fact that the decomposition is not autocatalytic, in spite of the production of potassium hydrogen sulphate during the course of the reaction, was explained by Green and Masson on the assumption that no hydrogen ions are produced, ionisation being limited to the formation of potassium and hydrogen sulphate ions, but this hypothesis is shown to be untenable, and the observations are readily explained by the hypothesis that the sulphate ion exerts an intrinsic retarding influence approximately equal to the accelerating influence of the hydrogen ion. The retarding influence of alkali sulphates and the autocatalysis occurring in cases where the sulphate ion is removed either as an insoluble or a practically non-ionised sulphate, observed by Green and Masson, are thus readily explained. Empirical intrapolation formulæ in which the unimolecular coefficient at 25° and 99·4°, respectively, is expressed as a function of the potassium-ion concentration and the difference between the hydrogen- and sulphate-ion concentrations are deduced both for the assumption of partial and complete dissociation, agreement between the calculated and observed values being fairly good. A similar formula is applied with equal success to the observations of Green and Masson. The addition of toluene increases the velocity of decomposition of an aqueous solution of potassium persulphate, but this is not due to reaction between the toluene and the liberated oxygen, since a diminution in the partial pressure of the latter does not increase the velocity of decomposition. J. W. BAKER.

Interaction of potassium *m*-tolyloxide with aliphatic esters in aqueous-alcoholic solutions. E. L. SMITH (J.C.S., 1927, 170—178).—An equilibrium is established between potassium tolyloxide, water, cresol, and potassium hydroxide; the ester is hydrolysed by the last-named substance. Constants are calculated which are the product of an equilibrium constant and a velocity coefficient. The equilibrium constant in aqueous solution has been measured by a dynamic and by an electrometric method. The constants decrease appreciably as the water concentration increases. Certain esters react abnormally, giving rise to the corresponding *m*-tolyl ethers (cf. Gyngell, A., 1926, 1134). The value of the temperature coefficient has been determined. *Ethyl* m-*tolyloxyacetate* is an oil, b. p. 264° (slight decomp.). W. THOMAS.

Rate of hydrolysis of solutions of proteins in acids as measured by the formation of amino-nitrogen. D. M. GREENBERG and N. F. BURK (J. Amer. Chem. Soc., 1927, 49, 275—285).—The hydrolysis of gelatin and silk fibroin by sulphuric and hydrochloric acids (0·75—3·0*N*) has been studied at 96—98°, 130°, and 142°. The rate of hydrolysis, as measured by the increase in amino-nitrogen, conforms to the equation for a bimolecular reaction. The rate of hydrolysis of wheat gliadin (cf. Vickery, A., 1922, ii, 754) also conforms to this order of reaction, whilst that of casein (cf. Dunn, *ibid.*, 1925, i, 1477) conforms to the equation for a unimolecular reaction. The catalytic effect of acids on the hydrolysis of proteins is shown to be proportional to the thermodynamic activity of the hydrogen ion, and an equation connecting the rate of hydrolysis of gelatin with temperature is derived. F. G. WILLSON.

Kinetics of dissolution of aluminium in acids and alkalis. K. JABŁCZYNSKI and E. HERMANOWICZ (Rocz. Chem., 1926, 6, 466—482).—The velocity of dissolution of aluminium in 0·1*N*-hydrochloric acid or sodium hydroxide is independent of the rate of stirring, and increases by 126% and 137%, respectively, per 10° rise in temperature, showing that this is a purely chemical reaction. The velocity is proportional to the concentration of the acid, whence it follows that this is a unimolecular reaction. The metal may be rendered passive by immersion in oxidising solutions, the effect being greatest with hydrogen peroxide, less with potassium permanganate, and least with bromine water. It may then be activated by contact with a platinum wire, but more

vigorously by the addition of mercuric chloride, which so accelerates the rate of dissolution that the process becomes one of diffusion; in this case, the temperature coefficient is small and the velocity depends on the rate of stirring. The velocity of dissolution in 0·1*N*-sodium hydroxide is 18·5 times as great as that in acid. R. TRUSZKOWSKI.

Thickness of the passive surface layer, and the velocity of dissolution of aluminium. M. CENTNERSZWER (Rocz. Chem., 1926, 6, 383—395).—Metallic aluminium may be covered with a passive layer, in which active nuclei form continuously. The thickness of this layer is greater than unimolecular, attaining from 30 to 84 μ, according to the nature of the treatment applied for passivation. On activation, there is first an induction period, during which the passive layer dissolves with continuously increasing velocity, after which further solution proceeds at uniform velocity. The velocity of solution is virtually independent of stirring, and its temperature coefficient is from 1·7 to 2·4 per 10°. This velocity depends, not on the dissociation constant of the given acid, but on its individual character, *i.e.*, on the affinity of aluminium for its anions. The addition of chlorides to hydrochloric acid increases the velocity of dissolution by increasing the concentration of undissociated acid, whilst sulphates and nitrates, which augment dissociation, have the opposite effect. These facts indicate that the dissolution of aluminium in acids is determined by a reaction between the metal surface and undissociated anions [?]; it is not an ionic reaction. R. TRUSZKOWSKI.

Rate of formation of insoluble anhydrite. P. P. BUDNIKOV (Z. anorg. Chem., 1926, **159**, 87—95).—In the determination of the rate of formation of the insoluble modification of calcium sulphate with regard to time and temperature of heating, an electrical conductivity method was adopted. The amount of insoluble anhydrite formed depends on the temperature, the time, and the state of division of the gypsum. Excessive time of heating and a high temperature favour the formation of insoluble anhydrite, which lowers the quality of the plaster of Paris. M. CARLTON.

Influence of moisture on the reaction between nitric oxide and oxygen. E. BRINER (J. Chim. phys., 1926, **23**, 848—850).—A short discussion of recent work in which it is concluded that, although water may act as a catalyst, it is not essential to the reaction. R. W. LUNT.

Acid and salt effects in catalysed reactions. IV. Derivation of a general equation for the catalytic activity of acids. General catalytic catenary. H. M. DAWSON (J.C.S., 1927, 213—222).—The equation derived is $r=\frac{1}{2}(10^{4p_H}+10^{-4p_H})$, in which r is the velocity due to the positive and negative ions expressed in terms of the velocity for the corresponding *M.V.* mixture, and is the difference between the p_H values of the solution in question and of the *M.V.* mixture. The expression, which corresponds with a catenary curve, may be termed the general or reduced catalytic catenary. It appears to be capable of wide application and is independent of the nature of the catalysing acid and of its concentration, of the temperature, of the nature of the solvent, and of the nature of the catalysed reaction. It has been tested by reference to observations on the velocity of the acetone–iodine reaction and to Karlsson's data for the rate of hydrolysis of methyl and ethyl acetates by the addition of acetic acid and sodium acetate (A., 1922, ii, 40). W. THOMAS.

Period of induction in chemical reactions. Interaction of mercuric chloride and sodium hydrogen carbonate. P. NEOGI and S. NEOGI (J.C.S., 1927, 30—37).—The period of induction is inversely proportional to the concentrations of each reactant. It diminishes with rise of temperature. Light has no effect on the period. Glycerol, *n*-propyl alcohol, chlorides, oxalates, and citrates increase the period, whilst methyl, ethyl, and *iso*propyl alcohols, and tartrates diminish it. The period of induction is not influenced by dextrose, sucrose, mannitol, and dulcitol. A decrease in the period of induction is believed to be due to an increase in the ionisation of the mercuric chloride under certain conditions. Sodium chloride inhibits the reaction owing to the formation of double salts with mercuric chloride. W. THOMAS.

Velocity of autocatalytic decomposition of bromosuccinic acid in aqueous solutions. J. ZAWIDZKI and W. WYCZALKOWSKA (Rocz. Chem., 1926, 6, 415—465).—Various equations for the autocatalytic decomposition of bromosuccinic acid are derived. The addition of hydrobromic acid to the reaction mixture changes the reaction velocity equation from $dx/dt=k_0(a-x)/x$ to $k_0(a-x)/(b+x)$, where b is the concentration of hydrogen bromide and k_0 remains constant (0·0000768). The addition of equivalent quantities of sodium sulphate, which combines with the hydrogen ions produced in the reaction, changes the velocity equation to $k(a-x)/\sqrt{\rho x}$, where k is twice as great as k_0, and ρ is the degree of dissociation of the hydrogen sulphate ion. The same equation holds for the velocity of decomposition of aqueous acid bromosuccinates, substituting for ρ the degree of dissociation of bromosuccinic acid. The normal sodium and potassium salts are hydrolysed according to the equation $dx/dt=k(a-x)^{3/2}/\sqrt{x}$. The retarding influence of nitric acid is half as great as that of equivalent quantities of hydrochloric or hydrobromic acids, the velocity in this case being $k_0(a-x)/\{(b/2)+x\}$, where b is the concentration of nitric acid. The addition of potassium bromide changes the velocity of reaction to $k_0(a-x)/\{(b/2n)+x\}$, where $n>1$. Since, therefore, the velocity of reaction is retarded by both hydrogen and bromine ions, the original equation should be expressed as $k_0(a-x)/2x$, whence it follows that the real value of k is 0·000154. R. TRUSZKOWSKI.

Catalytic minimum point. M. BERGSTEIN and M. KILPATRICK, jun. (J. Physical Chem., 1926, **30**, 1616—1622).—The catalytic minimum point for the reaction between iodine and acetone lies at p_H 4·8, and the value is unaffected by change of temperature over the range examined, viz., 25—45°, and by the presence of neutral salts. The results do not support the unhydrated ion theory of catalysis (Rice, A., 1924, ii, 98). L. S. THEOBALD.

Formation of ammonia from its elements by the silent discharge in Siemens tubes. E. WARBURG and W. RUMP (Z. Physik, 1926, **40**, 557—573).—In contrast with ozone formation, the production of ammonia is mainly a surface effect, the yield per coulomb is much smaller, and reduction of pressure has less influence in reducing the yield. The differences are accounted for by the much greater energy needed to dissociate nitrogen, collisions of ions in the volume of the gas being less effective than catalytic action on the walls; in presence of a suitable catalyst, the formation of ammonia can take place at the ordinary temperature, whilst that of ozone cannot. The formation of hydrogen iodide from its elements resembles that of ozone, being catalysed by the collision of ions. E. B. LUDLAM.

Decomposition of ethyl alcohol at the surface of thoria. I. G. I. HOOVER and E. K. RIDEAL (J. Amer. Chem. Soc., 1927, **49**, 104—115).—The decomposition of ethyl alcohol into ethylene and into acetaldehyde in presence of thoria at about 300° was investigated. The activation energy is 30,000 g.-cal. for the ethylene reaction and 24,000 g.-cal. for the aldehyde reaction. The presence of water vapour or acetaldehyde diminishes the reaction velocity of the ethylene reaction to a greater extent than that of the aldehyde reaction, which indicates that the two reactions proceed on different active areas of different adsorptive capacities. Whereas these poisons are reversible, excess of chloroform vapour forms an irreversible poison; minute amounts diminish both reactions, and larger quantities cause displacement of the adsorbed ethylene on the catalyst surface, although a promoter effect on the ethylene reaction and a simultaneous poisoning of the aldehyde reaction are also apparent. At pressures of 6 and of 1 mm., the ratio of the extents of the ethylene and aldehyde reactions is 2 : 1, in comparison with 1·25 : 1 at atmospheric pressure. This is proved to be due to the removal of poisons from the catalyst surface; the relative amount of ethylene is greater at low pressures, in harmony with the fact that those patches of the catalyst surface active towards the ethylene reaction are the more easily poisoned. The temperature coefficients are less at low pressures, indicating that the reactions at atmospheric pressure are being mutually poisoned by the reaction products. Thoria catalysts are more active when supported; they then promote the ethylene reaction almost completely, in agreement with the view that the two reactions are promoted by different active areas.

S. K. TWEEDY.

Decomposition of ethyl alcohol at the surface of thoria. II. Adsorption on the thoria catalyst. G. I. HOOVER and E. K. RIDEAL (J. Amer. Chem. Soc., 1927, **49**, 116—123; cf. preceding abstract).—The adsorption isotherms for hydrogen, nitrogen, and ethylene at 0° and at 100°, and ethyl alcohol vapour at 52·3° and at 100°, on thoria were investigated for pressures up to 760 mm. Nitrogen and hydrogen are adsorbed to an extent proportional to the pressure; the surface does not even approach saturation (cf. Lowry and Morgan, A., 1925, ii, 1053). A saturation maximum for ethylene at 0° occurs at about 600 mm.; an irregularity in the low-pressure portion of the 0° and 100° isotherms is attributed to a specially active area. A similar irregularity occurs in the alcohol isotherms. Adsorption and capillary condensation or surface liquefaction occur with alcohol both at 52·3° and at 100°. About 1·3% of the specific catalyst surface is active. The latent heat of capillary condensation of alcohol is about 9900 g.-cal./mol. and that of surface adsorption 14,000 g.-cal./mol. S. K. TWEEDY.

Attempts to activate copper for catalytic hydrogenation by oxidation and reduction. R. N. PEASE and C. W. GRIFFIN (J. Amer. Chem. Soc., 1927, **49**, 25—28).—A copper catalyst of low porosity and high activity was prepared by low-temperature oxidation and reduction of well-sintered copper. The resulting catalyst was only temporarily active in the hydrogenation of ethylene. This deactivation was uninfluenced by the temperature of oxidation or reduction of the copper and by the temperature of evacuation of the catalyst bulb. Neither was it due to the fixation of surface crystals on the catalyst. Apparently an atomic reaction occurs on the metal surface as a result of catalytic action, whereby the atoms become momentarily labile and may subsequently become oriented to a crystal. S. K. TWEEDY.

Catalytic oxidation of ammonia and hydrogen cyanide. III. J. ZAWADZKI and I. LICHTENSTEIN (Rocz. Chem., 1926, **6**, 824—837).—The oxidation of ammonia to nitric oxide, using a platinum catalyst, commences at 250°; that of hydrogen cyanide at about 400°. In this reaction, if the rate of flow of the reaction mixture is small, a considerable quantity of free nitrogen is found among the products; at velocities of more than 60 litres per hr. for ammonia and 23 litres per hr. for hydrogen cyanide, part of these gases passes unchanged at a temperature of 600°. The concentration of substrate in the reaction mixtures does not appear greatly to influence the reaction, the course of oxidation depending more on duration of contact and temperature. The yield of nitric oxide at a given temperature at first increases to a maximum and then decreases with increasing rate of flow, the optimal value for the latter increasing with temperature. By selecting appropriate values for the above two factors, yields of up to 100% of nitric oxide may be obtained.

R. TRUSZKOWSKI.

Mechanism of the catalytic decomposition of esters by nickel. J. N. PEARCE and C. N. OTT (J. Physical Chem., 1927, **31**, 102—114; cf. A., 1924, ii, 843; Sabatier and Mailhe, *ibid.*, 1912, i, 156).—The products of the catalytic decomposition of methyl, ethyl, and propyl acetates, and of methyl propionate by finely-divided nickel, prepared by ignition of the nitrate at 400—450° and subsequent reduction by hydrogen at the lowest possible temperature, have been studied for various temperatures between 300° and 735°. The approximate temperatures at which the esters begin to decompose are: methyl acetate, 310°; ethyl acetate, 280°; propyl acetate, 330°, and methyl propionate, 360°. The proportions of carbon dioxide and methane in the decomposition

products increase with rise in temperature, whilst those of hydrogen and carbon monoxide decrease. Hydrocarbons higher than ethane are formed only in traces, and no free acid or other liquid decomposition products appear at any temperature. The addition of hydrogen, one of the products, to the vapour before passage over the catalyst produces no change in the nature of the decomposition products, but the activity of the catalyst is affected by some of the products resulting from the decomposition. The mechanism of decomposition is discussed.

L. S. THEOBALD.

Catalytic power of [animal] charcoal. V. PODROUZEK.—See B., 1927, 95.

Ammonia catalysts. A. T. LARSON and A. P. BROOKS.—See B., 1927, 72.

Pure iron and promoted iron catalysts for ammonia synthesis. J. A. ALMQUIST and E. D. CRITTENDEN.—See B., 1927, 72.

Electrolysis in the fused state of oxygenated compounds. Preparation of metals and borates. ANDRIEUX (Compt. rend., 1927, **184**, 91—92).—The electrolysis with high cathode current densities in an apparatus previously described (A., 1926, 248) of a molten mixture of a metallic oxide, boric anhydride, or borax, and a fluoride (to produce a stable and homogeneous mass), usually yields the metal of the oxide in the molten or the crystalline state, according as the metal is easily fusible (*e.g.*, lead, zinc, cadmium), or refractory (*e.g.*, tungsten, molybdenum). Most metals the heats of oxidation of which are less than that of sodium have been prepared. Borates of the alkaline earths are produced using low current densities at 1000—1200°, the fluoride in the mass being that of the metal concerned, or that of a metal more difficult to oxidise.

J. GRANT.

Structure of electro-deposited metals. F. FOERSTER and J. FISCHER.—See B., 1927, 78.

Actinic absorption of chlorine gas with respect to the hydrogen-chlorine reaction. W. TAYLOR (Trans. Faraday Soc., 1927, **23**, 31—37).—Using an actinometric arrangement similar to that of Bunsen and Roscoe, the rate of combination of hydrogen and chlorine, under the influence of a "white" beam from a "pointolite" lamp, which has passed through a light filter of gaseous chlorine of variable pressure, has been studied. The effect of the varying sensitivity due to the presence, in different proportions, of an anti-catalyst, probably oxygen, is eliminated by the use of a second source of white illumination "B," used as a standard of reference. Exposure was first made with "B," which, by means of a switch, was then exchanged for the illumination under examination, the latter being finally replaced by "B" again. The rate for "B" before and after was, in general, constant. Volume change, due to absorption of hydrogen chloride by water, when plotted against time, for any single pressure of chlorine in the filter, gives a straight line after the Draper expansion has taken place. The curve obtained by plotting reaction velocity against pressure of chlorine is not exponential, although somewhat similar in form. It indicates that, although the greater part of the activating power of the light is cut down by a relatively small thickness of chlorine, there is a "residual effect" which is only slightly reduced by a further increase in concentration of absorbing gas. The shape of the curve is not in accordance with the view that only a narrow range of frequencies is effective in promoting activation. The extinction coefficient of about 45 does not agree with that of 17·17 found by Bunsen and Roscoe. This may be due to the difference in the source of light employed.

M. S. BURR.

Residual effect in the actinic absorption of chlorine. W. TAYLOR and A. ELLIOTT (Trans. Faraday Soc., 1927, **23**, 38—41).—With the view of investigating the "residual effect" observed in the actinic absorption of chlorine (cf. preceding abstract), experiments have been carried out with increased concentration of chlorine in the filter obtained by the use of solutions of chlorine in carbon tetrachloride, and also by increasing the thickness of the absorbing layer to be traversed by the light. The curves thus obtained agree in showing the residual effect. It has also been found that certain types of radiation present in ordinary white light, although only feebly absorbed by chlorine, yet appear capable of bringing about an appreciable amount of activation.

M. S. BURR.

Photochemical decomposition of potassium persulphate. I. J. L. R. MORGAN and R. H. CRIST (J. Amer. Chem. Soc., 1927, **49**, 16—25).—Many organic and inorganic per-compounds were found to be photo-sensitive and the case of potassium persulphate was examined in detail. The reaction is $K_2S_2O_8+H_2O=2KHSO_4+0{\cdot}5O_2$, no intermediate equilibria being apparent; it is suitable for actinometric use, and the technique is described in detail. The reaction is of the first order when the solution is dilute or when the light intensity is high; it is of zero order when the solution is concentrated and the light intensity is low. The order for intermediate solutions is an accelerated unimolecular one. The reaction is irreversible, since the rate is uninfluenced by variation in the oxygen concentration, although it is increased in the presence of hydrogen or nitrogen. The effect of ageing of the lamp was also studied. Ultra-violet light decomposes solid potassium persulphate also.

S. K. TWEEDY.

Synthetic formaldehyde from carbon monoxide and hydrogen. Mechanism of the sensitised photochemical reaction. A. L. MARSHALL (J. Physical Chem., 1926, **30**, 1634—1640; cf. A., 1926, 919).—The dependence of the rate of formation of formaldehyde on the concentrations of hydrogen and carbon monoxide has been studied in the photochemical reaction sensitised by mercury. An equation of the form $d[CH_2O]/dt=Kp_H^{\frac{1}{2}}\cdot p_{CO}(1/p_{total})^{\frac{1}{2}}$ has been deduced theoretically, but the results actually obtained indicate that the equation $d[CH_2O]/dt=Kp_{H_2}^{\frac{1}{2}}\cdot p_{CO}$ determines the velocity. Atomic hydrogen is thus one of the constituents taking part in the reaction, of which formaldehyde is the chief product.

L. S. THEOBALD.

Production of ions in chemical reactions and the mechanism of induced, photochemical, and catalytic reactions. N. R. DHAR (Z. anorg. Chem.,

1926, **159**, 103—120; cf. A., 1924, ii, 746; 1925, ii, 214).—There are many indications which favour the view that ionisation takes place in chemical reactions, more especially in exothermic reactions. Atoms and molecules become activated by the adsorption of ions or electrons or by collision with other stimulated atoms or molecules under suitable conditions. The explanation of induced oxidation, decomposition, etc. depends on the formation of electrons and ions in the primary exothermic reaction and the consequent activation of inactive molecules by adsorption of ions which lead to the secondary reaction. The abnormally large yield obtained in some photochemical reactions is probably due to formation of ions in the chemical transformation. In presence of water vapour or a substance with a high dielectric constant, the mobility of the ions is reduced, and the tendency to formation of complexes consisting of ion, water vapour, and reactant is greatly increased. Consequently in presence of such substances the reacting substance has more opportunity of adsorbing ions and an increased reactivity results.

Adsorption of gases by solid substances is considered as an exothermic chemical reaction in which ions and electrons are produced which lead to the activation of the reacting substances in the presence of the catalyst. M. CARLTON.

Photochemistry of complex compounds. II. R. SCHWARZ and K. TEDE (Ber., 1927, **60**, [*B*], 63—69; cf. A., 1925, ii, 576).—Measurements of the photochemical decomposition of cobalt-tetrammine salts in aqueous solution according to the scheme, $[Co(NH_3)_4X_2]Y+3H_2O=Co(OH)_3+2NH_4X+NH_4Y+NH_3$, by determination of the electrical conductivity show that the stability of the complex nucleus diminishes with increasing electroaffinity of the co-ordinatively united anion, $CO_3'' > C_2O_4'' > NO_2' > Br' > Cl' > SO_4''$. The inverse position of the C_2O_4'' and NO_2' ions is doubtless due to stereochemical factors and probable ring formation in the case of the oxalato-residue. In the cobaltpentammine series, the sequence is $CO_3'' > Cl' > C_2O_4'' > SO_3'' > NO_2' > NO_3' = SO_4''$; the exceptional position of the chlorine ion is attributable to its non-complex character. The observed exceptions indicate that the electroaffinity of the nuclear united acid radical is not the only factor governing the stability of the complex. The presence of water molecules in the complex increases its tendency towards hydrolysis. The complex compounds of chromium are generally less stable than those of cobalt and more susceptible to photochemical change. Examination of the photochemical decomposition of the stereoisomeric salts, $[Co(NH_3)_4(SO_3)_2]NH_4$, shows that the dark brown is less stable than the reddish-brown variety, and hence has the *cis*-configuration. Attempts to apply a similar method to the compounds $[Co(NO_2)_3(OH)_3]X_3$ were unsuccessful, since they are too readily hydrolysed in absence of light. H. WREN.

Photochemistry of complex compounds. III. The hexacyano-complexes of tervalent iron, cobalt, chromium, and manganese. R. SCHWARZ and K. TEDE (Ber., 1927, **60**, [*B*], 69—72).—Potassium ferricyanide is little sensitive to light, decomposition taking place only to the extent of a small percentage after intense illumination. The change consists in hydrolysis to aquo-complex salts and ultimately ferric hydroxide, and in the oxidation of hydrocyanic acid to cyanogen with production of potassium ferrocyanide. With potassium cobalticyanide, the change is $K_3[Co(CN)_6]+H_2O=K_3[Co(CN)_5OH]+HCN$ and $K_3[Co(CN)_6]+H_2O=KCN+K_2[Co(CN_5)H_2O]$. The corresponding chromium compound behaves similarly to the cobalticyanide, whereas the manganese compound is rapidly decomposed in the absence of light into manganic hydroxide, hydrocyanic acid, and potassium cyanide. H. WREN.

Decomposition of ammonia by optically excited mercury atoms. R. G. DICKINSON and A. C. G. MITCHELL (Proc. Nat. Acad. Sci., 1926, **12**, 692—696; cf. Taylor and Bates, following abstract).—The photochemical decomposition of ammonia at low pressures is sensitised by mercury vapour activated by absorption of the line 2537 Å. The sensitised decomposition is accompanied by a diffuse band fluorescence in the green and ultra-violet. The mol. fraction of hydrogen in the non-condensible reaction products is about 0·70. This is to be regarded as a minimum value, since some hydrogen is possibly adsorbed on the walls of the reaction vessel. No evidence of products other than nitrogen and hydrogen was obtained. In the case of the direct photochemical decomposition by light of shorter wave-length, the mol. fraction of hydrogen is about 0·87. Since a mol. fraction 0·75 corresponds with the decomposition, $2NH_3=3H_2+N_2$, it is suggested that probably some condensible product containing more nitrogen than does ammonia, *e.g.*, hydrazine, may have been formed. J. S. CARTER.

Photosensitised decompositions by excited mercury atoms. H. S. TAYLOR and J. R. BATES (Proc. Nat. Acad. Sci., 1926, **12**, 714—717).—Experiments on the photosensitised decomposition of water, ammonia, ethylene, methyl and ethyl alcohols, hexane, benzene, acetone, formic acid, and ethylamine by light of wave-length 2536·7 Å. in presence of mercury vapour demonstrate the extraordinary efficiency of the excited mercury atom in the disruption of the linkings C·H, N·H, and O·H. The decompositions obtained are often many hundredfold those obtained by exposure in quartz apparatus to the whole ultra-violet spectrum of the cooled mercury arc. Since the energy of the excited mercury atom is 112 kg.-cal. per g.-atom it follows that the energies of the linkings C·H, N·H, and O·H are all less than 112 kg.-cal., a conclusion in agreement with available thermal data. Oxygen in addition to hydrogen was identified in the products of decomposition of water (cf. Senftleben and Rehren, A., 1926, 768). Acetaldehyde and its decomposition products, carbon monoxide and methane, in addition to hydrogen, were obtained from ethyl alcohol. With benzene, diphenyl was detected, but the gaseous residue contained hydrocarbons in addition to hydrogen. Hexane yielded nearly pure hydrogen. From ethylene, hydrogen, acetylene, and some saturated hydrocarbons

were identified. With ammonia, the percentage of hydrogen in the reaction products was greatly in excess of that required by the simple stoicheiometric decomposition to the elements. It is hence concluded that the decomposition of ammonia occurs in stages, in the first of which hydrogen is eliminated from ammonia molecules, *e.g.*, $2NH_3 \longrightarrow N_2H_4+H_2$. The residual gas from ethylamine is, however, practically free from nitrogen. J. S. CARTER.

Chemical actions of radiations. P. VILLARD (Compt. rend., 1927, **184**, 131—134).—A general theory of the phenomenon of the destruction by ordinary light of a latent image produced by *X*-rays is proposed. The *X*-rays produce a disturbance in the equilibrium of the lower optical levels of the atoms of silver and bromine. This constitutes a latent image. Ordinary light will now set up electronic vibration, which restores the equilibrium and the sensitiveness of the plate to *X*-rays, but destroys the latent image. The suitability of a particular radiation depends on its quantum. The phenomenon first observed in certain cases by Becquerel of the continuation by red rays of the photographic action started by violet rays is equivalent to photographic development, and depends on the presence of a soluble silver salt and of a reducing agent. Thus, tartaric acid will not develop an exposed plate containing a soluble silver salt other than with the help of outside energy in the form of radiation, the quantum of which is such that it supplies the energy without itself affecting the plate. The phenomenon is independent of the intensity of the radiation. J. GRANT.

Chemical actions of radiations. A. G. DE MONCETZ (Compt. rend., 1927, **184**, 284—285; cf. preceding abstract).—The author summarises earlier observations (Compt. rend., 1908, **146**, 1032; 1909, **148**, 406). A plate exposed to *X*-rays has its image weakened if it is subsequently exposed to radiations of 800—920 Å., and intensified if radiations of 920—1350 Å. are used. If ordinary light replaces *X*-rays, the image is always destroyed. If the plate is solarised, the infra-red region of the spectrum subsequently used produces a blackening, the violet-blue region destroys the grey colour of the plate, and the ultra-violet (250—394 Å.) appears white or black on the plate according as the initial exposure is short or long. J. GRANT.

Deoxidation of potassium, sodium, and lithium permanganates in alkaline solution. A. A. MAXIMOV (J. Russ. Phys. Chem. Soc., 1926, **57**, 347—371).—In alkaline solution, sodium and potassium permanganates are decomposed thus: (1) $2M'MnO_4+2M'OH=2M_2'MnO_4+H_2O+0{\cdot}5O_2$; (2) $M'_2MnO_4+H_2O=MnO_2+2M'OH+0{\cdot}5O_2$. When a permanganate is formed by the fusion of an alkali hydroxide with manganese dioxide, the presence of an alkali peroxide assists the reaction. It is supposed that even when no peroxide is added, some is formed during the reaction. In these circumstances, whereas cæsium, potassium, rubidium, and sodium should form the manganate and permanganate on fusion of their hydroxides with manganese dioxide, lithium, which does not form a peroxide, should not undergo the reaction. This has been found to be the case. Lithium permanganate could be formed only by the addition of lithium sulphate to barium permanganate. Under the conditions in which potassium permanganate gave the manganate in potassium hydroxide solution, lithium permanganate in lithium hydroxide solution does not change, except exceedingly slowly, a change which is attributed to the presence of sodium in the glass of the containing vessel.

Hydrogen peroxide so accelerates the reaction that no manganate is formed, and only manganese dioxide. The reaction has been carried out quantitatively by titrating standard solutions of the permanganates with hydrogen peroxide until (i) a green colour is formed and (ii) a grey precipitate appears. This has been accomplished for lithium as well as for potassium. The results obtained are in accord with the equations: (i) $2M'MnO_4+H_2O_2+2M'OH=2M'_2MnO_4+2H_2O+O_2$; (ii) $2M'_2MnO_4+H_2O_2=2M_2'O+2H_2O+2MnO_2+2O_2$. Sodium permanganate in the presence of sodium peroxide undergoes the change: $2Na_2MnO_4+2Na_2O_2+4H_2O=2MnO_2+8NaOH+2O_2$. In the presence of potassium ferricyanide, the reaction is reversed (Dieffenbach, A., 1908, ii, 697). The reaction was effected as follows. Dry sodium hydroxide is added to a little water, and the mixture heated to boiling, when dry manganese dioxide is added. On adding sodium peroxide to the mixture, a gas is evolved with the formation of sodium manganate.

The following scheme is given for the oxidations and reduction of manganese salts: $MnO_2+4KOH+{\cdot}O{\cdot}O{\cdot}=MnO_2(OK)_2+KO{\cdot}OK+2H_2O$; $2KMnO_4+K_2O_2=2MnO_2(OK)_2+O_2$; $MnO_2(OM')_2+HO{\cdot}OH=O_2+Mn(OH)_2(OM')_2=H_2MnO_3+M_2'O+O_2$.

E. ROTHSTEIN.

Combination of potassium with carbon. K. FREDENHAGEN and G. CADENBACH (Z. anorg. Chem., 1926, **158**, 249—263).—Potassium, rubidium, and cæsium react vigorously with different forms of carbon with evolution of heat. Whilst carbides are not formed by the reaction, the resulting product contains 0·24, 0·12, or 0·06 mol. of alkali metal per mol. of carbon, according to the temperature, and has a definite colour, depending on the alkali metal content. Although it is suggested that an adsorption process may be responsible for the phenomena, it is remarkable that different forms of carbon, having different powers of adsorption, should exhibit very little difference in behaviour. With sodium, definite results were not obtained. A. S. CORBET.

Formation of gold from mercury. A. MIETHE and H. STAMMREICH (Z. anorg. Chem., 1926, **158**, 185—243).—Passage of electric discharges through mercury vapour frequently resulted in the appearance of gold. Experiments in liquid dielectrics, such as paraffin, water, etc., gave positive results, but only traces of gold resulted from electric discharges in gaseous dielectrics such as carbon dioxide and hydrogen. Traces of gold only were found by spark discharges through solid paraffin and through quartz and by conduction experiments through iron. The passage of a current through a long mercury column gave negative results. In general, the analytical procedure was that adopted previously (Stammreich, A., 1925, ii, 1208).

Although the majority of a large number of experiments were negative, some series were almost exclusively positive and the results indicate a close dependence of the appearance of gold on the nature of the electric discharge. The most favourable conditions, however, are not yet definitely known.

A. S. CORBET.

Magnesium–silver alloys. P. LAFFITTE (Bull. Soc. chim., 1927, [iv], **41**, 32—34).—Ethyl iodide and anhydrous ether extract all the magnesium from magnesium alloys containing not more than 74·5% of silver, irrespective of whether it is combined or not.

S. K. TWEEDY.

Behaviour of sparingly soluble metallic oxides in solutions of their salts. Magnesium oxide. I. W. FEITKNECHT.—See B., 1927, 73.

Volatile barium sulphate. F. L. HAHN.—See B., 1927, 106.

Salts of hydrofluoboric acid. II. H. FUNK and F. BINDER (Z. anorg. Chem., 1926, **159**, 121—124; cf. A., 1926, 1015).—The following *salts* of hydrofluoric acid have been prepared and analysed: $Mn(BF_4)_2,6H_2O$; $Cu(BF_4)_2,6H_2O$; $Tl(BF_4),H_2O$; $Ag(BF_4),AgF,HF,5H_2O$; $Pb(BF_4)_2,PbF_2,5H_2O$ (also the corresponding *stannous* salt, which was too unstable to give a satisfactory analysis), N_2H_4,HBF_4, and *benzenediazonium fluoborate*. The fluoborates of the heavy metals are characterised by their great solubility, deliquescence, and instability at higher temperatures. The hydrazine and diazonium salts may be included among the alkali salts; they give anhydrous crystals and are not hygroscopic.

M. CARLTON.

Recovery of alumina from natural silicates. H. KASSLER.—See B., 1927, 105.

Reaction of "aluminon" with hydroxides of scandium, gallium, indium, thallium, and germanium. R. B. COREY and H. W. ROGERS (J. Amer. Chem. Soc., 1927, **49**, 216—217).—Scandium produces a red lake with "aluminon" (cf. Middleton, A., 1926, 930) which is insoluble in ammonia solution, but is readily soluble in ammonium carbonate solution. Gallium lake forms slowly, but otherwise resembles the aluminium lake. Indium gives a red solution, which is fairly stable in presence of ammonia, but is decolorised by ammonium carbonate. The lake of tervalent thallium forms with difficulty and is unstable both in ammonia and ammonium carbonate solutions. Germanium forms no stable lake, although the solution becomes distinctly turbid on keeping.

S. K. TWEEDY.

Fixation of nitrogen as aluminium nitride. H. J. KRASE, J. G. THOMPSON, and J. Y. YEE.—See B., 1927, 73.

Constitution of N_2O_4 and N_2O_3; additive compounds of nitro- and nitroso-compounds with tin and titanium tetrachlorides. H. REIHLEN and A. HAKE (Annalen, 1927, **452**, 47—67).—Experiments on the structure of nitrogen tetroxide which involve fission (*e.g.*, Wieland, A., 1921, i, 778) can give no satisfactory results. The N_2O_4 molecule has now been studied as a whole in additive compounds, in which it behaves as $(O:)_2N\cdot O\cdot N:O$. Co-ordination compounds of nitro-compounds are first investigated; those with aluminium halides are unsuitable, owing to the variability of the co-ordination valency, and hence stannic chloride and titanic chloride, in which it is always six, were used. The following compounds were obtained as crystalline solids: *nitrobenzene stannic chloride*, $Ph\cdot NO_2,SnCl_4$, m. p. 11°, and *titanic chloride*, m. p. 77·5°; *m-dinitrobenzene dititanic chloride*, $C_6H_4(NO_2)_2,2TiCl_4$, m. p. 64°; *p-dinitrobenzene titanic chloride*, $C_6H_4(NO_2)_2,TiCl_4$. The titanic compounds are all yellow, as are *nitromethane titanic chloride*, m. p. 48°, and *nitroethane titanic chloride*, m. p. 51°, which can be sublimed without decomposition, and must be derivatives of the true nitro-forms of nitromethane and nitroethane; they show that the nitro-group, and not the aromatic nucleus, is responsible for co-ordination in the other compounds. In preparing the nitromethane compound, a white solid was always obtained, $CH_3O_4NCl_4Ti_2$, regarded as *nitromethane di-titanic oxychloride*, $NMe[:O \ldots TiOCl_2]_2$. The above compounds show that the nitro-group can combine with 1 mol. of stannic or titanic chloride, and thus supplies two co-ordination valencies.

The nitroso-group behaves differently. Nitrosobenzene yields an amorphous *di-nitrosobenzene stannic chloride*, and with titanic chloride, yellow and red amorphous products. Nitrosyl chloride gives dinitrosyl stannic chloride or titanic chloride (cf. Weber, Annalen, 1863, **118**, 476). The latter is also obtained by the action of tetranitromethane on titanic chloride, in which titanic carbonato-chloride and nitric oxide are formed, or very slowly by the action of chlorotrinitromethane. These compounds indicate that the nitroso-group supplies one co-ordination valency. Accordingly, if nitrogen tetroxide is symmetrical, it should give a complex, $Cl_4M<\overset{O}{\underset{O}{>}}N-N<\overset{O}{\underset{O}{>}}MCl_4$; if it is nitronitrite, $Cl_4M[\ldots O{:}N\cdot O\cdot N<\overset{O}{\underset{O}{>}}MCl_4]_2$. It is found that at 0° in carbon disulphide a brown *bis(nitrogen tetroxide) tri-stannic chloride*, $O_8N_4Cl_{12}Sn_3$, is obtained, showing that nitrogen tetroxide reacts in the second, nitronitrite form. If excess of solid nitrogen tetroxide is added to stannic chloride at −60° and the mixture is allowed to warm up in a freezing mixture, a yellow *tri(nitrogen tetroxide) bis-stannic chloride*, $O_{12}N_6Cl_8Sn_2$, is obtained. A titanic analogue of the latter is apparently formed, but this decomposes in the presence of nitrogen tetroxide to give *titanic (tetra)nitrate*, $Ti(NO_3)_4$, stable yellow crystals, decomposed by water.

Nitric oxide and nitrous oxide do not combine with stannic or titanic chloride, even at −25° (cf. Kuhlmann, Annalen, 1841, **39**, 319; carbon monoxide is similarly inert). Nitrogen pentoxide is decomposed by stannic and titanic chlorides.

Nitrogen trioxide reacts at −40° with stannic chloride in carbon tetrachloride to give an almost colourless product, which may be derived from a colourless tautomeric form of the oxide, $O{:}N\cdot O\cdot N{:}O$.

E. W. WIGNALL.

Addition of nitrosyl chloride to metallic salts. H. GALL and H. MENGDEHL (Ber., 1927, **60**, [*B*], 86—91).—The action of nitrosyl chloride on metallic

halides consists in the primary formation of an additive product, which may be stable or may become transformed into the compound of nitric oxide and the higher chloride by transference of the chlorine atom from the nitrosyl chloride to the metal. If the latter compound is unstable, nitric oxide is evolved, and the residual higher chloride may unite with nitrosyl chloride. The *compound*, $MnCl_3NO$, obtained from manganous chloride and nitrosyl chloride at −10°, is immediately decomposed by water with evolution of nitrous fumes, and, when heated, affords nitric oxide, chlorine, and manganous chloride. Under similar conditions, cuprous chloride gives the compound $CuCl_2,NO$, decomposing when heated with evolution of pure nitric oxide and yielding a dark blue solution in a little acetone or alcohol (cf. Manchot, A., 1914, ii, 567). Sublimed ferrous chloride yields the substance $FeCl_3,NOCl$ (cf. Sudborough, J.C.S., 1891, 59, 655), which is a secondary product, since evidence of the existence of the substance $FeCl_3,NO$ is also adduced. Antimony trichloride affords the *compound*, $SbCl_5,NOCl$, whereas the substance $AlCl_3,NOCl$ is obtained from aluminium chloride. Mercurous chloride is slowly converted into the *compound* $HgCl_2,NOCl$, which is also derived from mercuric chloride. The individual nature of the compounds is established by measurement of the vapour tension at a constant temperature. H. WREN.

Ammonium monometaphosphate. Phosphate. III. S. J. KIEHL and T. M. HILL (J. Amer. Chem. Soc., 1927, **49**, 123—132).—*Ammonium monometaphosphate* was prepared as white, monoclinic crystals, *d* 2·2084, from the sodium salt by way of the lead salt. The procedure is described in detail. The solubility of the salt is 25—30 g. per 100 c.c. of water at the ordinary temperature, the solution being neutral to litmus and precipitating insoluble monometaphosphates of some heavy metals from solutions of their salts. The conductivities at 25° of solutions of ammonium and sodium monometaphosphates are recorded. S. K. TWEEDY.

Formation of polythionates. E. JOSEPHY and E. H. RIESENFELD (Ber., 1927, **60**, [*B*], 252—254).—The reaction between thiosulphate and sulphur dioxide, which with the potassium salt gives pure potassium trithionate, with the aniline salt affords homogeneous aniline tetrathionate, thus giving a simple method for the preparation of the latter substance. The possibility of separating tri- or tetrathionate from the same solution according to the nature of the cation is due to the presence of all three polythionates and crystallisation of the most sparingly soluble salt. *Aniline pentathionate* is prepared from its components. H. WREN.

Colour of selenium dioxide. J. MEYER and M. LANGNER (Ber., 1927, **60**, [*B*], 285).—Selenium dioxide melts to an orange-yellow liquid when heated and gives a yellowish-green vapour. The change is reversible and not attributable to dissociation into selenium and oxygen. Solutions of the oxide in warm, concentrated sulphuric or selenic acid are distinctly yellow, but become lighter in colour when cooled. H. WREN.

Heterotri-acids and heterotri-salts. IV. G. CANNERI (Gazzetta, 1926, **56**, 871—889; cf. A., 1926, 258; this vol., 33).—Most of the analytical data for salts of complex tri-acids are too complicated for deductions of structure to be made; this is due to mixed crystal formation. Crystallographic study shows that ammonium tungstovanado-phosphates and -arsenates retain an isomorphous tetragonal structure under considerable variations in composition; variations in density are continuous. Ammonium tungstovanadophosphate gives an insoluble, red, crystalline *barium* salt from which the free *acid* is obtained in red, tetragonal crystals, in which the ratio $WO_3 : V_2O_5$ varies roughly between 2 and 5 by weight. Correspondingly, preparations of *tungstovanadoarsenic acid* are made. These two acids form mixed crystals among one another, as do their ammonium salts. Similar mixed crystals of tungstovanado- with the corresponding molybdovanado-phosphates or -arsenates, and of all four salts together, are obtained; the general type is thus

$$R_6H[(P,As)(Mo_2O_7,W_2O_7)_x(V_2O_6)_y],nH_2O.$$

E. W. WIGNALL.

Univalent manganese. W. MANCHOT and H. GALL (Ber., 1927, **60**, [*B*], 191—194).—Potassium manganocyanide is reduced by aluminium filings or Devarda's alloy in aqueous-alkaline solution under definite conditions of temperature to the *compound* $K_2Mn(CN)_3$. The new compound is oxidised with extraordinary ease, and decomposes water, rapidly in boiling, slowly in cold solution, with evolution of hydrogen. It is distinguished from the manganocyanide, itself a powerful reducing agent, by its ability to bleach litmus, its intensely blue colour with hydrogen peroxide, red colour with anthraquinone and alcohol, precipitation of lead and cadmium from solutions of their salts, and reduction of Nylander's bismuth reagent. H. WREN.

Action of high temperatures on some metallic sulphides. PICON (Compt. rend., 1927, **184**, 98—99).—Metallic sulphides having the formulæ FeS, MnS, and $CrS_{1\cdot3}$ were heated in a furnace in a carbon tube under a vacuum of 0·001 mm. of mercury. The iron sulphide dissociated into its elements between 1100° and 1600°; manganese sulphide volatilised without decomposition at 1375°; chromium sulphide gradually lost its sulphur from 1350°, and melted at 1550° (the m. p. of the monosulphide). The composition then corresponded with the formula $CrS_{1\cdot06}$. The sulphides are thus more stable than the corresponding oxides. J. GRANT.

Nickel carbide. G. MEYER and F. E. C. SCHEFFER (Rec. trav. chim., 1927, **46**, 1—7; cf. this vol., 29).—A mixture of nickel oxide and asbestos was treated with hydrogen at 270° and after reduction the hydrogen was replaced by carbon monoxide, which was passed for some hours at 250°. The resulting product contained one or more carbides of nickel and gave a mixture of hydrogen and hydrocarbons when treated with hydrochloric acid. No perceptible amount of nickel carbonyl was present. Previous work (*loc. cit.*) indicated that nickel carbide should have a dissociation temperature of about 420°, in agreement with which the above treatment at high

temperatures (700°) gives a mixture of nickel and carbon only, the product being unaffected by hydrochloric acid owing to envelopment of the nickel grains by carbon. The formation of the carbide may be represented $x\mathrm{Ni}+2\mathrm{CO}=\mathrm{Ni}_x\mathrm{C}+\mathrm{CO}_2$, whilst at high temperatures the nickel acts as a catalyst for the action $2\mathrm{CO}\rightleftharpoons\mathrm{CO}_2+\mathrm{C}$. The gases evolved when the carbide is treated with acid are complex and contain both methane and unsaturated hydrocarbons.

W. HUME-ROTHERY.

Sources of error in quantitative chemical analysis by means of *X*-ray emission spectra. H. STINTZING (Physikal. Z., 1926, 27, 844).—The technique is described. R. A. MORTON.

Method of micro-titration. E. SCHILOV [in part with Z. A. OSSENNOVA] (Z. anal. Chem., 1927, 70, 23—34).—A burette for micro-titrations comprises a 1 c.c. calibrated pipette without stopcock, but connected at its upper end by means of a piece of rubber tubing with a manometer filled with a 50% solution of barium bromide. By raising one arm of the manometer, liquid is delivered from the pipette in any desired quantity; conversely, by lowering this arm with the tip of the pipette in the titrating solution, the pipette may be refilled. Arrangements for cleaning the pipette and for filling it directly from the stock bottle are described and illustrated, and examples of its use in volumetric analysis are given.

A. R. POWELL.

Rapid calibration of micro-burettes. E. SCHILOV (Z. anal. Chem., 1927, 70, 35—38).—Microburettes may be calibrated in a similar way to capillary tubes by displacement of a column of mercury supported between two columns of water, provided that the bore of the burette is less than 3 mm. in diameter. The mercury column is caused to move by adjusting the manometer (cf. preceding abstract). For details of the actual procedure and method of calculating the results, the original must be consulted.

A. R. POWELL.

Colorimetric determination of hydrogen-ion concentration. J. H. SHAXBY and O. M. JONES (J. Physiol., 1926, 61, Proc., xxvi—xxvii).—Dale and Evans' method of the determination of hydrogen-ion concentration is liable to error resulting from the use of unequal depths of liquid in the two tubes. A. A. ELDRIDGE.

Determination of hydrogen-ion concentration with colloid membranes containing indicators. P. WULFF (Kolloid-Z., 1926, 40, 341—342).—A method is described in which the indicator is adsorbed by a colloid membrane, which is dipped in the solution to be examined. On withdrawal, the colour is compared with a series of standard colours.

E. S. HEDGES.

Use of the quinhydrone electrode in electrometric titrations. A. J. RABINOWITSCH and V. A. KARGIN (Z. Elektrochem., 1927, 33, 11—14).—Limits to the accuracy of electrometric titrations of acids with alkali hydroxides using the quinhydrone electrode have been investigated. Not only does the quinhydrone electrode always give p_{H} values which are too low in solutions more alkaline than about p_{H} 8, but also in insufficiently buffered solutions of weak acids such errors appear at lower p_{H} values, *e.g.*, around p_{H} 6. Since the titration curves of such acids do not become vertical until the neutral point is approached and the vertical portion is short, the observed titration values will tend to be high. The weaker is the acid the greater becomes the error. But, since for a given acid the error (in terms of equivalents of alkali) is practically constant, it becomes important only when very small quantities of the acid are being titrated, *e.g.*, it is negligible when 20—50 c.c. of 0·1*N*-acetic acid are titrated with 0·1—0·5*N*-potassium hydroxide. Good results are usually obtained in the titration of animal fluids owing to their being well buffered. No error arises with strong acids, since their titration curves become vertical at relatively low p_{H} values. The above inaccuracies are attributed to the slightly acidic character of quinol, the ionisation of which not only furnishes hydrogen ions to the solution, but also causes a shift in the quinol–quinone equilibrium on which the potential of the electrode depends. Purity of the quinhydrone is important, since the presence of acid oxidation products may cause errors even in the titration of strong acids. H. J. T. ELLINGHAM.

Correction for the new citrate buffer solutions. I. M. KOLTHOFF and J. J. VLEESCHOUWER (Chem. Weekblad, 1927, 24, 78; cf. A., 1926, 1220).—The figures previously given were based on the assumption that the potassium citrate used was anhydrous; it is now found that the monohydrate was employed. Corrected tables are given.

S. I. LEVY.

Employment of the quinhydrone electrode in solutions of low buffer capacity. I. M. KOLTHOFF and W. BOSCH (Chem. Weekblad, 1927, 24, 78—80).—Quinhydrone prepared by the oxidation of quinol with ferric alum gives low p_{H} values with solutions having low buffer capacity; for such solutions more accurate figures are obtained by use of quinhydrone obtained from alcoholic solutions of quinol and quinone. The solution to be examined should be shaken with the quinhydrone, the measurement taken, the liquor poured off and replaced by fresh solution, this being continued until constant values are obtained. S. I. LEVY.

Measurement of moisture content. H. EBERT (Physikal. Z., 1926, 27, 869—870).—The aspiration psychrometer of Assmann gives values for moisture which are correct when the moisture content is high, but when it is low the results err on the high side.

R. A. MORTON.

Automatic apparatus for the determination of water. R. KATTWINKEL.—See B., 1927, 63.

Sensitiveness of some reagents for gaseous hydrogen sulphide. M. WILMET (Compt. rend., 1927, 184, 287—289).—The sensitiveness towards hydrogen sulphide of lead and cadmium acetates, lead nitrate, and copper sulphate impregnated on filter-papers, and strips of silver or copper polished by various means, has been tested by observing the time elapsing before stains are produced when the reagents are suspended in a still or moving atmosphere of gas. Lead acetate (10% solution) is the best reagent if used on filter-paper 9 sq. mm. in area.

The method may be made roughly quantitative by standardising the conditions, and the dynamic method will then determine the amount of air containing 0·1 mm.^{3} of gas. The sodium nitroprusside, Lauth's violet, and methylene-blue tests are least trustworthy, whilst copper or brass strips respond only for concentrations at which the gas is harmless to man. The odour is detectable for concentrations down to 1 : 700,000. J. GRANT.

Reaction between elementary phosphorus and potassium iodate and its utilisation in the volumetric determination of phosphorus. T. F. BUEHRER and O. E. SCHUPP, jun. (J. Amer. Chem. Soc., 1927, 49, 9—15).—The phosphorus is heated in a reflux apparatus for 3—4 hrs. with potassium iodate, dilute sulphuric acid, and a small volume (2 c.c.) of carbon tetrachloride. The liberated iodine is then distilled into slightly insufficient standard sodium thiosulphate solution at 0°, the slight excess of iodine being determined by titration. The result is checked by titration of the excess of iodate remaining in the distillation flask. The accuracy is about 0·3%. The nature of the reactions involved is discussed. S. K. TWEEDY.

Separation of phosphoric acid in qualitative analysis by means of zirconium salts. F. OBERHAUSER (Ber., 1927, 60, [*B*], 36—42; cf. Curtman, Margulies, and Plechner, A., 1925, ii, 68).—Zirconium hydroxide is appreciably soluble in dilute hydrochloric acid in which zirconium phosphate does not dissolve. In the presence of the hydroxide and hydrochloric acid, zirconium phosphate yields a soluble complex salt in which the phosphate radical cannot be detected by ammonium molybdate except after repeated evaporation with much concentrated nitric acid. In qualitative analysis, the separation of phosphate is effected by addition of saturated zirconium nitrate or oxychloride and ammonium chloride to the oxidised solution from which the customary metals and nickel and cobalt have been separated; the solution is heated to incipient boiling, made alkaline with ammonia, boiled for 3 min., and rendered distinctly acid with acetic acid. The precipitate contains all the phosphate as basic zirconium phosphate, excess of the reagent as the hydroxide, and the greater part of the iron, aluminium, and chromium; zinc, manganese, the alkaline-earth metals, magnesium, the alkali metals, and small amounts of iron, aluminium, and chromium are present as acetates in the filtrates. The precipitated zirconium phosphate appears to have the composition $4Zr(OH)PO_4,3Zr(HPO_4)_2$, and to pass when ignited into the *salt*, $2ZrO_2,5ZrP_2O_7$. Zirconium may be determined by means of an excess of phosphate in concentrated hydrochloric acid solution in presence of metals of the ammonium sulphide and carbonate group. The method is not adapted to the determination of phosphate. H. WREN.

Electrolytic determination and separation of arsenic, antimony, and tin. A. SCHLEICHER and L. TOUSSAINT (Z. anorg. Chem., 1927, 159, 319—324).—The mixture of salts is dissolved in concentrated hydrochloric acid, with addition of hydrazine sulphate and a little potassium bromide, and arsenious chloride is distilled off in an air-stream at the temperature of the water-bath. Arsenic is determined in the distillate by direct titration with 0·1*N*-potassium bromate; antimony and tin are determined in the residue electrolytically. The residue is neutralised with sodium hydroxide until a turbidity is produced, and the incipient precipitate is just redissolved in hydrochloric acid. Excess of hydrochloric acid may not be used, or the deposited antimony will contain antimony chloride. A cathode potential of 0·28—0·35 volt (against the calomel electrode) is used for the deposition of antimony, the solution being kept at 60—70°. The deposition of tin commences at a cathode potential of 0·6 volt, and the temperature is lowered to 35°, with addition of a little hydroxylamine hydrochloride. The whole process can be performed in 3 hrs. The separation of antimony and tin can be carried out between the limits Sb : Sn=100 : 1 and 1 : 100. E. S. HEDGES.

Iodometric titrations. II. Determination of arsenate. K. BÖTTGER and W. BÖTTGER (Z. anal. Chem., 1927, 70, 97—109; cf. A., 1926, 1221).—By carrying out the iodometric titration of arsenate in concentrated hydrochloric acid solutions, considerable economy may be effected in the amount of iodide required, and disturbing influences caused by the separation of insoluble iodides (*e.g.*, lead iodide) are avoided. For the determination of arsenic acid in commercial lead arsenate preparations, 0·5 g. is shaken in a stoppered flask with 30 c.c. of cold hydrochloric acid (*d* 1·19), 0·5 g. of potassium iodide is added and, after 15 min., the liberated iodine is titrated with 0·1*N*-thiosulphate. When only very small quantities of arsenic acid are being determined, an atmosphere of carbon dioxide is essential for accurate results, as iodine is liberated by the action of the air on strongly acid iodide solutions. A. R. POWELL.

Analysis of silicates. A. LASSIEUR.—See B., 1927, 108.

Analysis of rock salt. W. TOELDTE.—See B., 1927, 106.

Analysis of rubidium and cæsium. L. MOSER and E. RITSCHEL (Z. anal. Chem., 1927, 70, 184—189).—The results of a critical examination of the methods of separating rubidium and cæsium from potassium and from each other described by Strecker and Diaz (A., 1926, 261) are recorded. The alcohol separation of potassium and rubidium chlorides gives high and irregular figures for potassium, the chlorostannate method good results only when little rubidium is present with much potassium, and the antimony chloride precipitation of cæsium very erratic results even under carefully controlled conditions. A. R. POWELL.

Volumetric determination of calcium by precipitation as oxalate and titration with permanganate. F. L. HAHN and G. WEILER (Z. anal. Chem., 1927, 70, 1—22).—Precipitation of calcium oxalate with an excess of ammonium oxalate in neutral or ammoniacal solution yields a precipitate which may contain a certain amount of a basic salt, of a double salt, or of mixed crystals, so

that, whether the precipitate is titrated directly with permanganate or the excess of ammonium oxalate in the filtrate is determined, incorrect results are obtained for calcium. Pure calcium oxalate may, however, be precipitated from a solution containing 5 c.c. of 0·1*N*-hydrochloric acid and 10 c.c. of 2*N*-ammonium chloride per 100 c.c. by the addition of a slight excess of ammonium oxalate to the boiling solution, followed by ammonia to neutrality. Ammonium acetate may replace the ammonium chloride and 10 c.c. of glacial acetic acid the hydrochloric acid. Better results are obtained by using a known volume of ammonium oxalate solution and titrating the excess in an aliquot part of the filtrate, as calcium oxalate has a tendency to hydrolyse on washing. A. R. POWELL.

Determination [and separation] of calcium, strontium, and barium. L. SZEBELLEDY (Z. anal. Chem., 1927, **70**, 39—55).—The accuracy of Winkler's methods for the determination of calcium as CaC_2O_4,H_2O (A., 1919, ii, 34), strontium as SrC_2O_4,H_2O (*ibid.*, 1918, ii, 241), and barium as chromate (Z. angew. Chem., 1917, **30**, 301) and as sulphate (A., 1921, ii, 62) has been tested and his correction factors have been confirmed. For the separation of calcium from barium and strontium, the nitrate solution is evaporated to dryness and the residue heated for 30 min. at 132°, then for the same time at 180°. The mass is extracted twice with 2·5 c.c. of absolute alcohol, then once with 5 c.c. of *iso*butyl alcohol, the residue is dissolved in water, and evaporation, heating, and extraction are repeated, and, finally, the insoluble portion is redissolved in water for the separation of barium and strontium. The alcoholic filtrates are evaporated in a tared crucible and the residual calcium nitrate is converted into sulphate by heating with five times its weight of ammonium sulphate. Barium is separated from strontium by adding 15 c.c. of *N*-acetic acid and 5 g. of ammonium chloride to the nitrate solution, heating to boiling, and adding slowly 10 c.c. of 10% potassium chromate solution. The precipitate is collected next day on a Gooch crucible, washed with hot water, dried at 132°, and weighed as barium chromate. Strontium is recovered from the filtrate by adding 10 c.c. of *N*-ammonia solution, followed by 10 c.c. of 10% potassium oxalate solution. The latter salt, being more soluble than ammonium oxalate, is more suitable for precipitation of calcium or strontium oxalates. A. R. POWELL.

Titration of barium ions. R. F. LE GUYON (Bull. Soc. chim., 1927, [iv], **41**, 99—101; cf. A., 1926, 927).—Neutral solutions of barium salts may be determined volumetrically by titration with a standard chromate solution, using silver nitrate as an internal indicator. S. K. TWEEDY.

Determination of lead by oxidation with persulphate. P. EKWALL (Z. anal. Chem., 1927, **70**, 161—179).—A critical examination of Samter's method of determining lead by oxidation with persulphate in ammoniacal solution ("Analytische Schnellmethoden," Halle, 1911). Under no modification of the conditions could a better conversion to peroxide be obtained than 97%, the precipitate invariably containing small amounts of sulphate and monoxide. The use of potassium persulphate in sodium hydroxide solution gave no better results. A. R. POWELL.

Spot method of qualitative analysis. N. A. TANANAIEV (J. Russ. Phys. Chem. Soc., 1926, **58**, 219—222).—A rapid and simple systematic method is described for the detection of metals which give colour reactions, in presence of each other. A drop of a solution containing aluminium, chromium, iron, cobalt, nickel, zinc, manganese, mercury, lead, silver, bismuth, cadmium, or copper is brought in contact with suitably prepared filter-paper and further treated with appropriate reagents; *e.g.*, for aluminium, the paper is saturated with ferricyanide solution, and the spot of solution to be tested is treated with ammonia and an alcoholic solution of alizarin. A pink ring on a violet background is obtained. For nickel, the paper is saturated with sodium phosphate solution, and the spot moistened with dimethylglyoxime in alcohol, a pink ring being developed.

The method, which is sensitive and accurate, has been extended to other elements (cf. Feigl, A., 1921, ii, 278; 1923, ii, 508). M. ZVEGINTZOV.

Determination of ferrous iron. E. DITTLER (Z. anorg. Chem., 1926, **158**, 264—276).—The hydrogen sulphide, evolved by decomposition of minerals and meteorites containing sulphur with mineral acid, is collected and, after oxidation by nitric acid, determined as sulphate and the ferrous salt present calculated from the relation $FeS+H_2SO_4=FeSO_4+H_2S$. During the decomposition a brisk stream of carbon dioxide passed through the apparatus prevents any small amount of magnetic pyrites from being attacked and inhibits any reduction which may otherwise result from the reaction $Fe_2(SO_4)_3+H_2S=2FeSO_4+H_2SO_4+S$. A. S. CORBET.

Electrometric study of tungstic acid. H. T. S. BRITTON (J.C.S., 1927, 147—150).—A solution of tungstic oxide in excess of sodium hydroxide was titrated with hydrochloric acid. A sharp diminution in hydrogen-ion concentration occurred when the amount of hydrochloric acid necessary to react with the alkali in excess of that required to form the normal sodium tungstate (Na_2WO_4) was added. This explains the successful use of phenolphthalein as an indicator for the titration of the oxide. The inflexion in the hydrogen-ion concentration curve indicates that tungstic acid is not an ordinary dibasic acid. Meta- and para-tungstates are assumed to contain tungstic acid either in a polymerised form or in a semi-colloidal form. W. THOMAS.

Titration of tin with ferric chloride using indigo-carmine [as internal indicator]. W. SCHLUTTIG (Z. anal. Chem., 1927, **70**, 55—61).—Stannous chloride may be satisfactorily titrated with ferric chloride at the ordinary temperature, using indigo-carmine as indicator, if the solution contains at least half its volume of concentrated hydrochloric acid. The ferric chloride solution is made by dissolving 47 g. of the commercial salt in 160 c.c. of hydrochloric acid (*d* 1·19) and diluting to 1 litre, and for each titration 10 drops of a 0·5% solution of indigo-carmine are used. The yellow colour of the

indicator becomes pale green just before the end-point is reached; a further drop or two of the ferric chloride solution produces a sharp change to indigo-blue. Titrations should be carried out in an atmosphere of carbon dioxide, stannic solutions being previously reduced with iron or aluminium to the stannous state. A. R. POWELL.

Electrometric titration of dichromate using potassium ferrocyanide. K. SOMEYA (Z. anorg. Chem., 1926, **159**, 158—160).—The usual apparatus for electrometric titration was employed, using as electrodes a bright platinum wire and a calomel half-electrode. For a sharp end-point, the temperature must lie between 40° and 65° and the amount of concentrated hydrochloric acid be between 5 and 10 c.c. per 60 c.c. of the total volume. Under these conditions, a sharp fall in potential of about 250 millivolts is obtained. M. CARLTON.

Separation of minute quantities of gold from ferric oxide. E. WICHERS (Ind. Eng. Chem., 1927, **19**, 96).—The approximate determination of gold (of the order 0·005 mg.) in a residue consisting mainly of ferric oxide may be made by separating the ferric oxide by fusion with potassium pyrosulphate. The solution of the sample is absorbed on filter-paper, which is burned off in a porcelain crucible, and the residue fused with about 20 g. of potassium pyrosulphate. The clear mass is dissolved in water acidified with sulphuric acid, filtered through paper treated with paper pulp, and wet with dilute sulphuric acid. A very small amount of ferric oxide may still be present, and the fusion is repeated with a very small quantity of pyrosulphate. The papers are burned off and the slight residue is digested with chlorine water. On the addition of several drops of benzidine reagent, a positive test for gold is obtained, and by using comparative tests with known quantities of gold and comparing the depth of colour, the approximate proportion present may be determined. D. G. HEWER.

Hygrometer employing glycerol. E. GRIFFITHS and J. H. AWBERY (Proc. Physical Soc., 1926, **39**, 79—84).—The variation of refractive index of glycerol solutions in equilibrium with air of various humidities has been studied; the time for equilibrium to be reached, when thin films of glycerol are used, has also been investigated. A hygrometer, in which the refractive index of a thin glycerol film is measured, is described. The instrument is robust, and the scale can be engraved directly in humidities. The time-lag is about 15 min. C. J. SMITHELLS.

Clip for securing paper covers on funnels and beakers. N. H. HARTSHORNE (J.S.C.I., 1927, **46**, 40T).—A description of, and directions for making, a simple wire clip for securing paper covers placed on funnels and beakers to exclude dust or other foreign matter.

Regulating device for pinchcocks of burettes. M. WIKUL (Z. anal. Chem., 1927, **70**, 61—62).—A glass rod cut at one end to form a rough wedge is inserted between the arms of the pinchcock on the side remote from the loop. By gently twisting this rod, the solution may be delivered at any desired rate. A. R. POWELL.

Device for maintaining a constant level in water-baths. G. FOUQUE (Bull. Soc. chim., 1927, [iv], **41**, 115—116).—A simple non-siphoning device is described which can readily be constructed from glass tubing. S. K. TWEEDY.

Constant-level water-bath using distilled water. R. W. GERDEL (Ind. Eng. Chem., 1927, **19**, 50).—Through the 3-holed cork of a 10- or 15-litre bottle there pass a short tube with stopcock, for filling the bottle and for applying pressure to start the siphon; a tube bent twice at right angles, from the bottom of the bottle to the bottom of the water-bath, and another tube from the bottom of the bottle and connected by rubber tubing (for application of a pinchcock when starting up) to a wider glass tube (diameter at least 1 inch to overcome capillarity) reaching to the desired level in the water-bath. D. G. HEWER.

Gas-tight bearing for rotating laboratory apparatus. C. VAN BRUNT (Ind. Eng. Chem., 1927, **19**, 127).—The rotating horizontal member is in the form of an inner tube fitting as closely as possible into an outer bearing, and the seal is formed by a mercury jacket in a tube (supported against rotation), fixed by rubber tubing, which fits closely enough on the inner tube to hold the mercury under a small head, but not so tightly as to bind. The tubing may be rubbed inside with flake graphite. This bearing has run satisfactorily for days at about 25 r.p.m. D. G. HEWER.

Apparatus for the determination of moisture by distillation with xylene. J. PRITZKER and R. JUNGKUNZ.—See B., 1927, 63.

Simple apparatus for the removal of ammonium salts by volatilisation. K. FISCHER.—See B., 1927, 73.

Formation of films of lead sulphide on glass surfaces. H. L. SMITH (J. Sci. Instru., 1926, **4**, 115—118).—Thin films of lead sulphide can be deposited on the surface of lead glass or zinc crown glass by treatment with a mixture of an alkaline solution of lead tartrate and a solution of thiocarbamide at 50°. Other types of glass and quartz do not give satisfactory results. R. CUTHILL.

Apparatus for the purification of gases and the determination of vapour pressures. E. CARDOSO (J. Chim. phys., 1926, **23**, 829—840).—A simple and convenient apparatus in which gases can be purified and measurements made of their vapour pressures is described. Complete liquefaction at constant pressure and at two different constant temperatures constitutes the criterion of purity. R. W. LUNT.

Apparatus for the measurement of the speeds of absorption of gases by liquids. P. RIOU (Compt. rend., 1927, **184**, 195—197).—An apparatus is described the main feature of which is the gradual drawing of water into a graduated burette by means of the low pressure produced in the absorption tube. The speed is measured by a chronometer, the absorbing liquid in the meantime being automatically stirred.

For high rates of absorption, the absorbing vessel is replaced by a tube drawn out at the absorbing surface. The method gives concordant results and regular curves for a large range of rates of absorption, with or without chemical action. J. GRANT.

Application of eudiometer discharges to the demonstration of the synthesis of nitric oxide and the decomposition of methane. S. PLESNIEWICZ (Rocz. Chem., 1926, **6**, 741—742).—Two lecture demonstrations are described. R. TRUSZKOWSKI.

Mineralogical Chemistry.

Variations in density of the atmosphere. A. STOCK and G. RITTER.—See B., 1927, 74.

Radioactivity and the heat of the earth. R. W. LAWSON (Nature, 1927, **119**, 277—278).—Evans' view that an appreciable proportion of the energy liberated by the radio-elements, when they occur as rock constituents, is absorbed in ways other than raising the temperature of the rocks is contested. A. A. ELDRIDGE.

Walchowite. W. FUCHS and G. LANDSMANN (Ber., 1927, **60**, [*B*], 246—249).—Walchowite, an organic mineral from Mähren, *d* 1·1, hardness 1·5—2, acid value 0, saponification value 42·5, iodine value (Hanus) 33·2, is a polymerised resin which gives sesquiterpene alcohols when distilled with zinc dust. When mixed with silver powder and subjected to dry distillation, it yields a mixture of terpenes. It is converted by cold, concentrated sulphuric acid into an amorphous material soluble in chloroform which, according to its colour reactions, is related to the terpenes. H. WREN.

Uranium minerals of Katanga. A. L. HACQUAERT (Natuurwetensch. Tijdschr., 1926, **8**, 131—139).—Methods of identifying the minerals are described. Colour is determined by aid of the Ostwald atlas, optical properties with the polarising microscope; for coefficients of refraction, solid mixtures of piperine with arsenic or antimony iodides (n=1·8—2·07) or of sulphur and selenium (2·1—2·7) are required, as the indices of most of the minerals are too high for the ordinary liquids. Dehydration curves are constructed by heating for definite times to definite rising temperatures; the curves so obtained, and physical properties, serve to distinguish different varieties of the same or similar chemical composition. Uranium is best separated in solution as ammonium uranyl carbonate, precipitated and filtered as ammonium uranate, and weighed as U_3O_8. Uranium present as the dioxide is determined by dissolving in 15% sulphuric acid, in a Carius tube filled with carbon dioxide, at 180°, afterwards titrating with permanganate. For determination of the uranium where phosphates are present, the method of Schoep and Steinkuhler (A., 1922, ii, 530) is recommended. S. I. LEVY.

Helium content of some Japanese minerals. J. SASAKI (Bull. Chem. Soc. Japan, 1926, **1**, 253—254).—Travers' observation (A., 1899, ii, 769), that nearly half of the helium contained in most minerals is evolved on heating, is used to determine the helium content of fergusonite, monazite, and beryl. From the data thus obtained, the geological age of the two first-named minerals is discussed. A. S. CORBET.

Three South African meteorites. G. T. PRIOR (Min. Mag., 1926, **21**, 188.—193)—A mass of iron weighing about 26 lb. was found in 1918 on the Vaalbult farm, Prieska Division, Cape Province. The structure is that of a coarse octahedrite. Analysis gave Fe 92·18, Ni 6·99, Co 0·68, Cu 0·02, P 0·19, S trace, insoluble 0·02, total 100·08; *d* 7·62. On May 26, 1918, a stone fell near Witklip, Caroline District, Transvaal. It is a grey bronzite-chondrite. Two or more stones were seen to fall on April 30, 1925, near Queen's Mercy, Matatiele, Griqualand East. The material is classed as a veined grey bronzite-chondrite. Analysis gave Fe(+Co) (14·26), Ni 1·35, FeS 5·42, insoluble silicate 44·48, soluble silicate 34·49%. The insoluble silicate (pyroxene) gave SiO_2 53·98, Al_2O_3 4·78, Cr_2O_3 0·36, FeO 9·28, MnO trace, CaO 2·03, MgO 25·19, Na_2O and loss (4·38)%. L. J. SPENCER.

Aramayoite, a new mineral, from Bolivia. L. J. SPENCER (Min. Mag., 1926, **21**, 156—162).—This was found in 1925 in a silver–tin vein in the Animas mine at Chocaya. It shows a confused aggregate of cleavage plates with iron-black colour and brilliant metallic lustre. In addition to the perfect basal cleavage, there are also good cleavages following a steep tetragonal pyramid. The mineral is pseudo-tetragonal. Streak black, *d* 5·602, *H* 2½. The powdered mineral is slowly decomposed by hot concentrated nitric acid with separation of a white precipitate, but hot concentrated hydrochloric acid has no action. Analysis by E. D. MOUNTAIN gave S 20·87, Sb 29·95, Bi 13·75, Ag 34·74, Cu 0·53, Fe trace, total 99·84, agreeing with the formula $Ag(Sb,Bi)S_2$. L. J. SPENCER.

Schultenite, a new mineral, from South-West Africa. L. J. SPENCER (Min. Mag., 1926, **21**, 149—155; cf. A., 1926, 1022).—Colourless platy crystals were found on balydonite pseudomorphous after mimetite and anglesite from Tsumeb. They are monoclinic ($a:b:c$ =0·8643 : 1 : 0·7181, β=84° 36′) and flattened parallel to the plane of symmetry, which is also the direction of good cleavage. Many crystal forms are present, and the table of angles gives the angles from each face to the three axial planes. (This method combines the advantages of both the arrangement of interfacial angles in zones and the latitude and longitude angles of two-circle goniometry.) The crystals are optically positive, with the optic axial plane perpendicular to the plane of symmetry; 2V 58°14′, n_α 1·8903, n_β 1·9097, n_γ 1·9765 (Na); *d* 5·943, *H* 2½. Analysis by E. D. MOUNTAIN gave PbO 63·97, As_2O_5 32·18, H_2O 2·88, total 99·03, corresponding with the formula $PbHAsO_4$. L. J. SPENCER.

Organic Chemistry.

Indirect interatomic effects in organic compounds. F. SWARTS (2me. Cons. Chim. Inst. Intern. Chim. Solvay, 1926, 199—236).—A review and discussion of sterie hindrance and of various theories advanced to explain the effects of certain atoms or radicals when present in a molecule on the remaining portion of the molecule. CHEMICAL ABSTRACTS.

Exceptional instances of stereoisomerism. J. K. SENIOR (Ber., 1927, **60**, [*B*], 73—81).—The number of stereoisomeric forms of a carbon compound of given structure is generally assumed to be 2^k (where k is the number of asymmetric carbon atoms), provided the development of the full number of forms is not impeded by internal compensation or by the strain set up by the production of condensed ring systems. It is, however, possible to synthesise saturated non-cyclic compounds which contain a clearly-defined number of asymmetric carbon atoms and exist in optically active forms in number less than 2^k, although the molecules are free from strain and incapable of internal compensation (cf. the ethyl α-bromo-ββ-dibromodimethylpropanetricarboxylate of Beesley and Thorpe, J.C.S., 1920, **117**, 619). It is shown that if a is a symmetrical, saturated, non-cyclic substituent and x, y, z, and v are four structurally different non-cyclic substituents in which n, m, p, and q asymmetric carbon atoms are present in straight chains, the number of isomerides of the given types is given by the formulæ: $Caxxx$, $(2^{3n}+2^{n+1})/3$; $Caxxy$, 2^{2n+m}; $Caxyz$, $2^{n+m+p+1}$; $Nxxx$, $2^n(2^n+1)(2^n+2)/6$; $Nxxy$, $(2^{2n+m}+2^{n+m})/2$; $Nxyz$, 2^{n+m+p}; $Cxxxx$, $(2^{4n}+11\times2^{2n})/12$ (including 2^{n-1} non-divisible *meso*-forms; $Cxxxy$, $(2^{3n+m}+2\times2^{n+m})/3$; $Cxxyy$, $(2^{2n+2m}+2^{n+m})/2$; $Cxxyz$, 2^{2n+m+p}; $Cxxzv$, $2^{n+m+p+q+1}$. If k is the total number of asymmetric carbon atoms in the substituents, the number of isomerides is smaller than 2^k in the types, $Caxxx$, $Nxxx$, $Nxxy$, $Cxxxy$, and $Cxxyy$, although none of these types permits the existence of non-divisible *meso*-forms and the molecules are free from strain in all cases. H. WREN.

Crystalline, blue ψ-nitrole. H. RHEINBOLDT and M. DEWALD (Ber., 1927, **60**, [*B*], 249—251).—*ββ-ψ-Nitrole-αγ-diphenylpropane*, $(CH_2Ph)_2C{:}N_2O_3$, m. p. 88° (decomp.), is prepared by the action of ethyl nitrite and nitric acid (d 1·4) on an ethereal solution of dibenzyl ketoxime or from the latter substance and an excess of nitrogen tetroxide. The blue crystals retain their colour at the temperature of liquid air; in hydrocyanic acid at −10°, they are unimolecular. Although stable in the dark, they rapidly decompose on exposure to light, with production of *ββ-dinitro-αγ-diphenylpropane*, m. p. 132°, also prepared by oxidation of the ψ-nitrole with nitric acid in glacial acetic acid solution. H. WREN.

Decomposition of ethyl alcohol at the surface of thoria. I. II. G. I. HOOVER and E. K. RIDEAL. —See this vol., 215.

An erythritol of the acetylenic series. J. SALKIND and E. KOMAROWSKAJA (Ber., 1927, **60**, [*B*], 182—184).—Benzoin is converted by the magnesium derivative of dibromoacetylene into *αβεζ-tetrahydroxy-αβεζ-tetraphenyl-Δγ-hexinene*, m. p. 218—219°. The substance is acetylated with difficulty to the *triacetate*, m. p. 83—85°. Bromine is added very slowly. The constitution is established by its conversion by solid potassium hydroxide at 100° into acetylene and benzoic acid. It is oxidised by permanganate in acetone solution to carbon dioxide, benzaldehyde, and benzoic acid. H. WREN.

Mutual transformations of alkyl phosphites. M. JANCZAK (Rocz. Chem., 1926, **6**, 774—793).—Sodium diethyl, dipropyl, and di*iso*butyl phosphites are converted by the action of silver nitrate into the corresponding silver salts, which are also produced, although in smaller yield, from the corresponding acids. This supports the view that phosphorus is tervalent in the ester salts, but quinquevalent in the acid esters. Sodium ethoxide reacts with diethyl hydrogen phosphite to yield diethyl sodium phosphite, ethyl sodium hydrogen phosphite, EtO·PH(O)·ONa, ethyl ether, and alcohol. With diethyl ethylphosphite, it reacts as follows: $(EtO)_2PEt{:}O+Et{\cdot}ONa\longrightarrow EtO{\cdot}PEt(O){\cdot}ONa+Et_2O$, whilst no reaction takes place with triethyl phosphite, sodium ethyl hydrogen phosphite, or sodium ethyl hydrogen ethylphosphite, EtO·PEt(O)·ONa. R. TRUSZKOWSKI.

Resolution of asymmetric glycerides into their antipodes. I. Optically active glyceride sulphuric acids and the thermolability of the optical activity of their salts. II. Optically active glyceride phosphoric acids and the thermolability of the optical activity of their salts. A. GRÜN and R. LIMPÄCHER (Ber., 1927, **60**, [*B*], 255—265, 266—272).—I. αβ-Distearin is converted by cautious treatment with chlorosulphonic acid in the presence of light petroleum into αβ-distearin hydrogen sulphate (cf. Grün and Corelli, A., 1912, i, 409), from which the brucine and strychnine salts are readily obtained in quantitative yield. Under definite conditions, decomposition of the salts into alkaloid hydrogen sulphate and free diglyceride can be effected, but it is very difficult to prevent the conversion of a considerable proportion of the diglyceride into its structural isomeride. This greatly complicates the fractional crystallisation of the alkaloidal salts, but it has been found possible to separate l-*strychnine* dl-*αβ-distearin sulphate* into fractions exhibiting marked differences in solubility. The distearin preparations isolated from the individual fractions are practically inactive, and latent activity cannot be detected when they are examined in thionyl chloride solution. The result is, however, not unexpected, since activity has not been detected in preparations of α-monostearin etc. which are undoubtedly asymmetric and derived from initially active material. The potassium salts of *d*- and *l*-αβ-distearin sulphate, prepared by treating the separate fractions of the strychnine salt dissolved in acetone with alcoholic potassium hydroxide, are almost or completely inactive in solvents at tem-

peratures of 40° and above. If, however, they are cooled below 35°, whereby they assume the properties of typical colloidal solutions, great activity is observed. If the observations of the minimal activity at higher temperature are trustworthy, cooling causes first a diminution in specific rotation, which passes through zero and then increases with time to a constant maximum (up to about $[\alpha]_D$ 10,000° in very dilute solution) in the other direction. The process is reversible, since the cold, highly-active solution passes into an inactive (apparently true) solution when warmed, which again becomes active when cooled. The phenomenon is shown to be due to the optical activity of the potassium salt, and not to a physical cause such as the double refraction of the solution, since it is not exhibited by the potassium salt of the corresponding racemic compound or of the non-resolvable αγ-distearin sulphate.

Strychnine αγ-distearin sulphate, $[\alpha]_D^{17.5}$ −10·2 to 10·7° in chloroform, is described. Elimination of strychnine sulphate from it gives a product containing 93% of αγ-distearin and 7% of the αβ-isomeride. Fractional crystallisation of the strychnine salt and conversion of the individual fractions into the potassium salts yields optically inactive products in all cases except one, in which the activity is doubtless due to the αβ-compound formed by isomerisation.

II. The production of αβ-distearin hydrogen phosphate from αβ-distearin and phosphoric anhydride proceeds less smoothly than the analogous preparation of αβ-distearin hydrogen sulphate, since the primary ester readily becomes converted into secondary ester and phosphoric acid, $2(OH)_2PO\cdot OR = OH\cdot PO(OR)_2 + PO(OH)_3$. Although this change involves about a half of the primary ester, it does not cause serious further difficulty, since the salts of the two series differ widely in solubility. The αβ-ester and its salts, however, show a pronounced tendency towards isomerisation to the αγ-compound. Nevertheless, it has been found possible to separate the strychnine salt into fractions which, after transformation into the corresponding potassium salts, behave as optical antipodes. The thermolability of the specific rotation of these salts resembles that of the corresponding sulphates, but is less marked. The warm solutions do not exhibit appreciable activity, but become active when cooled to an extent which is very considerable in comparison with the activity of glycerides synthesised from optically active materials. The following substances are incidentally described: *strychnine* r-αβ-*distearin* γ-*phosphate*, m. p. about 195°, decomp. 200°, $[\alpha]_D^{17.5}$ −14·7° in chloroform, and the corresponding *potassium* salt; *strychnine di-αβ-distearin phosphate*, $[C_3H_5(O\cdot CO\cdot C_{17}H_{35})_2O]_2PO\cdot OH, C_{21}H_{22}O_2N_2$, m. p. 63—65° after softening at 59°, and the *potassium* salt.

H. WREN.

Glycerolphosphoric acids. P. KARRER and P. BENZ (Helv. Chim. Acta, 1927, **10**, 87—91).—The *diacetate*, $[\alpha]_D$ +2·0° (±0·1°), of barium *d*-glycerol-α-phosphate is hydrolysed by barium hydroxide to barium *d*-glycerol-α-phosphate (cf. A., 1926, 818). This is optically inactive, but when reacetylated yields a diacetate having $[\alpha]_D$ +1·8° (±0·2°). The hydrolysis is therefore not accompanied by a displacement of the phosphate radical to the β-position. Lecithin, which is hydrolysed by an exactly similar method, giving principally glycerol-β-phosphoric acid (*ibid.*, 384), must, accordingly, be for the most part a derivative of the latter (cf. Grün and Limpächer, preceding abstract).

H. E. F. NOTTON.

Synthesis of lecithins. II. A. GRÜN and R. LIMPÄCHER (Ber., 1927, **60**, [*B*], 147—150; cf. A., 1926, 827).—αγ-Distearin, heated somewhat above its m. p., is treated successively with phosphoric oxide and choline hydrogen carbonate, whereby the *endo*-salt of *choline αγ-distearoylglycerol-β-phosphate*, $\begin{matrix}NMe_3\cdot O\\ C_2H_4\cdot O\end{matrix}>PO\cdot O\cdot CH(CH_2\cdot O\cdot CO\cdot C_{17}H_{35})_2$, m. p. 195° after softening at 84°, decomp. 198°, is obtained. The new lecithin so closely resembles that derived from αβ-distearin (*loc. cit.*) that possible identity is not excluded. Two by-products, m. p. 166° after softening at 77° and m. p. 167° after softening at 82°, possibly choline salts of the composition $OH\cdot C_2H_4\cdot NMe_3\cdot O\cdot PO[O\cdot C_3H_5(O\cdot CO\cdot C_{17}H_{35})_2]_2$, are described.

H. WREN.

Syntheses of kephalins. A. GRÜN and R. LIMPÄCHER (Ber., 1927, **60**, [*B*], 151—156).—αβ-Distearin is treated successively at 71—72° with phosphoric oxide and β-hydroxyethylamine carbonate, whereby a mixture of β-aminoethyl phosphate and *β-aminoethyl hydrogen αβ-distearoylglycerol-γ-phosphate*, $C_2H_3(O\cdot CO\cdot C_{17}H_{35})_2\cdot CH_2\cdot O\cdot PO(OH)\cdot O\cdot C_2H_4\cdot NH_2$ (possibly formulated as the *endo*-salt), m. p. 176° after softening at 78—80°, decomp. above 185°, is produced. The kephalin is neutral towards lacmoid, acidic towards phenolphthalein. It is very readily hydrolysed by alkali hydroxide and rapidly suffers ester transformation in presence of alcoholic hydrogen chloride. αγ-Distearin similarly yields *β'-aminoethyl hydrogen αγ-distearoylglycerol-β-phosphate*, m. p. 177° after softening at 80°, decomp. 185°. The properties of the two kephalins are so nearly identical that it is regarded as possible that the same kephalin or mixture of symmetrical and unsymmetrical kephalins is obtained from both distearins. Indications of the presence of isomerides have not been obtained.

H. WREN.

Simple reaction for the thiol group. H. RHEINBOLDT (Ber., 1927, **60**, [*B*], 184—186).—Solid sodium nitrite is covered with a solution of the substance under investigation in ether, alcohol, light petroleum, chloroform, carbon tetrachloride, benzene, or other solvent, and dilute sulphuric acid is added so that a rapid stream of nitrous gases passes through the liquid; if glacial acetic acid is the solvent, sodium nitrite crystals are cautiously added. The colours are developed immediately (cf. Rheinboldt, A., 1926, 819). Alternatively, if possible, the alcoholic solution of the substance is mixed with an aqueous-alcoholic solution of sodium nitrite and acidified with acetic acid; the colours develop gradually and are stable in concentrated but evanescent in exceedingly dilute solution. The limits of sensitiveness are ethylmercaptan (1 : 7500), thiophenol (1 : 25,000), triphenylthiocarbinol (1 : 7500). The method is more delicate than that of Lecher and Siefken (this vol., 39).

H. WREN.

Lengthened chain compounds of sulphur. P. C. RAY (Nature, 1927, **119**, 124).—Polemical (cf. Bennett, A., 1926, 1123). A. A. ELDRIDGE.

Trichloromethylsulphonyl chloride. M. BATTEGAY and W. KERN (Bull. Soc. chim., 1927, [iv], **41**, 34—47).—Trichloromethylsulphonyl chloride is slowly decomposed by cold water, the rate of decomposition being rather greater than in the case of *p*-toluenesulphonyl chloride. Sulphurous acid appears to be formed first, $CCl_3{\cdot}SO_2Cl \longrightarrow CCl_3{\cdot}SO_3H \longrightarrow CCl_2(OH){\cdot}SO_3H \rightarrow CCl(OH)_2{\cdot}SO_3H \rightarrow CO(OH){\cdot}SO_3H \rightarrow CO_2+SO_2+H_2O$, but is immediately oxidised by the dichlorocarbinolsulphonic acid to sulphuric, hydrochloric, and trichloromethylsulphinic acids, the last ultimately decomposing into chloroform and sulphur dioxide. With ethyl alcohol, trichloromethylsulphinic acid is formed directly, the alcohol undergoing reduction to acetaldehyde, the sulphinic acid as before affording finally chloroform and sulphur dioxide. A similar reaction occurs with ammonia or with primary amines, the corresponding sulphinate being formed, accompanied by the evolution of nitrogen in the case of ammonia, and of sulphur dioxide in the case of amines, the amine being partly oxidised to indulines (cf. McGowan, A., 1884, 1126). The *aniline*, m. p. 145°, and *m-toluidine*, m. p. 140°, salts of trichloromethylsulphinic acid are described. *o*-Phenylenediamine in alcohol affords 2 : 3-diaminophenazine. No reaction was obtained with 2-aminoanthraquinone in solvents other than nitrobenzene, in which the trichloromethylsulphonyl chloride attacked the solvent, liberating carbonyl chloride, which afforded 2 : 2′-dianthraquinonylcarbamide. Aluminium chloride and benzene yield triphenylcarbinol, with evolution of sulphur dioxide and hydrogen chloride. Keten was not obtained by the action of zinc, or of a mixture of zinc and copper, or of iron in dry ether, the reaction product, m. p. 180°, being contaminated with unchanged sulphonyl chloride. R. BRIGHTMAN.

Organic molecular compounds with co-ordination centres. I. H. RHEINBOLDT.—See this vol., 242.

Addition of alkali alkoxide to esters. III. Addition of alkali alkoxide to ethyl formate. F. ADICKES (Ber., 1927, **60**, [*B*], 272—277; cf. A., 1925, i, 1378; this vol., 41).—Contrary to the observations of Scheibler (A., 1926, 711), the addition of sodium ethoxide to ethyl formate leads to the production, not of sodiumoxyethoxymethylene, but of *sodiumoxydiethoxymethane*, $CH(ONa)(OEt)_2$, the composition of which is deduced from analyses and is in harmony with the insolubility of the compound in ether or light petroleum and its free solubility in alcohol. Unlike other additive compounds, it is decomposed by water thus: $CH(ONa)(OEt)_2+H_2O \longrightarrow NaOH+CH(OH)(OEt)_2 \longrightarrow H_2O+C(OEt)_2$. Scheibler's conception of the hydrolysis, $C(ONa)(OEt)+H_2O \longrightarrow NaOH+CO+Et{\cdot}OH$, cannot be maintained, since carbon monoxide is evolved only in minimal amounts. The production of sodium hydroxide by the hydrolysis is not quite quantitative, since a small proportion of the metal is found as sodium formate. Sodiumoxydiethoxymethane is transformed by phosphoryl chloride and sodium ethoxide into diethoxymethylene (carbon monoxide diethylacetal) thus: $2CH(ONa)(OEt)_2+POCl_3 \longrightarrow CHCl(OEt)_2+NaCl$; $CHCl(OEt)_2=C(OEt)_2+HCl$; $HCl+Na{\cdot}OEt \longrightarrow NaCl+EtOH$. H. WREN.

Mechanism of the catalytic decomposition of esters by nickel. J. N. PEARCE and C. N. OTT.—See this vol., 215.

Preparation of ethoxalyl chloride. R. BARRE (Bull. Soc. chim., 1927, [iv], **41**, 47—49).—Yields of 84% of ethoxalyl chloride are obtained by mechanical agitation of the mixture of phosphorus pentachloride and ethyl oxalate at 110—115°, and decomposition of the dichloride, $CO_2Et{\cdot}CCl_2{\cdot}OEt$, with reduced platinum. At 125—135°, the yield is only 55%. R. BRIGHTMAN.

Velocity of autocatalytic decomposition of bromosuccinic acid in aqueous solutions. J. ZAWIDZKI and W. WYCZALKOWSKA.—See this vol., 214.

Penthian series. I. Action of sodium ethoxide on ethyl β-thiodipropionate. G. M. BENNETT and L. V. D. SCORAH (J.C.S., 1927, 194—200).—Ethyl β-thiodipropionate undergoes the Dieckmann reaction with sodium ethoxide, forming the enolic ester *ethyl* Δ^3*-penthien-4-ol-3-carboxylate*, b. p. 150—151°/16 mm., d_4^{20} (vac.) 1·2011, n^{20} 1·51574, n_β^{20} 1·52938 (*phenylpyrazolone*, m. p. 219°; p-*bromophenylpyrazolone*, m. p. 221·5°; p-*nitrophenylpyrazolone*, m. p. 210·5°). The enolic ester, on keeping, deposits crystals of the keto-tautomeride *ethyl penthian-4-one-3-carboxylate*, m. p. 59°; *barium* salt (from either ester). Hydrolysis of the cyclic ester yields *penthian-4-one*, m. p. 65—66°; *oxime*, m. p. 84—85°; *semicarbazone*, m. p. 151°; 2 : 4-*dinitrophenylhydrazone*, m. p. 186°; *dibenzylidene* derivative, m. p. 149—151°; *dipiperonylidene* derivative, m. p. 181°; *chloroplatinate*; *sulphonium methiodide*, m. p. 112—113° (decomp.). B. W. ANDERSON.

Alkali and alkaline-earth salts of bismuthotartaric acid. C. PRADEL (Anal. Fís. Quím., 1926, 24, 600—610; cf. Portillo, A., 1926, 1025).—The preparation of *salts* of the composition $[Bi_3(C_4H_4O_6)_7]R'_4{,}xH_2O$ or $[Bi_3(C_4H_4O_6)_7]R''_2{,}xH_2O$, where R′=potassium, sodium, or ammonium, and R″=barium or calcium, is described. In addition, new *compounds*, $K_2[BiO(C_4H_3O_6)]{,}5H_2O$, $(NH_4)_2[BiO(C_4H_3O_6)]{,}2H_2O$, $Na[BiO(C_4H_4O_6)]$, and $NH_4[BiO(C_4H_4O_6)]$, are described. G. W. ROBINSON.

Double citrates of quadrivalent vanadium. G. CANNERI (Gazzetta, 1926, 56, 901—902).—A correction (cf. this vol., 42); to the formula of each citrate described there should be added one oxygen atom, through which the two vanadium atoms are joined. E. W. WIGNALL.

Mechanism of the formation of citric and oxalic acids from sugars by *Aspergillus niger*. I. F. CHALLENGER, V. SUBRAMANIAM, and T. K. WALKER (J.C.S., 1927, 200—208).—When the sugar in Molliard's culture medium is replaced by citric acid, *Aspergillus niger* produces malonic acid, glyoxylic acid, and acetone. With calcium acetate, glyoxylic

and oxalic acids are formed, and with dipotassium saccharate there are strong indications of citric acid being produced. B. W. ANDERSON.

d-Galacturonic acid from pectins. K. SMOLEŃSKI and W. WŁOSTOWSKA (Rocz. Chem., 1926, **6**, 743—746).—A *monohydrate* of *d*-galacturonic acid, m. p. 116—120°, isolated from beet pulp, is described. R. TRUSZKOWSKI.

β-Chloroglutaconic anhydride. R. MALACHOWSKI and T. KALIŃSKI (Rocz. Chem., 1926, **6**, 768—773; cf. A., 1926, 732).—*β-Chloroglutaconic anhydride*, m. p. 113—114°, is obtained from the corresponding acid. From it are prepared, by condensation with cinnamaldehyde, *4-chloro-6-hydroxy-5-cinnamylidene-α-pyrone*, m. p. 171—172°, with diazobenzene, *4-chloro-6-hydroxy-α-pyrone-5-phenylhydrazone*, m. p. 204°, and by bromination *3-chloro-2-bromo-6-hydroxy-α-pyrone*, m. p. 107·5°, which on hydrolysis yields *β-chloro-α-bromoglutaconic acid*, m. p. 131—132°. R. TRUSZKOWSKI.

Optical superposition. VIII. *l*-Menthylamine, brucine, and strychnine salts of mucic and *allo*mucic acid. T. S. PATTERSON and J. D. FULTON (J.C.S., 1927, 50—53).—The preparation and optical examination of the following salts were carried out in duplicate: *menthylamine mucate*, m. p. 198° (decomp.), $[\alpha]_{5461}^{19\cdot5}$ −32·25° and −31·75°; *menthylamine* allo*mucate*, m. p. 173° (decomp.), $[\alpha]_{5461}^{19\cdot5}$ −31·50° and −31·00°; *brucine mucate*, decomp. 150°, +1·35°, $[\alpha]_{5461}$ +1·15°; *brucine* allo*mucate*, decomp. 170°, $[\alpha]_{5461}^{17}$ −1·10°, $[\alpha]_{5461}^{20}$ −0·95°; strychnine mucate, decomp. 273°, +7·93°, +7·57°; *strychnine* allo*mucate*, decomp. 269°, $[\alpha]_{5461}^{17\cdot5}$ +7·07°, $[\alpha]_{5461}^{5}$ +6·86°. These results, in opposition to the principle of optical superposition, show that mucic and *allo*mucic acids differ in their effect in determining the rotation of compounds formed from these acids and the same active base. B. W. ANDERSON.

Preparation and properties of arabono- and ribono-lactones. V. HASENFRATZ (Compt. rend., 1927, **184**, 210—213).—Arabono- and ribono-lactones are obtained by modifications of the methods of Bauer (A., 1886, 869) and of Fischer and Piloty (*ibid.*, 1892, 437), respectively. An aqueous solution of arabinose is oxidised by bromine, the solution neutralised with potassium hydroxide, and treated with crystalline calcium chloride. The syrup of the arabonolactone (*dibenzoate*, m. p. 200°; *tribenzoate*, m. p. 120°) obtained by decomposition of the calcium arabonate with oxalic acid and concentration in a vacuum crystallises spontaneously. To convert it into ribonolactone, the arabonolactone (500 g.) is heated under reflux with 280 g. of pyridine and 65 g. of water for 3 hrs., neutralised with milk of lime, and the pyridine distilled off in a vacuum. Calcium arabonate is removed from the filtrate by crystallisation, the lactone freed from its calcium salt by oxalic acid, the solution of ribonic acid boiled with cadmium oxide, filtered, and the cadmium salt caused to crystallise by the addition of one fifth the volume of alcohol. Decomposition of the cadmium salt in aqueous solution with hydrogen sulphide and concentration of the solution of the lactone yields a syrup which readily crystallises. Crystallised from alcohol, ribonolactone has m. p. 84—86° (Fischer and Piloty, *loc. cit.*, give 72—74°) (*tribenzoate*, $[\alpha]_D$ +11·1°). On distillation, either lactone gives a 35% yield of a mixture of pyromucic and *iso*pyromucic acids. J. W. BAKER.

Reactions of nitrosyl chloride. III. Action of nitrosyl chloride on aliphatic aldoximes. H. RHEINBOLDT and M. DEWALD (Annalen, 1927, **451**, 273—281).—The chloronitroso-derivatives formed by the action of nitrosyl chloride on aliphatic aldoximes in ethereal solution, unlike the corresponding aromatic derivatives (this vol., 245), are comparatively stable, crystalline, colourless bimolecular solids of penetrating odour, which dissociate when heated alone, or in solution, into deep blue, unimolecular liquids, the change being reversible. On keeping, they pass more or less rapidly into the corresponding chloro*iso*nitroso-derivatives. Liebermann's and other nitroso-reactions are positive. The *αα-chloronitroso*-derivatives of methane, m. p. 62°, with previous sintering; ethane (cf. Piloty and Steinbock, A., 1902, i, 735); propane, m. p. 56—57°; *n*-butane, m. p. 41—42°; *iso*butane, $CHMe_2{\cdot}CH_2{\cdot}CHCl{\cdot}NO$, m. p. 36—38°, and *n*-heptane, m. p. 43°, are described. The compounds prepared analogously from *n*-octylaldoxime, *iso*valeraldoxime, and phenylacetaldoxime could not be obtained crystalline. H. E. F. NOTTON.

Condensation of oximes with thiocarbimides. Autoxidation of the additive compounds from oximes and thiocarbimides. C. V. GHEORGHIU (Bull. Soc. chim., 1927, [iv], **41**, 50—53; cf. Pawlewski, A., 1904, i, 237).—The additive compounds of oximes with thiocarbimides are unstable; those derived from aldoximes (*syn-* and *anti-*) decompose spontaneously into a nitrile, a thiocarbanilide, and carbonyl sulphide. The mechanism is probably $[R{\cdot}CH{:}NO{\cdot}CS{\cdot}NHR'] \longrightarrow R{\cdot}CN+[R'{\cdot}NH{\cdot}CS{\cdot}OH]$: $2[R'{\cdot}NH{\cdot}CS{\cdot}OH]=CS(NHR')_2+COS+H_2O$. There is also some separation of sulphur, probably from autoxidation. Ketoximes afford additive compounds which undergo autoxidation to products identical with those obtained by Goldschmidt from the condensation of oximes with carbimides (cf. A., 1893, i, 707), *e.g.*, $Ph{\cdot}NCS+CMe_2{:}N{\cdot}OH=CMe_2{:}NO{\cdot}CS{\cdot}NHPh$

$$CMe_2{\cdot}NO{\cdot}C(NHPh)\!<\!\overset{S}{O}\!>\!O \longrightarrow$$

$CMe_2{:}NO{\cdot}CO{\cdot}NHPh+[SO]$; the thiosulphuric anhydride decomposes into sulphur and sulphur dioxide, and the latter is finally oxidised to sulphuric acid, the separation of sulphur affording an indication of the extent of the reaction. The autoxidation is not inhibited by iodine, ether, acetaldehyde, or quinol, these substances exerting a positive instead of their usual negative catalytic action. Solvents do not affect the autoxidation, but the reaction is slower in hydrocarbons than in alcohol or ether. The oximes of diketones, phenylhydroxamic acid, oximinolævulic acid, and tetramethyldiaminobenzophenoneoxime do not react with thiocarbimides. Resacetophenoneoxime does not react with *o*-tolylthiocarbimide. The behaviour of α- and β-benzaldoximes, acetaldoxime, heptaldoxime, salicylald-

oxime, α- and β-anisaldoxime, and α- and β-furfuraldoxime with phenylthiocarbimide, and, in the first three cases, with *o*- and *p*-tolylthiocarbimides; the reactions of these three thiocarbimides with the oximes of acetone, acetophenone, methyl ethyl ketone, and methyl *iso*butyl ketone, and of phenyl thiocarbimide with those of resacetophenone, benzophenone, methyl *p*-tolyl ketone, methyl propyl ketone, and camphor were also examined. The O-*phenylcarbamates* of methyl ethyl ketoxime (m. p. 135°), diethyl ketoxime (m. p. 96—98°), methyl propyl ketoxime (m. p. 146°), methyl *iso*butyl ketoxime (m. p. 117°), resacetophenoneoxime (m. p. 126°), *p*-tolyl methyl ketoxime (m. p. 112°), and camphoroxime (?) (m. p. 148°) are described, together with the O-o-*tolylcarbamates* of methyl ethyl ketoxime (m. p. 80°), acetoxime (m. p. 146—147°), methyl *iso*butyl ketoxime (m. p. 184°), and acetophenoneoxime (m. p. 108—109°), and the O-p-*tolylcarbamates* of methyl ethyl ketoxime (m. p. 146—147°), acetoxime (m. p. 105—106°), and acetophenoneoxime (m. p. 126°). R. BRIGHTMAN.

Relation between rotatory power and structure in sugar group. I. C. S. HUDSON (U.S. Bur. Standards Sci. Paper 533, 1926, **21**, 241—384).—A summary of the author's earlier work, and a collection of 10 papers published during 1924—1925. A table of the rotatory powers of 104 pure substances examined during the course of the work is given.

H. BURTON.

Degradation of *d*-glucose and *d*-α-glucoheptose. G. ZEMPLEN and D. KISS (Ber., 1927, **60**, [*B*], 165—170).—Penta-acetylgluconononitrile, m. p. 84°, $[\alpha]^{22}$ +46·2° in chloroform, is prepared in 56·8% yield by the action of acetic anhydride and sodium acetate on crude *d*-glucoseoxime freed as far as possible from water. It is converted by sodium methoxide in presence of chloroform into *d*-arabinose in 71·5% yield. Deacetylation of the nitrile previous to degradation causes somewhat poorer yields of *d*-arabinose.

d-α-Glucoheptonolactone is converted by alcoholic ammonia into d-α-*glucoheptonamide*, m. p. 129°, $[\alpha]_D$ +9·1° in water, which is transformed into its *acetate*, m. p. 165°, $[\alpha]^{20}$ +17·4° in chloroform, and thence by phosphoryl chloride into d-α-*hexa-acetylglucoheptononitrile*, m. p. 112·5—113·5°, $[\alpha]_D^{21}$ +24·6° in chloroform; the latter substance is also derived from α-glucoheptose by successive oximation and acetylation. When degraded in the usual manner, it affords dextrose, identified as *d*-β-penta-acetyl glucose.

Penta-acetyl-d-*gluconamide*, m. p. 183·5—184°, $[\alpha]_D^{18}$ +20·8° in pyridine, is prepared from the corresponding nitrile by the action of glacial acetic acid and hydrogen bromide. H. WREN.

Deamination of γ-aminohexoses. P. A. LEVENE and H. SOBOTKA (J. Biol. Chem., 1926, **71**, 181—185).—After deamination of epiglucosamine, and treatment of the resulting solution with phenylhydrazine acetate, there was obtained an *osazone*, m. p. 160°, decomp. 185—190°, $[\alpha]^{20}$ −24° to −44°, mutarotating to −8° in methyl alcohol. This osazone appears to be different from that of the γζ-anhydroglucose of Fischer and Zach (A., 1912, i, 239), indicating the possibility that the product of deamination of epiglucosamine is γζ-anhydroallose.

C. R. HARINGTON.

Acetone sugars. XI. Synthesis of a ζ-glucosidogalactose. K. FREUDENBERG, A. NOE, and E. KNOPF (Ber., 1927, **60**, [*B*], 238—241; cf. following abstract).—Di*iso*propylidenegalactose is converted by acetobromoglucose and silver oxide in the presence of carbon tetrachloride into *tetra-acetylglucosidodi*iso*propylidenegalactose*, m. p. 141°, $[\alpha]_D^{22}$ −52·6° in *s*-tetrachloroethane, which is hydrolysed by barium hydroxide to *ζ-glucosidodi*iso*propylidenegalactose*, m. p. 84—88°, $[\alpha]^{20}$ −67·5° in water. The latter compound is transformed by very dilute acid mainly into *ζ-glucosidogalactose*, $[\alpha]_D^{19}$ +8·2° to +20·6° in water (*osazone*, m. p. 200°).

Amended instructions are given for the preparation of di*iso*propylidenegalactose and acetobromoglucose.

H. WREN.

Acetone sugars. X. γ-Thioglucose. K. FREUDENBERG and A. WOLF (Ber., 1927, **60**, [*B*], 232—238; cf. A., 1926, 601).—Di*iso*propylideneglucose is converted by successive treatment with sodium, carbon disulphide, and methyl iodide into *methyl di*iso*propylideneglucose-γ-xanthate*, b. p. 156—162°/1 mm., m. p. 61°, $[\alpha]_{5780}^{18}$ −12·82° in *s*-tetrachloroethane, which is transformed at 290—300° into *methyl di*iso*propylideneglucose-γ-dithiocarbonate*, m. p. 142°, $[\alpha]_{5}^{16}$ −59·91° in *s*-tetrachloroethane. The latter ester is converted by methyl-alcoholic ammonia in the absence of air into methylmercaptan, carbamide, and the non-crystalline *γ-thioglucose di*iso*propylidene ether*, which when treated successively with sodium and methyl iodide affords *γ-methylthioglucose di*iso*propylidene ether*, m. p. 43°, $[\alpha]_{5780}^{22}$ −26·5° in *s*-tetrachloroethane. The non-crystalline *γ-methylthioglucose*, obtained by hydrolysis of the di*iso*propylidene ether with dilute sulphuric acid, gives a *tetra-acetate*, m. p. 94°, $[\alpha]_{5}^{21}$ + 24·65° in *s*-tetrachloroethane. *Bisdi*iso*propylideneglucosyl disulphide*, m. p. 163°, $[\alpha]_{5780}^{21}$ −330·1° in *s*-tetrachloroethane, is described; it is hydrolysed to *diglucosyl disulphide*, $[\alpha]_{5780}^{20}$ +29·85° in water.

In an analogous manner, mannose di*iso*propylidene ether yields *methyl di*iso*propylidenemannosexanthate*, m. p. 80—82°, $[\alpha]_{5780}^{1}$ +69·30° in *s*-tetrachloroethane, and the corresponding *thiocarbonate*, m. p. 158—159°. Mannose di*iso*propylidene ether is converted by oxalyl chloride and pyridine in the presence of chloroform into the corresponding *oxalate*, m. p. 138°, $[\alpha]_{5780}$ +83·44° in *s*-tetrachloroethane, which when heated gives small yields of the *carbonate*, m. p. 186—187°. *Methyl di*iso*propylidenegalactosexanthate*, m. p. 162—163°, $[\alpha]_{5780}^{16}$ −67·3° in *s*-tetrachloroethane, is described. A modified method is given for the preparation of mannose di*iso*propylidene ether, which is transformed by phosphorus pentachloride into *di*iso*propylidenemannose-α-chlorohydrin*, b. p. 119°/1 mm., $[\alpha]_D^{21}$ + 85·7°. H. WREN.

Constitution of disaccharides. R. WEIDENHAGEN (Z. Ver. Deuts. Zucker-Ind., 1927, 73—85).—An account of recent work on the constitution of disaccharides. H. BURTON.

Position of the sugar nucleus in the quercitin glucosides. G. F. ATREE and A. G. PERKIN (J.C.S., 1927, 234—240).—Rutin (quercetin in union with rutinose), xanthorhamnin (rhamnetin in union with rhamninose) and *iso*quercitrin (quercetin in union with glucose) were methylated with diazomethane and the products hydrolysed, forming, in each case, 5 : 7 : 3′ : 4′-tetramethoxyflavonol. Thus all contain the sugar nucleus in the 3 position. Using less diazomethane, xanthorhamnin yielded a trimethyl ether (?), m. p. 175—178°. Quercimeritrin, on methylation, forms a pentamethyl ether(?), m. p. 203—205° (sinters 197°), which yields, on hydrolysis, 5 : 3 : 3′ : 4′-*tetramethoxyflavonol*, m. p. 284—285° (*acetyl* derivative, m. p. 174—176°); the sugar nucleus in quercimeritrin therefore has the 7 position.

B. W. ANDERSON.

[Constitution of cellulose.] H. PRINGSHEIM (Annalen, 1927, **451**, 308—312).—Polemical against Schultze and Hess (cf. A., 1926, 942; this vol., 44).

H. E. F. NOTTON.

Synthesis of γ-ketoalkylamines from β-ketonic acids, amines, and formaldehyde. C. MANNICH and K. CURTAZ (Arch. Pharm., 1926, **264**, 741—751).—The reaction described by Mannich and Bauroth (A., 1924, i, 947) appears to be general for substituted β-ketonic acids and secondary amines. The yields vary from 40 to 60% of the theoretical. When a primary amine or ammonia is used, a complicated interaction takes place, and the products have not been identified. With unsubstituted β-ketonic acids, both hydrogen atoms of the methylene group may be replaced; acetoacetic acid, for example, yields a mixture of monoamine and diamine, $Me{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}NR'R''$ and $Me{\cdot}CO{\cdot}CH[CH_2{\cdot}NR'R'']_2$.

In these preparations, it is not necessary to isolate the ketonic acid; the potassium salt is obtained in solution by dissolving the ethyl ester in a slight excess of cold 2·5% aqueous potassium hydroxide and keeping the solution for about 2 days. This solution is then exactly neutralised and the amine hydrochloride is added, followed by the formaldehyde. The cold solution is stirred while hydrochloric acid is added to keep it from becoming alkaline; carbon dioxide is evolved. In subsequently isolating the base, sodium hydrogen sulphite is added if necessary, to render inactive any excess of formaldehyde. Ethyl benzylacetoacetate, piperidine, and formaldehyde yield *δ-phenyl-γ-piperidinomethylbutan-β-one*, b. p. 180—183°/14 mm. The *hydrochloride*, m. p. 145°, and *oxime hydrochloride*, m. p. 216—217°, are described. When reduced by aluminium amalgam in moist ether, the ketone affords the corresponding *alcohol* (a mixture of stereoisomerides), which has m. p. 62°. The *hydrochloride*, m. p. 187·5°, of the *benzoyl* derivative is an anæsthetic. *δ-Phenyl-γ-diethylaminomethylbutan-β-one*, b. p. 157—162°/16 mm., yields a deliquescent *hydrochloride*. The *alcohol* (mixture) has b. p. 164—174°/16 mm.; its *benzoyl* derivative (*hydrochloride*, m. p. 187—190°) possesses pronounced anæsthetic properties. The p-*nitrobenzoyl* derivative (*hydrochloride*, m. p. 191—193°) yields by reduction with hydrogen and palladised charcoal the p-*aminobenzoyl* derivative (*hydrochloride*, m. p. 211—213°), which also is an anæsthetic. *γ-Dimethylaminomethyl-Δ$^{\epsilon}$-hexen-β-one*, b. p. 75—78°/14 mm., is obtained from allylacetoacetic esters. The salts are deliquescent, with the exception of the *picrate*, m. p. 110°. The *oxime hydrochloride* has m. p. 154°. *γ-Piperidinomethyl-Δ$^{\epsilon}$-hexen-β-one*, b. p. 121°/12 mm., is somewhat unstable. The *hydrobromide*, m. p. 118°, and *oxime hydrochloride*, m. p. 192—193°, are described. Reduction affords the corresponding *alcohol*, b. p. 131°/13 mm., a mixture, from the crude *benzoyl* derivative, b. p. 208—210° (*hydrochloride*, m. p. about 122°), of which can be separated a purer *hydrochloride*, m. p. 149°, or *hydrobromide*, m. p. 168°. This compound is a strong anæsthetic. *γ-Dipropylaminomethylpentan-β-one* has b. p. 119—120° (*chloroaurate* and *oxime hydrochloride*, m. p. 155°). *γ-Piperidinomethylbutan-β-one* has b. p. 101—102°/13 mm. (*hydrochloride*, very hygroscopic, m. p. 146°; *picrate*, m. p. 128°). *γ-Dimethylaminomethylbutan-β-one*, b. p. 56—58°/15 mm. (*chloroaurate*, m. p. 102°; *picrate*, m. p. 135°), is the parent of "Tutocaine." When dimethylammonium acetoacetate interacts with formaldehyde, the product consists of δ-dimethylaminobutan-β-one and *δ-dimethylamino-γ-dimethylaminomethylbutan-β-one*, b. p. 85—90°/12 mm. (*picrate*, m. p. 136·5°; *chloroplatinate*, m. p. 181°), in almost equal amounts. ω-Piperidinopropiophenone (Mannich and Lammerling, A., 1923, i, 43) and ω-dimethylaminopropiophenone (Mannich and Heilner, *ibid.*, 1922, i, 351) are obtained when the appropriate amine benzoylacetate is treated with formaldehyde.

W. A. SILVESTER.

Imide chlorides and imide bromides of aliphatic acids. I. J. VON BRAUN, F. JOSTES, and A. HEYMONS (Ber., 1927, **60**, [*B*], 92—102).—The statement that the imide chlorides of aliphatic acids are readily transformed by loss of hydrogen chloride into complex bases is too general, since the compounds derived from di- and tri-chloroacetethylamide are relatively or completely stable at high temperatures. The base, $C_{16}H_{15}N_2Cl$, obtained from acetphenylimide chloride, is identified as *diphenylchlorovinylacetamidine*, $NPh{\cdot}CMe{\cdot}NPh{\cdot}CCl{:}CH_2$, since when catalytically reduced it passes into diphenylethylacetamidine, b. p. 189—192°/15 mm., characterised by the *picrate*, m. p. 162°, by hydrolysis to acetic acid, aniline, and ethylaniline, and by comparison with the compound obtained from ethylaniline and acetphenylimide chloride (which, contrary to the literature, could not be caused to crystallise). During hydrogenation, acetaldehyde, ethyl alcohol, and aniline are produced in small amount. The production of the compound is attributed to the migration of a hydrogen atom in the chloride, $CH_3{\cdot}CCl{:}NPh \longrightarrow CH_2{:}Cl{\cdot}NHPh$. This possibility is established on lines similar to those used with acyl bromides. Thus, *isobutyrethylamide*, b. p. 105—107°/14 mm., m. p. 68°, is converted by the successive action of phosphorus pentachloride and bromine into a mixture of the compounds $CMe_2Br{\cdot}CCl{:}NEt$ and $CMe_2Br{\cdot}CBr{:}NEt$, from which *α-bromoisobutyrethylamide*, m. p. 57°, is derived by the action of water. *α-Bromopropionethylamide*, b. p. 114—115°/16 mm., m. p. 60°, with somewhat greater difficulty gives the expected mixture of chlorinated and brominated compounds from which *αα-dibromo-*

propionethylamide, m. p. 61°, is obtained. Dichloroacetethylamide, after treatment with phosphorus pentachloride, reacts very readily with bromine, giving a mixture of substances from which *dichlorobromoacetethylamide*, m. p. 65—66°, is derived by treatment with warm water. α-Bromo*iso*butyrethylamide, αα-dibromopropionethylamide, and dichlorobromoacetethylamide, which do not contain hydrogen attached to the α-carbon atom, are completely stable to bromine after treatment with phosphorus pentachloride. Similarly, *α-chloroisobutyrethylamide*, b. p. 80°/15 mm., m. p. 38—39°, is converted by phosphorus pentachloride into *α-chloroisobutyrethylimide chloride*, b. p. 160°/atmos. pressure, which is indifferent to bromine, and *fencholethylamide*, b. p. 152°/11 mm., gives the corresponding stable *imide chloride*, b. p. 109—111°/13 mm. If the ethyl group of dichloroacet-, α-bromopropion-, or *iso*butyr-ethylamide is replaced by a phenyl, tolyl, or naphthyl residue, bromination of the nucleus cannot be avoided during the course of the changes; *dichloroacet-p-bromoanilide*, m. p. 147—148°, is incidentally described.

Propionethylamide, b. p. 100°/10 mm., is very readily converted by the successive action of phosphorus pentachloride and bromine (2 mols.) into a mixture of the dibrominated imide chloride and bromide, from which αα-dibromopropionethylamide, m. p. 61°, is derived by action of water; if, however, only 1 mol. of halogen is used and the product is treated with water, an inseparable mixture of propionethylamide and its mono- and di-bromo-derivatives is produced. Somewhat similar difficulties are encountered with acetethylamide; *dibromoacetethylamide*, m. p. 96°, is described. Chloroacetethylamide is converted by treatment with phosphorus pentachloride and bromine (1 mol.), followed by water, into *chlorodibromoacetethylamide*, m. p. 46°. H. WREN.

Structure of hydroxyureas [hydroxycarbamides] and of carbamazides. C. D. HURD and L. U. SPENCE (J. Amer. Chem. Soc., 1927, **49**, 266—274).—When the aqueous solution of *N*-hydroxy-*N'N'*-diethylcarbamide (cf. Hantzsch and Sauer, A., 1898, i, 171) is treated with benzoyl chloride and alkali, a *product*, m. p. 101—102°, is obtained, which is not the expected benzoyl ester, together with dibenzhydroxamic acid, m. p. 156—157°, and a *product*, m. p. above 270°. *N*-Hydroxy-*N'N'*-diethylcarbamide was obtained as an oil by the action of hydroxylamine on diethylcarbamyl chloride in ethyl acetate solution. When heated at 150—160°/25 mm., it decomposes with formation of a charred residue and an oil which, on distillation with alkali, yields diethylhydrazine, and is therefore probably carbonyldiethylhydrazine, NEt_2·NCO, formed by rearrangement of the hydroxydiethylcarbamide. Treatment of the hydroxydiethylcarbamide with excess of cold acetic anhydride affords the *acetyl* derivative as an oil which, on treatment with alkali, yields diethylhydrazine. *Phenylcarbimidediethylhydrazone*, m. p. 125·5—126°, is obtained by the action of diethylhydrazine on phenylcarbimide in dry ether. As carbamazide and hydroxycarbamide and their monosubstituted derivatives, NHR·CO·N_3 and NHR·CO·NH·OH, do not undergo the rearrangement typical of the ·CO·N_3 and ·CO·NH·OH groups, it is concluded that these compounds have the structures NR:C(OH)·N_3 and NR:C(OH)·NH·OH.

F. G. WILLSON.

Reactions of carbohydrazide. I. A. C. BROWN, E. C. PICKERING, and F. J. WILSON (J.C.S., 1927, 107—112).—The following were prepared from carbohydrazide and the appropriate ketone or aldehyde: *diacetonecarbohydrazone*, m. p. 156°; *di(methyl ethyl ketone)carbohydrazone*, m. p. 113°; *diacetophenonecarbohydrazone*, m. p. 204°; *acetophenone-δ-aminosemicarbazone*, m. p. 188° (benzaldehyde reacts with this compound to form *benzaldehyde acetophenone carbohydrazone*, m. p. 160°); *benzophenone-δ-aminosemicarbazone*, m. p. 223—224° (decomp.); *benzaldehyde-δ-aminosemicarbazone*, m. p. 173°; *benzilmono-δ-aminosemicarbazone*, m. p. 172—174°; and *diacetylmono-δ-aminosemicarbazone*, m. p. 260°. Acetylacetone and carbohydrazide gave 3 : 5-dimethylpyrazole. Dibenzaldehydecarbohydrazone decomposed in boiling alcoholic solution, giving dibenzaldehydehydrazicarbohydrazone and benzylideneazine; similarly, diacetophenonecarbohydrazone gave *diacetophenonehydrazidicarbohydrazone*, m. p. 239—240°, and phenyl methyl ketazine. When heated without solvent, these carbohydrazones gave 4-aminourazole and azine. Benzaldehyde-δ-aminosemicarbazone in boiling toluene decomposed into hydrazidicarbohydrazide and benzylideneazine, and heated alone above the m. p. it gave 4-aminoaurazole, hydrazine, and benzylideneazine, the first two compounds evidently resulting from the hydrazidicarbohydrazide.

B. W. ANDERSON.

Complex compound of biuret with copper and nickel. W. TRAUBE and W. WOLFF (Ber., 1927, **60**, [*B*], 43—50; cf. A., 1922, i, 718).—The following complex *derivatives* of biuret are obtained by evaporating an aqueous solution of the substance, treated with an excess of organic alkali and saturated with copper or nickel hydroxide, in a vacuum over sulphuric acid at the atmospheric temperature. The compounds, when freed from mother-liquor, are generally unstable, absorbing carbon dioxide from the air and depositing the metallic hydroxide:

$[(C_2H_3O_2N_3)Cu](NMe_4)_2,4H_2O$;
$[(C_2H_3O_2N_3)Cu](SEt_3)_2,4H_2O$;
$[(C_2H_3O_2N_3)_2Cu](PEt_4)_2,4H_2O$;
$[(C_2H_3O_2N_3)_2Cu][CH_6N_3]_4,2H_2O$;
(?)$[C_2H_3O_2N_3][Cu(CH_5N_3)_2],2H_2O$;
$[(C_2H_3O_2N_2)_2Cu][Ni\,en_3],4H_2O$;
$[(C_2H_3O_2N_3)_2Cu][Zn\,en_3],4H_2O$;
$C_2H_3O_2N_2Cu\,Cd\,en_3,4H_2O$;
$[(C_2H_3O_2N_3)_2Cu][Co\,en_3],4H_2O$;
$[(C_2H_3O_2N_3)_2Ni][NMe_4]_2,4H_2O$;
$[(C_2H_3O_2N_3)_2Ni][CH_6N_3]_2,2H_2O$;
$[(C_2H_3O_2N_3)_2Ni][Ni\,en_3],4H_2O$;
$[(C_2H_3O_2N_3)_2Ni][Cd\,en_3],4H_2O$;
$[(C_2H_3O_2N_3)_2Ni][Ag(NH_3)_2]_2,6H_2O$.

H. WREN.

[Thiocyanogen chloride.] H. P. KAUFMANN (Ber., 1927, **60**, [*B*], 58—59; cf. Kaufmann and Liepe, A., 1924, i, 209).—A reply to Lecher and Joseph (this vol., 46). H. WREN.

Free, crystalline gluconononitrile. G. ZEMPLEN (Ber., 1927, **60**, [*B*], 171—173).—*Gluconononitrile*, m. p.

about 115—120° (decomp.), $[\alpha]_D^{21}$ +8·8° in water, is prepared by hydrolysing its penta-acetate with aqueous-alcoholic sulphuric acid under definite conditions. Separation of the crystalline substance from solutions shown analytically to contain the greatest quantity of it is not easy, whereas little difficulty is experienced when hydrolysis is continued until about 50% of the nitrile has been transformed into ammonium gluconate. H. WREN.

Prussian blue and complex metallic cyanides. H. REIHLEN and W. ZIMMERMANN (Annalen, 1926, **451**, 75—107).—The properties of a number of complex metallic cyanides and ammonium compounds are reviewed, and the conclusion is reached that the cyanides are better represented as complex polynuclear structures than as salts of hydroferrocyanic acid. Such a conception offers an explanation for the structure, conductivity, colour, and general reactions of the complex cyanides, and for the fundamental difference between these substances and the complex ammonium compounds. Whilst the decomposition of the ammonium compounds would be independent of the nature of the central atom, the formation of polynuclear structures by the complex cyanides will depend on the relative ionic volumes of the metals concerned, and the character of the complex formed will depend on the nature of the central atom. The properties of the complex cyanides seem to be directly opposed to the co-ordination theory of valency. R. W. WEST.

Carbylamines. XV. Reactions with aliphatic carbylamines. M. PASSERINI.—See this vol., 149.

Grignard synthesis of certain organic arsenic derivatives. E. GRYSZKIEWICZ-TROCHIMOWSKI and E. ZAMBRZYCKI (Rocz. Chem., 1926, **6**, 794—803).—Arsenious oxide added to ethereal solutions of various magnesium organic derivatives yields with magnesium aryl salts partly oxidised products, whilst alkyl salts produce trialkylarsines. Thus the following compounds are prepared: diphenylarsine oxide, dibenzylarsenious acid, di-α-naphthylarsine oxide, trimethylarsine, b. p. 48—51°, triethylarsine (whence *chlorodiethylarsine*, b. p. 155°, is prepared), tri-*n*-propylarsine, and *triallylarsine*, b. p. 104°/37 mm.

R. TRUSZKOWSKI.

Synthesis of bromovinylarsines. E. SCHMIDT (Bull. Soc. chim., 1927, [iv], **41**, 49—50).—The action of acetylene at 31—35° on a mixture of 2 mols. of aluminium bromide or chloride and 1 mol. of arsenious bromide affords *ββ'β''-tribromotrivinylarsine*, m. p. 65·5—67° (odour of geranium), in addition to the primary and secondary arsines described by Lewis and Stiegler (A., 1925, i, 1470). R. BRIGHTMAN.

Constitution of organo-magnesium derivatives. P. JOLIBOIS (Compt. rend., 1926, **183**, 971—973).—Reasons are stated for adopting the bimolecular formula $MgR_2 \cdot MgX_2$ for organo-magnesium compounds. The argument is based primarily on the work of Terentjev (A., 1926, 1130).

L. F. HEWITT.

Constitution of magnesium organo-compounds. A. JOB and M. DUBIEN (Compt. rend., 1926, **184**, 155—157).—A criticism of the argument advanced by Jolibois (preceding abstract).

W. ROBSON.

Reaction of organomagnesium compounds on nitriles. Glutaronitrile and magnesium benzyl chloride. P. BRUYLANTS and A. DEWAEL (Bull. Acad. roy. Belg., 1927, [v], **12**, 464—476).—The action of magnesium benzyl chloride on glutaronitrile yields the *hydrochloride*, m. p. 246° (*chloroplatinate*, decomp. 270°), of the cyclic *base* $\begin{matrix} C(CH_2Ph)_2 \cdot NH \cdot CR \\ | \\ CH_2 \text{---} CH_2 \text{---} CH_2' \end{matrix}$, m. p. 172° (R=NH). The *nitrite*, m. p. 144°, and *iodide* are described. With phenylthiocarbimide, it yields the *phenylthiocarbamate*, m. p. 147—149°. On boiling with 10% sodium hydroxide solution for several hours, the base is converted into the cyclic *amide* (R=O), m. p. 159—160°, which does not exhibit basic properties, but when treated in alcohol–ether solution with dry hydrogen chloride gives a *hydrochloride*, m. p. 205—207° (decomp.), completely hydrolysed in aqueous solution. When heated with excess of fuming hydrochloric acid in a sealed tube at 170° for 6 hrs., the amide yields a small quantity of a *hydrochloride*, m. p. 193°, probably derived from the corresponding open-chain amino-acid; on treatment with ammonia, the original lactam is regenerated.

J. W. BAKER.

Action of organomagnesium compounds on *cyclo*heptene oxide. M. GODCHOT and P. BEDOS (Compt. rend., 1927, **184**, 208—210).—*cyclo*Heptene oxide (cf. Boeseken and Derx, A., 1921, i, 663), when treated with magnesium methyl iodide, yields 1-methyl*cyclo*heptan-1-ol, identical with the product obtained from suberone itself. The seven-ring oxide therefore behaves differently from the analogous five- and six-ring compounds (cf. Godchot and Bédos, *ibid.*, 1922, i, 334), isomerisation to *cyclo*heptanone preceding the addition of the Grignard reagent.

J. W. BAKER.

Organometallic derivative of gold. A. LUMIERE and F. PERRIN (Compt. rend., 1927, **184**, 289—291).—Addition of a concentrated solution of gold chloride to sodium thiopropanolsulphonate yields the amorphous *gold* salt, $CH_2SAu \cdot CH(OH) \cdot CH_2 \cdot SO_3Na$, which is stable in 2% aqueous solution and has but feeble toxicity. Hence intramuscular injections are free from the disadvantages which accompany the use of sodium gold thiosulphate. J. W. BAKER.

Optical activity and the polarity of substituent groups. VI. Optically active acids and bases. H. G. RULE (J.C.S., 1927, 54—59).—In the polar series corresponding with the relative influence of substituents on benzene substitution and the rotatory power of optically active compounds, the ionic complex $-NH_3^{\cdot}$ ranges itself with the positive substituents, and the complex $-CO \cdot O'$ with the negative substituents. The polar influence may be intramolecular, and sudden changes of activity may take place as the chain attached to the asymmetric atom attains a length of 5, 10, or 15 atoms, due to the close proximity of the end of the chain to the asymmetric atom. Further, the influence of polar groups on neighbouring molecules leads to changes in rotatory power.

B. W. ANDERSON.

Nitration of decahydronaphthalene. S. S. NAMETKIN and O. S. MADAJEVA-SITSCHEVA (J. Russ. Phys. Chem. Soc., 1926, **57**, 382—389).—Decahydronaphthalene is slowly converted by boiling nitric acid (d 1·2) into tert.-*nitrodecahydronaphthalene*, b. p. 96—97°/2 mm., d_4^{20} 1·0847, n_D^{20} 1·4944; from the residue, after the fractionation of the tertiary decahydronaphthalene, crystals of *dinitrodecahydronaphthalene*, m. p. 164°, are obtained. The tertiary nitro-compound is reduced with zinc and acetic acid to the corresponding *amine*, b. p. 98°/15 mm., d_4^{20} 0·9435, n_D^{20} 1·4932, *benzoyl* derivative, m. p. 148—149°. The hydrochloride when boiled for 24 hrs. with potassium nitrite yields an *octahydronaphthalene*, b. p. 88—89°/1·4 mm., d_4^{20} 0·9200, n_D^{20} 1·4979, the residue from which yields tert.-*decahydronaphthol*, m. p. 65°. α-*Nitrodecahydronaphthalene*, b. p. 108—109°/14 mm., d_4^{20} 1·0815, n_D^{20} 1·4978, yields on oxidation α-decahydronaphthalone. E. ROTHSTEIN.

Reduction of nitro-compounds with iron and soluble chlorides. R. E. LYONS and L. T. SMITH (Ber., 1927, **60**, [*B*], 173—182).—Sodium chloride or ferric chloride may replace hydrochloric acid in the reduction of nitrobenzene, *p*-nitrotoluene, *m*-dinitrobenzene, *p*-nitrophenol, or picric acid to the corresponding amines or nitroamines by iron. Only a small proportion of the salts is necessary (1·672—2·675 g. of ferric chloride or 1·523—2·9 g. of sodium chloride for 100 g. of nitro-compound). Amines are obtained in 95—100% yield from nitrobenzene, *p*-nitrotoluene, and *m*-dinitrobenzene when the concentration of chlorine as ferric or sodium chloride lies between 0·0183 and 0·035 g. per c.c. of solution. Theoretical yields of amine are obtained from *p*-nitrophenol or picric acid when the corresponding concentrations are 0·009. Iron passed through an 80-mesh sieve gives the best results with reduction extending over a short period; coarser iron is correspondingly less active. Under similar conditions, the activity of sodium chloride is 84% of that of ferric chloride. *p*-Nitrophenol and picric acid are much more readily reduced by iron in presence of the salts named than are nitrobenzene, *p*-nitrotoluene, or *m*-dinitrobenzene, Picric acid is reduced by iron alone. The presence of a hydroxyl group in the *p*-position greatly diminishes the resistance of the nitro-group towards reducing agents. H. WREN.

Additive products of sulphur dioxide and aromatic hydrocarbons. I. II. F. DE CARLI (Atti R. Accad. Lincei, 1926, [vi], **4**, 460—466, 523—530; cf. A., 1926, 944).—I. Sulphur dioxide forms with toluene the *compounds*, $C_6H_5Me,2SO_2$, m. p. —85·5°, and $C_6H_5Me,3SO_2$, m. p. —80°. The f.-p. curve for the system mesitylene–sulphur dioxide exhibits two eutectics, at —72·5° and —76·5°, corresponding with 10% and about 90% SO_2, and a maximum, —49·4°, corresponding with the compound $C_6H_3Me_3,SO_2$. The isomeric *compound* with ψ-cumene has m. p. —60°, and the system shows two eutectics, at —71° and —82°, corresponding with 15% and 68% SO_2, respectively.

II. Sulphur dioxide forms the following additive *compounds*. With ethylbenzene, C_8H_{10},SO_2, m. p. —91°, and $C_8H_{10},2SO_2$, m. p. —78·5°; the system exhibits two eutectics, at —93° (60% SO_2) and —82·5° (about 42% SO_2). With cymene, $C_{10}H_{14},SO_2$, m. p. —89°, $C_{10}H_{14},2SO_2$, m. p. —83°. With tetrahydronaphthalene, $C_{10}H_{12},SO_2$, m. p. —58°, $C_{10}H_{12},2SO_2$, m. p. —66·2°, and $C_{10}H_{12},3SO_2$, m. p. —70°; two eutectics exist, at —64·5° and —76·5°, respectively. T. H. POPE.

Two forms of cobaltous β-naphthalenesulphonate. W. BILTZ and E. BIRK (Z. anorg. Chem., 1926, **159**, 125—128).—Cobaltous β-naphthalenesulphonate hexahydrate gives rise to two forms of the anhydrous salt depending on the method of dehydration: a rose-coloured (α-) form by direct and rapid dehydration at 130—150° in an air-oven, also a blue (β-) form which is the result of slow dehydration by way of the monohydrate. These forms differ in their optical and crystallographic properties. The α-modification is the more stable form. M. CARLTON.

Fluorene series. C. COURTOT and C. VIGNATI (Bull. Soc. chim., 1927, [iv], **41**, 58—64).—Repeated crystallisation from 90% alcohol raises the m. p. of 2-bromofluorene, prepared by Matthews and Hodgkinson's method (J.C.S., 1883, **43**, 163), to 111·5°; dibromofluorene, m. p. 162—163°, has been isolated from the mother-liquors. Diels' 2-aminofluorene (A., 1901, i, 521) with the diazo-reaction affords the same 2-bromofluorene; the reverse transformation is effected with ammonia and cuprous chloride at 180°. On oxidation, 2-bromofluorene affords 2-bromofluorenone, m. p. 142—143° (oxime, m. p. 194—195°), identical with the bromofluorenone, m. p. 134°, obtained by Schmidt and Bauer (*ibid.*, 1906, i, 28). The halogen therefore enters the same position, whether introduced in the fluorene or the fluorenone molecule. Aqueous ammonia in the presence of cuprous chloride at 200° converts 2-bromofluorenone into the aminofluorenone obtained by Diels (*loc. cit.*) from 2-nitrofluorene. On hydrogenation, 2-bromofluorenone affords 2-*bromofluorenol*, m. p. 129—130°, the product, m. p. 101—102°, obtained, but not analysed, by Schmidt and Bauer (*loc. cit.*) being 9-*chloro*-2-*bromofluorene*; the latter is formed on warming the fluorenol with hydrochloric acid. Nitration of 2-bromofluorene with nitric and acetic acids at 100° affords 2-*bromo*-7(?)-*nitrofluorene*, m. p. 236°, reduced by zinc and alcoholic ammonia to 2-*bromo*-7(?)-*aminofluorene*, m. p. 146°. Oxidation of the bromonitrofluorene affords a bromonitrofluorenone, m. p. 230° (oxime, m. p. 249°), identical with that described by Schmidt and Bauer (*loc. cit.*) and regarded by them as 2-bromo-7-nitrofluorenone. Hydrogen sulphide in alcoholic ammonia converts this bromonitrofluorenone into 2-*bromo*-7(?)-*aminofluorenone*, brownish-red, m. p. 233—234°; with zinc dust the pale yellow 2-*bromo*-7(?)-*aminofluorenol*, m. p. 186—187°, is obtained. R. BRIGHTMAN.

Coloured hydrocarbons. II. Synthesis of ketones, carbinols, hydrocarbons, and halogen derivatives of the fluorenes. A. A. VANSCHEIDT (J. Russ. Phys. Chem. Soc., 1926, **58**, 55—68; cf. this vol., 140).—The ketones can be regarded as the starting points for the syntheses of the whole series. They can often be obtained from the hydrocarbons,

however; thus chrysofluorenone is obtained by the oxidation and subsequent distillation with lead oxide of chrysene, whilst di-α-naphthafluorenone is formed in 90% yield by the agitation in air of an acetone solution of the hydrocarbon in the presence of alcoholic potassium hydroxide, m. p. 272° (cf. Schmidlin and Huber, A., 1910, i, 833, impure, 255°). The carbinols are obtained from the ketones by the action of zinc dust in boiling glacial acetic acid. The di-α-naphthafluorenol has m. p. 265° (decomp.), 20° higher than found by Tschitschibabin. Alkaline reduction results largely in autoxidation. The halogen derivatives (or "*meso*halofluorenes") can, with the exception of the iodides, be prepared by Staudinger's method (A., 1906, i, 824) by the action of halogen acid on an acetic acid solution of the carbinol. The following new compounds were synthesised: *chrysofluorenyl chloride*, $\begin{matrix}C_6H_4\\C_{10}H_6\end{matrix}>CHCl$, m. p. 146° (decomp.); *bromide*, m. p. 142° (decomp.); *di-α-naphthafluorenyl chloride*, $\begin{matrix}C_{10}H_6\\C_{10}H_6\end{matrix}>CHCl$, m. p. 224°, *bromide*, m. p. 234°. The iodides were obtained by double decomposition in acetone solution of the bromo-compounds with sodium iodide. *Fluorenyl iodide* decomposes at 98° with evolution of iodine; *chrysofluorenyl iodide*, decomp. 130°; *di-α-naphthafluorenyl iodide*, decomp. 160°. The chlorides and bromides decompose on fusion, with formation of the coloured hydrocarbons and evolution of halogen acid: $2<Ar_2>CHX \longrightarrow <Ar_2C{:}CAr_2>$. They all dissolve in sulphuric acid, giving blue solutions for the chrysofluorenes, and green for the others, probably due to halochromism: $<Ar_2CHX+H_2SO_4 \rightleftharpoons <Ar_2CH{\cdot}SO_3H+HX$. They are coloured, the chloride lemon-yellow, bromide yellow, and iodide orange. The colour deepens with the introduction of naphthalene nuclei. By the action of hydrogen iodide on the carbinols in glacial acetic acid and boiling, instead of the iodide, the hydrocarbon is formed quantitatively and with great ease. This simple method seems never to have been previously employed. M. Zvegintzov.

Arylamine salts of some sulphonic acids of the benzene series. II. *m*-Nitrobenzenesulphonic acid. C. M. Keyworth (J.S.C.I., 1927, **46**, 20T).—The preparation of *m*-nitrobenzenesulphonic acid is briefly discussed. The arylamine salts of *m*-nitrobenzenesulphonic acid are similar in properties to those of benzenemonosulphonic acid, except that they are much less soluble in water. They are also much less soluble in water than the inorganic salts of *m*-nitrobenzenesulphonic acid. The benzidine salt is very sparingly soluble and may be used for determining *m*-nitrobenzenesulphonic acid in absence of sulphuric acid or sulphates. A table is given showing the principal properties of the commoner arylamine salts, together with a comparison of the corresponding salts of benzenesulphonic acid. The m. p. of the m-*nitrobenzenesulphonates* prepared are: aniline, 222°; *o*-toluidine, 193°; *m*-toluidine, 195°; *p*-toluidine, 222°; α-naphthylamine, 221°; β-naphthylamine, 250°; benzidine and tolidine, above 300°; dianisidine, 279—281°; *m*-xylidine, 185°; *o*-chloroaniline, 204°; *p*-chloroaniline, 234°.

Complex-isomerism. E. Hertel and J. Mischnat (Annalen, 1926, **451**, 179—208).—Existing data are reviewed and it is shown that the predictions of Pfeiffer ("Organische Molekülverbindungen," 1922, 226) are fulfilled with regard to the existence of two types of additive compounds of aromatic substances with polynitrophenols. With picric acid and an aromatic amine, type I is the "true picrate" in which the hydroxylic hydrogen atom is united by a subsidiary valency to the basic nitrogen atom, and in type II the subsidiary valency of the nitro-groups of picric acid is saturated by the residual valency field of the aromatic nucleus of the base, $OH{\cdot}C_6H_2(NO_2)_3 \ldots . R{\cdot}NH_2$. With a strong phenol (picric acid) and a strong base (α-naphthylamine), only type I is obtained, whilst weak components (2 : 6-dinitrophenol and 2 : 4-dichloro-α-naphthylamine) yield only type II. Between these limits, it is possible with suitable components (2 : 6-dinitrophenol and 4-bromo-α-naphthylamine) to obtain both types of the additive compound. Type I compounds are much lighter in colour and of lower m. p. than the type II isomerides. Hydroxyl groups in the *o*-position to the nitro-groups have a deepening effect on the colour of the type II compounds, the colour of molecular compounds with picric acid being darker than those with trinitrobenzene, although the m. p. of the two series of compounds are of the same order.

Although in general type I is the stable isomeride (cf. Skraup and Eisemann, A., 1926, 999), it sometimes happens, as with 1 : 6-dibromo-β-naphthylamine picrate, that type I is obtained only at low temperatures and readily passes into type II, which is stable at all temperatures from 0° to its m. p. In the system 4-bromo-α-naphthylamine–2 : 6-dinitrophenol the compound of type I is stable, whilst II is unstable and decomposes rapidly into its components on being isolated, but may be preserved under its solution in bromobenzene.

Comprehensive tables are included illustrating the difference in colour and m. p. of the two types of molecular compounds. R. W. West.

Acetylation of aniline in anhydrous glycerol. E. Sakellarios (Ber., 1927, **60**, [*B*], 218—219; cf. Gasopoulos, A., 1926, 1131).—The use of glycerol in the acetylation of aniline with glacial acetic acid is disadvantageous, since a portion of the acid is consumed in converting the glycerol into acetin and the liberated water dilutes the acid. The disadvantage is more pronounced in the case of *o*-toluidine. A 50% economy of acid is effected by addition of xylene. Aniline is converted into acetanilide by monoacetin at 200°, but not to an appreciable extent at 130°. H. Wren.

Sulphonation of *o*-toluidine and preparation of sodium 6-chloro-5-nitro-*m*-toluenesulphonate. M. N. Schultz and H. J. Lucas (J. Amer. Chem. Soc., 1927, **49**, 298—302).—Sulphonation of *o*-toluidine to the 5-sulphonic acid is best effected by heating the base with 2 mols. of fuming sulphuric acid (20% SO_3) for 10 hrs. at 180° (yield, 77%). The presence of iodine is detrimental, as it increases charring (cf. Ray and Dey, J.C.S., 1920, **117**, 1405). Treatment

of the diazotised sulphonic acid with cuprous chloride gives a 98·2% yield of 6-chloro-*m*-toluenesulphonic acid, most of which separates out direct, the remainder being obtained on evaporating the solution, removal of copper being unnecessary (cf. Davies, *ibid.*, 1922, **121**, 785). Treatment of the dried sulphonic acid with phosphorus pentachloride affords the sulphochloride in 85% yield, nitration of which according to Davies' method (*loc. cit.*) gives a 75% yield of the 5-nitro-derivative. Subsequent hydrolysis to sodium 6-chloro-5-nitro-*m*-toluenesulphonate, also by Davies' method, gives a yield of 80%. F. G. Willson.

M. p. of pure *s*-*p*-bromophenyl-*n*-hexylthiocarbamide. R. F. Hunter and C. Soyka (Chem. News, 1927, **134**, 13).—The m. p. of *s*-*p*-bromophenyl-*n*-hexylthiocarbamide was erroneously given in a recent paper (cf. this vol., 263) as 189°. The correct m. p. is 106°. W. J. Powell.

Rearrangement of alkylanilines. W. J. Hickinbottom (J.C.S., 1927, 64—67; cf. *ibid.*, 1920, **117**, 103).—Ethyl- and butyl-anilines, when heated at 220—290° in open tubes in presence of cobalt, zinc, cadmium, or manganese chlorides, silver sulphate, or copper phosphate, rearrange, giving *p*-aminoethyl- and *p*-aminobutyl-benzenes. The presence of water has no effect on the change. Ethylaniline hydrochloride heated at 220—290° gave chiefly aniline, with a small amount of an unidentified amine, whereas dry butylaniline hydrochloride gave *p*-amino-*n*-butylbenzene. These results do not support the view that the reaction takes place with intermediate formation of alkyl chloride, according to the scheme: $2NHR\cdot C_6H_5+MCl_2+H_2O \longrightarrow 2RCl+2C_6H_5\cdot NH_2+MO \longrightarrow 2R\cdot C_6H_4\cdot NH_2+MCl_2+H_2O$. H. Burton.

Alternating effect in carbon chains. XI. Substitution of benzylamine salts. J. W. Baker and C. K. Ingold (J.C.S., 1927, 261—264; cf. A., 1926, 1131).—Nitration of (*a*) α-phenylethylamine, (*b*) α-phenyl*iso*propylamine, (*c*) α-nitro-α-phenylethane, gave the following amounts of *meta*-substituted product: (*a*) 40%, (*b*) 26%, (*c*) 43%. These results are in agreement with those previously obtained (*loc. cit.*), confirming the view that phenylnitromethane derivatives are nitrated in the *meta*-position to approximately the same extent as substituted benzylamines. H. Burton.

Alternating effect in carbon chains. X. Nitration of some derivatives of β-phenylethylamine. F. R. Goss, W. Hanhart, and C. K. Ingold (J.C.S., 1927, 250—261; cf. A., 1926, 1132).—Nitration of (*a*) β-phenylethylamine, (*b*) methyl-β-phenylethylamine, (*c*) dimethyl-β-phenylethylamine picrate, (*d*) trimethyl-β-phenylethylammonium picrate, gives the following amounts of *m*-nitro-derivative, isolated as a suitable salt, or by oxidation to the corresponding nitrobenzoic acids with subsequent analysis: (*a*) 12%, (*b*) 15%, (*c*) 13%, (*d*) 19%. Nitration of *trimethylbenzylammonium picrate*, m. p. 168—169°, yields 88% of the *m*-nitro-derivative. These results show that the directive effect of an ionic centre situated in a side-chain of saturated carbon atoms does not alternate, but diminishes with increasing distance from the nucleus. The following salts have been isolated during the investigation: β-o-*nitrophenylethylammonium chloride*, m. p. 162—163°; β-m-*nitrophenylethylammonium oxalate*, m. p. 200° (decomp.), and *chloride*, m. p. 204—205°; *dimethyl*-β-o-*nitrophenylethylammonium picrate*, m. p. 160—161°; *dimethyl*-β-m-*nitrophenylethylammonium oxalate*, m. p. 186°, and *picrate*, m. p. 166—167°; *dimethyl*-β-p-*nitrophenylethylammonium picrate*, m. p. 162°; *trimethyl*-β-o-*nitrophenylethylammonium picrate*, m. p. 146—147°; *trimethyl*-β-m-*nitrophenylethylammonium picrate*, m. p. 147—148°; *trimethyl*-β-p-*nitrophenylethylammonium iodide*, m. p. 206°, and *picrate*, m. p. 144—145°; m-*nitrobenzyltrimethylammonium picrate*, m. p. 180—180·5°; and p-*nitrobenzyltrimethylammonium picrate*, m. p. 194°. The quaternary ammonium picrates were made usually by treating the tertiary base with a solution of trinitroanisole. H. Burton.

Preparation of α-naphthylthiocarbimide from α-naphthylamine and thiocarbonyl chloride. G. Dyson and R. F. Hunter (Chem. News, 1927, **134**, 4—5).—See A., 1926, 718.

Substitution products of 2-aminodiphenyl. H. A. Scarborough and W. A. Waters (J.C.S., 1927, 89—97).—2-Nitrodiphenyl on reduction with tin and hydrochloric acid (cf. Blanksma, A., 1906, i, 345) gives 5-chloro-2-aminodiphenyl (60%) and 2-aminodiphenyl (cf. Hübner, *ibid.*, 1882, 180). Chlorination of 2-aminodiphenyl in carbon tetrachloride solution yields 3 : 5-*dichloro*-2-*aminodiphenyl hydrochloride*, m. p. 140—145° (all m. p. are corr.). 3 : 5-*Dichloro*-2-*aminodiphenyl*, m. p. 51° (*benzoyl* derivative, m. p. 207°), on deamination gives 3 : 5-*dichlorodiphenyl*, b. p. 180°/15 mm. Sodium hypochlorite converts 2-acetamidodiphenyl into N-*chloro*-2-*acetamidodiphenyl*, m. p. 86°, which when treated with acetic acid gives a mixture of substances. Further treatment of this mixture with sodium hypochlorite followed by acetic acid gives 5-*chloro*-2-*acetamidodiphenyl*, m. p. 122·5° (*benzamido*-derivative, m. p. 142—143°). 2 : o-*Dichlorodiphenyl* has b. p. 171°/15 mm. Monobromination of 2-aminodiphenyl in carbon tetrachloride furnishes 5-*bromo*-2-*aminodiphenyl hydrobromide*, m. p. 226°, whilst dibromination in acetic acid in presence of sodium acetate gives 3 : 5-*dibromo*-2-*aminodiphenyl*, m. p. 51—52° (*benzoyl* derivative, m. p. 218°). Deamination of this base yields 3 : 5-dibromodiphenyl, b. p. 208°/15 mm. 2-Acetamidodiphenyl furnishes o-*bromo*-2-*acetamidodiphenyl*, m. p. 130°, which on hydrolysis with alcoholic hydrobromic acid gives 5-*bromo*-2-*aminodiphenyl*, m. p. 57·5° (*benzoyl* derivative, m. p. 162°). 2 : o-*Dibromodiphenyl* has b. p. 209°/15 mm. *N*-Bromo-2-acetamidodiphenyl was not obtained pure, and the crude substance on treatment with acetic acid gives 5-bromo-2-acetamidodiphenyl and 2-acetamidodiphenyl.

Nitration of the last substance gives 4′-*nitro*-2-*acetamidodiphenyl*, m. p. 199°, and 5(or 3) : 4′-*dinitro*-2-*acetamidodiphenyl*, m. p. 211°. Hydrolysis of these compounds furnishes 4′-*nitro*-2-*aminodiphenyl*, m. p. 158°, and 5(or 3) : 4′-*dinitro*-2-*aminodiphenyl*, m. p. 238°, deamination of the latter giving 3 : 4′-dinitrodiphenyl. 2-*Bromo*-4′-*nitrodiphenyl*, m. p. 82·5°, on

oxidation with chromic acid gives *p*-nitrobenzoic acid, whilst oxidation of the dihalogenodiphenyls gives the dihalogenobenzoic acids. H. BURTON.

Occurrence of free radicals in chemical reactions. V. H. WIELAND, A. HINTERMAIER, and I. DENNSTEDT [with J. LORENZO] (Annalen, 1927, **452**, 1—34; cf. A., 1926, 61).—p-*Phenylbenzoyl chloride*, m. p. 113°, gives with hydrazine s-*di*-p-*phenylbenzoylhydrazine*, m. p. 260—270° (decomp.), but *ethyl* p-*phenylbenzoate*, m. p. 46°, b. p. 178°/10 mm., gives p-*phenylbenzhydrazide*, m. p. 189°. This condenses with triphenylmethyl chloride to give p-*phenylbenzoylhydrazotriphenylmethane*, m. p. 183° (decomp.). The p-*phenylbenzoylazotriphenylmethane*, m. p. 82° (decomp.), obtained from this by oxidation is very unstable, decomposing to p-*phenylbenzoyltriphenylmethane*, m. p. 178°, or in a stream of oxygen to *p*-phenylbenzoic acid and triphenylmethyl peroxide, which is also obtained from all the azo-compounds mentioned below.

Acetylazotriphenylmethane decomposes vigorously at 70°, or in xylene at 40°, to *acetyltriphenylmethane*; in oxygen to diacetyl peroxide. iso*Butyrylazotriphenylmethane*, m. p. 60—61° (decomp.), obtained from the *hydrazo*-compound, m. p. 170—172°, by the action of hypochlorous acid (potassium ferricyanide or bromine in chloroform having no action), is extremely unstable, evolving nitrogen from a chloroform solution at −7°. In oxygen, *di*isobutyryl *peroxide* is obtained; in nitrogen a syrup, from which, by distillation, triphenylmethane, and, by aerial oxidation, *iso*butyric acid are obtained. The pinacolin (*iso*butyryltriphenylmethane) cannot be isolated, nor can it be obtained from magnesium triphenylmethyl chloride and an alkyl *iso*butyrate. Pivalyl chloride gives with hydrazine *dipivalylhydrazine*, but by heating ethyl pivalate with hydrazine hydrate at 140°, *trimethylacethydrazide*, m. p. 65°, b. p. 113°/12 mm., is obtained; *trimethylacetylazotriphenylmethane*, m. p. 71° (decomp.), obtained from the *hydrazo*-compound, m. p. 123°, decomposes readily, evolving nitrogen and carbon monoxide to form ααα-triphenyl-ββ-dimethylpropane, m. p. 189·5°; in oxygen, *tert.*-butyl peroxide is formed.

The above three acylazotriphenylmethanes show during decomposition in an indifferent solvent the carmine-red colour associated with free acyl radicals. The *iso*butyryl compound on decomposition gives in ether an intense red colour, which fades on cooling and reappears on warming again, indicating an association and deassociation of free radicals. An ethereal solution of the trimethylacetyl compound shows an absorption spectrum with two bands between 580 and 590 μμ, as well as the triphenylmethyl band at 520 μμ.

Phenylacetylazotriphenylmethane, m. p. 68° (decomp.), obtained from the *hydrazo*-compound, m. p. 181—183° (decomp.), forms moderately stable yellow crystals, but in light petroleum solution turns red and then yellow, forming *as*-tetraphenylethane; with oxygen, the peroxide of phenylacetic acid is formed. *Diphenylacetylazotriphenylmethane*, m. p. 76° (decomp.), is obtained by oxidation of the *hydrazo*-compound, m. p. 184—186° (decomp.), by calcium hypochlorite (potassium ferricyanide not reacting); it decomposes much more slowly than the phenylacetyl compound, giving a solution with an absorption band at 580 and evolving 70% of the theoretical carbon monoxide to give pentaphenylethane, with some pentaphenylacetone, isolated only from the product of decomposition in oxygen. *Triphenylacethydrazide*, m. p. 196° (decomp.), formed, with some *bistriphenylacetylhydrazine*, decomp. 253°, from the acid chloride, gives, with triphenylmethyl chloride, *triphenylacetylhydrazotriphenylmethane*, m. p. 170—172° (decomp.), oxidised by calcium hypochlorite to the *azo*-compound, which decomposes at 53—54°, or immediately in solution, giving carbon monoxide and triphenylmethyl, which when shaken with air or oxygen gives its peroxide. The triphenylacetyl radical is thus very unstable, and no hexaphenylacetone is formed. An attempt to obtain this by another method has also failed. Carbohydrazide with triphenylmethyl chloride gives s-*bistriphenylcarbohydrazide*, m. p. 178—181° (decomp.), after drying in a vacuum, 200—202°, which is oxidised by bromine water to *bis*-ββ′-*triphenylmethylcarbazone*, $CPh_3{\cdot}NH{\cdot}NH{\cdot}CO{\cdot}N{:}N{\cdot}CPh_3$, m. p. 96—97° (decomp.). This cannot be oxidised to the bisazo-compound, decomposition always occurring. It is the most stable of these azo-compounds, not decomposing in petroleum until heated to 80°, when the orange colour of triphenylmethyl is observed, and triphenylacetylhydrazotriphenylmethane (see above) is obtained. *Triphenylmethylsemicarbazide*, m. p. 190—192°, when oxidised by bromine water, gives *triphenylmethylazoformamide*, $CPh_3{\cdot}N{:}N{\cdot}CO{\cdot}NH_2$, m. p. 200—225° (decomp.), which decomposes in solution to triphenylacetamide; in oxygen, no peroxide, $[NH_2{\cdot}CO{\cdot}]_2O$, can be obtained. *Triphenylmethylhydrazoformanilide*, m. p. 198° (decomp.), is not sufficiently soluble to be oxidised.

Benzenesulphonazotriphenylmethane is not obtainable: the *hydrazo*-compound decomposes on oxidation, giving *benzenesulphontriphenylmethane*; the dibenzenesulphonylhydrazine also decomposes, giving diphenylsulphone.

The hydrazo-compound from benzylhydrazine and triphenylmethyl chloride cannot be isolated, undergoing autoxidation in air to *as*-tetraphenylethane; it is concluded that benzylazotriphenylmethane is very unstable. p-*Anisylhydrazotriphenylmethane*, m. p. 114° (decomp.), is also very susceptible to autoxidation; it yields the *azo*-compound, m. p. 114° (decomp.), which decomposes in xylene at 70—80° to a product from which no *p*-methoxytetraphenylmethane can be isolated, but only triphenylmethane. E. W. WIGNALL.

Metallic derivatives of o-amino- and o-hydroxy-azo-compounds. G. CHARRIER and A. BERETTA [with I. PAPPOFF] (Gazzetta, 1926, **56**, 865—871).—Cupric, nickelous, and cobaltous ammonium hydroxides react with *o*-amino- and *o*-hydroxy-azo-compounds to give crystalline compounds, which were at first thought to be salts in which the azo-compound had replaced the ammonia, but which proved to have the general formula $M[Az]_2$, where M is the metal and Az the azo-compound. These compounds, especially those of copper, are readily converted on

heating into triazoles, and may be intermediate products in the formation of the latter by way of metal ammonia derivatives. They are stable to alkali, but are decomposed by acid. The following are described: *Copper bisbenzeneazo-β-naphthylamine*, red, m. p. about 130°, soluble in benzene, and the corresponding *nickel*, green, m. p. 260—265° (decomp.), and *cobalt*, dark brown, sinters 215—220°, m. p. about 265°, compounds; *copper bis-o-tolueneazo-β-naphthylamine*, decomp. below m. p.; *copper bisbenzeneazo-β-naphthol*, m. p. about 278°, and the corresponding *nickel* and *cobalt* compounds, which decompose below m. p.; *copper bis-p-tolueneazo-β-naphthol*, m. p. 285—290° (decomp.), and the corresponding *nickel* compound. E. W. WIGNALL.

Spectrochemical studies of hydroxyazo-compounds. I. T. UEMURA, N. YOKOJIMA, and C. TAN (Bull. Chem. Soc. Japan, 1926, **1**, 260—266).—The relation between the colour and constitution of hydroxyazo-compounds has been studied spectrochemically. The colour change from yellow, through red, to bluish-violet, observed on addition of alkali to *p*-nitrobenzeneazo-β-naphthol, and considered by Suitsu and Okuma (J. Soc. Chem. Ind. Japan, 1926, **29**, 132) to be due to the azo-, mono- and diquinonoid forms, respectively, has now been observed in simpler compounds.

p-Hydroxyazobenzene, benzeneazoresorcinol, benzeneazo-*p*-cresol, *p*-nitrobenzeneazophenol, and *m*-nitrobenzeneazoresorcinol all show the first colour change on addition of alkali, whilst the violet diquinonoid forms of *p*-nitrobenzeneazoresorcinol and *p*-nitrobenzeneazo-*p*-cresol are obtained on further addition of alkali. These results are in agreement with the curves obtained by plotting the oscillation frequencies against the relative thicknesses of 0·0001*N*-solutions of the hydroxyazo-compounds. A. S. CORBET.

Molecular rearrangement of some new unsymmetrical hydrazines. E. C. GILBERT (J. Amer. Chem. Soc., 1927, **49**, 286—292).—*α-Benzoyl-β-p-toluoylhydrazine*, m. p. 220—221°, is obtained by the action of *p*-toluoyl chloride on benzoylhydrazine in suspension in benzene. When heated at 450° for 5 min., it yields a mixture of aniline (80%) and *p*-toluidine (20%). When heated at 350° for 30 min., the product contained the *compound* $Me{\cdot}C_6H_4{\cdot}C(:O){\cdot}N{\cdot}N{:}CPh$, m. p. 114—115°, which forms an additive *compound* with silver nitrate (1 : 1), m. p. 260° (decomp.). *α-Benzoyl-β-p-chlorobenzoylhydrazine*, m. p. 222—223°, obtained by the action of *p*-chlorobenzoyl chloride on benzoylhydrazine in aqueous alkaline solution, yields aniline and *p*-chloroaniline, when heated at 410° for 3 min., in the proportion of 1 : 3. The results obtained are in accordance with the Stieglitz theory of the rearrangement (A., 1922, i, 778). F. G. WILLSON.

Organic salts of hydrofluoboric acid. E. WILKE-DORFURT and G. BALZ (Ber., 1927, **60**, [*B*], 115—118).—Attention is directed to the striking resemblance between perchloric and hydrofluoboric acids in their salts. The following *fluoborates* are described: *benzenediazonium*, volatile at 100°, and *o-toluenediazonium*, characterised by unusual stability, *tetramethylammonium*; *tetraethylammonium*; *neurine*, $C_2H_3{\cdot}NMe_3,BF_4$; *brucine*, not molten below 250°; *strychnine*, not molten below 280°; *morphine*; *cocaine*. *Brucine persulphate* and the corresponding *fluorosulphonate* are described. H. WREN.

Stereochemistry of dicyclic ring systems. II. Decahydronaphthalene and its derivatives. II. β-Substituted decahydronaphthalenes. W. HUCKEL, R. MENTZEL, E. BRINKMANN, and E. KAMENZ (Annalen, 1926, **451**, 109—132).—The previous investigation (A., 1925, i, 258) has been extended, and second *cis*- and *trans*-forms of 2-hydroxydecahydronaphthalene (β-decalol) and 2-aminodecahydronaphthalene (β-decalylamine) have been isolated. That each of these compounds should exist in four isomeric forms supports the views of Mohr (*ibid.*, 1922, i, 243).

Hydrogenation by Skita's method of β-naphthol and *ar*-tetrahydro-β-naphthol yields 33% of decahydronaphthalene (75% *cis*- and 25% *trans*-) and 67% of β-decalol (mainly the *cis*-form, m. p. 105°), whilst with *ac*-tetrahydro-β-naphthol the relative quantities of the products are reversed. Separation of the mixture of β-decalols may be effected by crystallisation of the hydrogen phthalates and yields *cis*-β-decalol, m. p. 105°, *trans*-β-decalol, m. p. 75° (*hydrogen phthalate*, m. p. 180°), and a new *cis*-form (*hydrogen phthalate*, m. p. 153°; *phenylurethane*, m. p. 102°), which after further purification through its *oxalate*, m. p. 131—132°, has m. p. 17°.

Catalytic reduction of β-naphthyl methyl ether yields only the tetrahydro-derivative, whilst β-naphthyl benzoate gives a mixture which, after hydrolysis, yields mainly decahydronaphthalene and 20% of *cis*-β-decalol, m. p. 105°.

Reduction of *cis*-β-decalone (*cis*-2-ketodecahydronaphthalene) by sodium and alcohol yields a mixture of the two *cis*-β-decalols, mainly m. p. 105°, whilst the *trans*-ketone on reduction by Willstatter's and Skita's methods gives a mixture of *trans*-β-decalol, m. p. 75°, and a new *trans*-form (*phenylurethane*, m. p. 99°), which after further purification through the *oxalate*, m. p. 143°, has m. p. 53°.

Technical β-decalol may be separated into the four isomerides by fractional distillation followed by fractional crystallisation of the hydrogen phthalates and further purification through the oxalates.

Hydrogenation of *cis*-β-decaloneoxime yields only the known *cis*-β-decalylamine (*acetyl* derivative, m. p. 154°; *benzoyl* derivative, m. p. 202°; *benzoate*, m. p. 218°), but reduction by sodium and alcohol yields a mixture from which a second *cis*-β-decalylamine (*benzoyl* derivative, m. p. 127°) can be isolated. Similarly, *trans*-β-decaloneoxime yields two *trans*-β-decalylamines, the known form with acetyl derivative, m. p. 130° (*benzoyl* derivative, m. p. 177°; *benzoate*, m. p. 217°), and the new form (*acetyl* derivative, m. p. 163°; *benzoyl* derivative, m. p. 174°).

Experiments with decahydronaphthalene and β-decalone show that the *cis*-form has a slightly higher heat of combustion than the *trans*-form in each case. R. W. WEST.

Stereochemistry of dicyclic ring systems. III. Hexahydrohydrindene and its derivatives. W.

HUCKEL and H. FRIEDRICH (Annalen, 1926, **451**, 132—160).—Models constructed similarly to those of Mohr (A., 1922, i, 243) suggest that *cis*-hexahydrohydrindol should exist in two *meso*-forms, whilst the *trans*- should exist in one racemic form. These isomerides have now been isolated.

When *cis*- and *trans*-β-decalols are heated with potassium hydrogen sulphate, they yield *cis*- and *trans*-Δ^2-octahydronaphthalenes (cf. Borsche and Lange, A., 1924, i, 32), which, on oxidation with alkaline potassium permanganate, give good yields of *cis-cyclo*hexane-1 : 2-diacetic acid (*dianilide*, m. p. 212—214°; *diethyl* ester, b. p. 187°/24 mm., d_4^{20} 1·030, n_D^{20} 1·4581), and the *trans*-acid (*monoanilide*, m. p. 179°; *dianilide*, m. p. 283°; *diethyl* ester, b. p. 182°/21 mm., d_4^{20} 1·0246, n_D^{20} 1·4566). The *trans*-acid, m. p. 167°, may be resolved through its cinchonidine salt into enantiomorphs having m. p. 148—150°. This favours the view that the *trans*-hexahydrohydrindol should be a racemic form. Ethyl *cis-cyclo*hexane-1 : 2-diacetate by the Dieckmann reaction yields ethyl *cis*-hexahydro-β-hydrindone-α-carboxylate, b. p. 170—173°/21 mm., which by acid hydrolysis gives *cis*-hexahydro-β-hydrindone, m. p. 10°, b. p. 109°/23 mm., d_4^{20} 0·998, n_D^{16} 1·48457 (semicarbazone, m. p. 215—216°; oxime, m. p. 80°), which is also obtained by heating the *cis*-diacetic acid with acetic anhydride. Similarly, the *trans*-compounds yield ethyl *trans*-hexahydro-β-hydrindone-α-carboxylate, b. p. 160—163°/20 mm., and *trans*-hexahydro-β-hydrindone, m. p. −12°, b. p. 98°/19 mm., d_4^{20} 0·978, 1·47687 (semicarbazone, m. p. 243°; oxime, m. p. 161°).

Reduction of hexahydro-β-indone by Willstatter's method yields mainly hexahydrohydrindene with some hexahydro-β-hydrindol, which can be partly separated through the *hydrogen phthalates*, m. p. 109—110° and m. p. 80—85° (still impure) (*phenylurethanes*, m. p. 102—103° and m. p. 82°), and a small quantity of *cis*-hexahydro-β-hydrindone. Reduction by Skita's method in neutral solution gives a 50% yield of mixed ketone and alcohol. By reduction, *cis*-hexahydro-β-hydrindone yields a mixture of the two *cis*-hexahydro-β-hydrindols, whilst the *trans*-ketone yields *trans*-hexahydro-β-hydrindol, m. p. 17°, b. p. 102°/13 mm. (*phenylurethane*, m. p. 114°).

Oxidation of *cis*-hexahydro-β-hydrindol by chromic acid in acetic acid solution yields *cis*-hexahydro-β-hydrindone and *cis-cyclo*hexane-1-acetic-2-propionic acid. The *trans*-isomeride of the latter acid is obtained by oxidising *trans*-hexahydro-β-hydrindone with alkaline potassium permanganate solution.

The heat of combustion of *cis*-hexahydro-β-hydrindone is slightly higher than that of the *trans*-isomeride. R. W. WEST.

Action of methyl alcohol on phenol at high temperature and pressures; formation of xanthen. W. IPATIEV, N. ORLOV, and A. PETROV (Ber., 1927, **60**, [*B*], 130—133; cf. A., 1926, 281).—Methyl alcohol and phenol in presence of aluminium hydroxide at 440° and 220 atm. (maximum) afford *o*-cresol, anisole, xanthen, and smaller amounts of ethylene, carbon monoxide, hydrogen, carbon, and traces of benzene. The isomeric cresols are not produced. The formation of hexamethylbenzene could not be established. Anisole is doubtless formed by direct etherification of phenol under the influence of the catalyst. The production of *o*-cresol appears due to isomerisation of anisole and that of xanthen to the action of phenol on *o*-cresol with loss of water and hydrogen. Phenol when heated in the presence of aluminium hydroxide yields diphenylene oxide and small amounts of diphenyl ether. H. WREN.

Substituted diaryl ethers. I. Di-*p*-tolyl ether. J. REILLY, P. J. DRUMM, and H. S. B. BARRETT (J.C.S., 1927, 67—73).—Di-*p*-tolyl ether, prepared from potassium *p*-tolyloxide and *p*-bromotoluene in presence of copper bronze and *p*-cresol, has m. p. 50° (see Gladstone and Tribe, J.C.S., 1882, **41**, 9). Oxidation of the ether with chromic acid gives *di*-p-*carboxydiphenyl ether* (*silver* salt). Nitration of di-*p*-tolyl ether with nitric acid in acetic acid solution yields 2-*nitrodi*-p-*tolyl ether*, m. p. 50°; with nitric acid alone, or by treatment with nitrogen peroxide, 2 : 2′-*dinitrodi*-p-*tolyl ether*, m. p. 126°; with nitric acid–sulphuric acid, the 2 : 2′-dinitro-compound and 2 : 6 : 2′(?) : 6′(?)-*tetranitrodi*-p-*tolyl ether*, m. p. 246°, this last substance being obtained also by nitration of 2 : 6-*dinitrodi*-p-*tolyl ether*, m. p. 98—100°. There are produced at the same time varying amounts of nitrated *p*-cresols. The above nitro-derivatives were also synthesised by preparing them from the requisite potassium nitrotolyloxides and bromonitrotoluenes. Di-*p*-tolyl ether condenses with acetyl chloride, benzoyl chloride, and phthalic anhydride in presence of aluminium chloride, giving monoketonic substances.

Di-*p*-tolylene oxide, m.p. 165° (Buch, A., 1885, i, 147, gave this as the m. p. of di-*p*-tolyl ether), is obtained by heating *p*-cresol with litharge. H. BURTON.

Reciprocal exchange of aromatically combined hydroxyl and halogen. II. Mechanism of the Ullmann–Nadai reaction. W. BORSCHE and E. FESKE (Ber., 1927, **60**, [*B*], 157—159; cf. A., 1918, i, 11).—Replacement of hydroxyl in polynitrophenols by chlorine (cf. Ullmann and Nádai, A., 1908, i, 525) occurs according to the scheme $(NO_2)_nC_6H_3\cdot OH + Cl\cdot SO_2\cdot C_7H_7 = (NO_2)_2C_6H_3\cdot O\cdot SO_2\cdot C_7H_7 + HCl$;

$(NO_2)_2C_6H_3\cdot O\cdot SO_2\cdot C_7H_7 + NPhEt_2 =$

$(NO_2)_2C_6H_3\cdot NPhEt_2\cdot O\cdot SO_n\cdot C_7H_7 \xrightarrow{+HCl}$

$(NO_2)_2C_6H_3\cdot NPhEt_2Cl \longrightarrow NPhEt_2 + (NO_2)_2C_6H_3Cl$.

3 : 5-Dinitro-*o*-tolyl *p*-toluenesulphonate dissolved in nitrobenzene and diethylaniline saturated with hydrogen chloride is converted at 120° into 2-chloro-3 : 5-dinitrotoluene, m. p. 61°, in 53% yield. The sulphonic ester merely becomes hydrolysed when heated with hydrochloric acid in acetic acid solution at 130° or 160°. When the ester is warmed with pyridine, the *compound* $(NO_2)_2C_6H_2Me\cdot NC_5H_5\cdot O\cdot SO_2\cdot C_7H_7$, m. p. 196°, is produced, which is converted by 5*N*-hydrochloric acid at 170° into 2-chloro-3 : 5-dinitrotoluene in 80% yield. 4-Chloro-3 : 5-dinitrotoluene is obtained in 10—15% yield from diethylaniline hydrochloride and 3 : 5-dinitro-*p*-tolyl *p*-toluenesulphonate at 110° or from dinitro-*p*-cresol and *p*-toluenesulphonyl chloride in diethylaniline. The yield rises to 70% when the *pyridinium* derivative of the sulphonate, m. p. 179°, is heated with hydrochloric acid. H. WREN.

Some aryl amides. S. Weil (Rocz. Chem., 1926, **6**, 756—767) [with (Mlle.) Bomberg].—m-*Nitrobenz*-o-*phenetidide*, m. p. 113°, yields on reduction m-*aminobenz*-o-*phenetidide* (I), m. p. 89—90°, which on condensation with *m*-nitrobenzoyl chloride gives m-3-*nitrobenzamidobenz*-o-*phenetidide*, m. p. 172°, giving by reduction m-3-*aminobenzamidobenz*-o-*phenetidide*, $NH_2 \cdot C_6H_4 \cdot CO \cdot NH \cdot C_6H_4 \cdot CO \cdot NH \cdot C_6H_4 \cdot OEt$ (II), m. p. 119—120°. The m-*nitrobenzamide* of *aminophenyldimethylpyrazolone*, m. p. 199°, is obtained by the action of *m*-nitrobenzoyl chloride on aminoantipyrine.

[With (Mlle.) Z. Wyszogród.]—*Ethyl* p-3-*nitrobenzamidobenzoate*, m. p. 177—178°, prepared by the action of *m*-nitrobenzoyl chloride on ethyl *p*-aminobenzoate, yields on reduction the corresponding *amine* (III), m. p. 176—177°, which is further condensed with *m*-nitrobenzoyl chloride to yield ethyl p-3-(m-*nitrobenzamido*)*benzamidobenzoate*, m. p. 218°, corresponding *amine*, m. p. 205—206°.

[With (Mlle.) C. Wierzbicka.]—2-*Nitro*-p-*toluoyl chloride*, m. p. 17°, on condensation with ethyl *p*-aminobenzoate yields *ethyl* p-2-*nitro*-4-*toluamidobenzoate*, m. p. 172°, giving the corresponding *amine* (IV), m. p. 173—174°, on reduction. The above condensation is repeated with this amine, yielding *ethyl* p-2-(2′-*nitro*-4′-*toluamido*)-4-*toluamidobenzoate*, m. p. 207—208°, which again, on reduction of the nitro-group, yields an *amine*, m. p. 181—182°.

[With J. Slifirski.]—Certain of the amines prepared as above are converted into carbamide derivatives by the action of carbonyl chloride. The *carbamides* have the following m. p.: from amine I, 224—225°; II, above 200° (decomp.); III, above 210° (decomp.); and IV, 180—181°. These carbamides possess considerable trypanocidal properties.

R. Truszkowski.

2 : 3-Dichloroquinol. E. Gebauer-Fülnegg and E. Malnič (Monatsh., 1926, **47**, 403—404; cf. Dimroth, Eber, and Wehr, A., 1926, 296).—Only moderate yields of 2 : 3-dichloroquinol are obtained (1) by the action of sulphuryl chloride on quinol in ether solution, (2) by the action of sulphur dioxide on *p*-benzoquinone dichloride (Peratoner and Genco, A., 1895, i, 362), and (3) by the method of Eckert and Endler (*ibid.*, 1922, i, 932). As stated by Hollander (*ibid.*, 1920, i, 559), this product is not obtained by the action of hydrogen chloride on an ethereal solution of monochlorobenzoquinone. The following derivatives of 2 : 3-dichloroquinol are prepared: *dimethyl ether*, m. p. 124°; 2 : 3-*dichloro*-4 : 5-*dibromo*-p-*benzoquinone*, m. p. 294°.

J. W. Baker.

Bromination of quinol monomethyl ether (*p*-methoxyphenol). F. M. Irvine and J. C. Smith (J.C.S., 1927, 74—77).—Monobromination of quinol monomethyl ether in carbon disulphide solution yields the 2-*bromo*-derivative, m. p. 44—45° (*benzoyl* derivative, m. p. 85°), whereas bromination of 4-*methoxyphenyl benzoate*, m. p. 87°, in formic acid solution gives 3-*bromo*-4-*methoxyphenyl benzoate*, m. p. 105·5°, which on hydrolysis furnishes 3-*bromoquinol monomethyl ether*, m. p. 77—78°. Dibromination of the ether in acetic acid solution yields 30—35% of the 2 : 5-dibromo-derivative, the main product being the 2 : 6-dibromo-isomeride (cf. Kohn and Guttmann, A., 1925, i, 1263). An improved method for the preparation of 2 : 6-dibromoquinol dimethyl ether is given.

H. Burton.

Synthesis of *p*-methoxyephedrine and *p*-hydroxy-*m*-methoxyephedrine. G. Koller (Monatsh., 1926, **47**, 397—402).—β-Bromo-α-methoxy-α-*p*-anisylpropane (prepared by the action of methyl alcohol on anethole dibromide) when heated with 2 mols. of a 33% methyl-alcoholic solution of methylamine at 110° for 8 hrs. yields β-*methylamino*-α-*methoxy*-α-p-*anisylpropane*, b. p. 142—143°/13 mm., which, when treated in an atmosphere of carbon dioxide with a solution of hydrogen chloride saturated at 0°, yields β-*methylamino*-α-*hydroxy*-α-p-*anisylpropane* (*p*-methoxyephedrine; cf. Späth and Koller, A., 1925, ii, 1086), m. p. 119—120° (*hydrochloride*, m. p. 169—170° in a vacuum). *iso*Eugenol dibromide treated with absolute methyl alcohol similarly yields β-bromo-α-methoxy-α-(*p*-hydroxy-*m*-methoxyphenyl)propane (β-bromo-α-methoxydihydro*iso*eugenol), m. p. 82—83° (Auwers, *ibid.*, 1902, i, 212, describes it as a syrup), which is added in small successive portions to a 33% alcoholic methylamine solution and the product hydrolysed with hydrochloric acid to remove the α-methoxy-group, when β-*methylamino*-α-*hydroxy*-α-(p-*hydroxy*-m-*methoxyphenyl*)*propane* (amorphous) is obtained. Physiologically, these compounds are much weaker in their action than ephedrine.

J. W. Baker.

Constitution of furoperylene. A. Rollett and L. Bayer (Monatsh., 1926, **47**, 447—448).—Dehydration of 1 : 12-dihydroxyperylene with zinc and zinc chloride at 250—320° for 0·4 hr. yields 1 : 12-furoperylene, m. p. 252°, which does not depress the m. p. of a purified specimen prepared from β-dinaphthalene oxide (Weitzenböck and Seer, A., 1913, i, 847), thus confirming the constitution there assigned.

J. W. Baker.

Dehydration of benzyl alcohol. S. S. Nametkin and D. N. Kursanov (J. Russ. Phys. Chem. Soc., 1926, **57**, 390—394).—By the xanthate reaction on acyclic hydroxy-compounds, it is possible to convert the latter into unsaturated hydrocarbons. This can occur in three ways. An unsaturated hydrocarbon containing a double linking may be formed (cf. A., 1904, i, 327; 1905, i, 71; 1925, i, 1146), or isomerisation may occur (cf. Qvist, *ibid.*, 1919, i, 165; and Komppa and Roschier, *ibid.*, 1922, i, 1167), or, finally, the dehydration may be 1 : 3 and not 1 : 2 (cf. Tschugaev and Budrick, *ibid.*, 1912, i, 480). None of these courses is possible in benzyl alcohol. Dehydration with vigorous dehydrating agents (Cannizzaro, Annalen, 1854, **92**, 114) yielded a compound $C_{14}H_{12}$, m. p. 163°. By the xanthate reaction, the authors find that the main product is stilbene: $2CH_2Ph \cdot O \cdot CS \cdot S \cdot Me \longrightarrow 2COS + 2MeSH + CHPh{:}CHPh$.

Methyl benzyl xanthate, m. p. 29°, is prepared by the action of methyl sulphate on benzyl xanthate. Ethyl sulphate yields the *ethyl* ester, b. p. 170—171°/14 mm., m. p. below 20°. It has the characteristic odour of mercaptan. The methyl ester is converted by ammonia at 0° in the course of two weeks into the *amide*, m. p. 61·5—62°. When the ester is heated a

350° in a flask carrying a condenser, the substance is decomposed with the formation of stilbene on the walls of the condenser. The residue in the flask was a *substance*, m. p. 184—185°, having an empirical formula, $C_{28}H_{26}S$. E. ROTHSTEIN.

Action of sulphur on organic compounds. IX. L. SZPERL (Rocz. Chem., 1926, **6**, 728—737).—*o*-Methylbenzyl alcohol, m. p. 33·7—34·2°, prepared from *o*-methylbenzyl bromide, yields, on heating at 200° with sulphur, *o*-methylbenzaldehyde, *o*-toluic acid, probably 2 : 2′-dimethylstilbene, and a number of unidentified products.

[With I. LIBRACH.]—*m*-Methylbenzyl alcohol when heated with sulphur yields m-*methylbenzyl ether*, b. p. 315—321°, *m*-methylbenzaldehyde, *m*-toluic acid, 3 : 3′-dimethylstilbene, and a number of unidentified products.

[With E. SZPIC.]—*p*-Methylbenzyl alcohol, similarly treated, gives *p*-methylbenzaldehyde, *p*-toluic acid, 4 : 4′-dimethylstilbene, and unidentified products. R. TRUSZKOWSKI.

Molecular transpositions. Preparation and dehydration of some β-phenyl-β-alkylethyl alcohols. (MME.) RAMART-LUCAS and (MLLE.) AMAGAT (Compt. rend., 1927, **184**, 30—32).—β-Phenyl-β-alkylethyl alcohols, on dehydration, yielded chiefly hydrocarbons of the symmetrical type, CHPh:CHR, with small amounts of the CPhR:CH_2 type, thus differing from *iso*butyl alcohol and the corresponding ββ-diaryl alcohols (cf. A., 1925, i, 658). The following are described: α-*phenyl*-n-*butyramide*, m. p. 84—85°, b. p. 185°/16 mm.; β-*phenyl*-n-*butyl alcohol*, b. p. 120—121°/15 mm.; β-*phenyl*-n-*butylamine*, b. p. 110°/13 mm., *hydrochloride*, m. p. 156°; α-*phenyl*-β-*methylbutyramide*, m. p. 110°; β-*phenyl*-γ-*methylbutyl alcohol*, b. p. 130°/15 mm.; β-*phenyl*-γ-*methyl*-n-*butylamine hydrochloride*, m. p. 128°. B. W. ANDERSON.

Action of Grignard reagents on amino-acids. II. Synthesis of peptide alcohols and their fission by acid and alkali. F. BETTZIECHE and R. MENGER (Z. physiol. Chem., 1926, **161**, 37—65).—Although amino-alcohols of the type NH_2·CHR·CR'_2·OH react almost quantitatively with chloroacetyl chloride, the resulting products are aminated with great difficulty to glycylamino-alcohols. On the other hand, benzoylglycylamino-alcohols are readily prepared by the use of hippuryl chloride. The diphenyl compounds (R′=Ph) are easily hydrolysed by acid, forming benzoic acid, ammonia, and a ketone or an aldehyde, R·CO·CHR'_2. The dibenzyl compounds (R′=CH_2Ph), on the other hand, give, with greater difficulty, first oxazolines and finally 2-benzylindenes. Hydrolysis of the peptide alcohols with alkali yields first glycine and the amino-alcohol, which then undergoes further fission into amine and ketone.

γ-*Bromoacetamido*-α-*phenyl*-β-*benzylisopropyl alcohol*, m. p. 87—88°, is prepared in 72% yield from the amino-alcohol and bromoacetyl bromide in presence of sodium hydroxide. β-*Chloroacetamido*-αα*β*-*triphenylethyl alcohol*, m. p. 218—219°, and β-*chloroacetamido*-αα-*diphenylpropyl alcohol*, m. p. 170—171°, are similarly obtained; the latter, treated with aqueous-alcoholic ammonia at 130°, gives a very small yield of β-*glycylamino*-αα-*diphenylpropyl alcohol*, m. p. 187·5°. γ-Bromoacetamido-α-phenyl-β-benzylbutan-β-ol is converted by ammonia into an oily γ-*glycylamino*-α-*phenyl*-β-*benzylbutan*-β-*ol*, which on benzoylation yields γ-*hippurylamino*-α-*phenyl*-β-*benzylbutan*-β-*ol*, m. p. 183°, more readily prepared from hippuryl chloride and γ-amino-α-phenyl-β-benzylbutan-β-ol. These two methods are also used for the preparation of β-*hippurylamino*-αα*β*-*triphenylethyl alcohol*, m. p. 213—214°, γ-*hippurylamino*-α*γ*-*diphenyl*-β-*benzyl*isopropyl alcohol, m. p. 188°, and β-*hippurylamino*-αα-*diphenylpropyl alcohol*, m. p. 188°. Hydrolysis of compounds of the type X·NH·CHR·CR'_2·OH with concentrated hydrochloric acid gives the following results. Where X=PhCO, R=Me, and R′=CH_2Ph, 2-phenyl-5 : 5-dibenzyl-4-methyloxazoline, m. p. 152—153°, and a non-basic *isomeride*, m. p. 90°, are isolated, but no benzoic acid. The non-acylated amino-alcohol is obtained in the case of the benzyl compounds (X=NH_2·CH_2·CO· or NHBz·CH_2·CO·, R=Me or Ph, R′=CH_2Ph), and is accompanied by an indene derivative, $C_6H_4<\begin{matrix}CR\\CH_2\end{matrix}>CR'$. γ-Glycylamino-α-phenyl-β-benzylbutan-β-ol is also formed from the corresponding β-hippurylamino-alcohol, and where X=NHBz·CH_2·CO·, R=Ph, R′=CH_2Ph there are isolated the benzoylamino-alcohol (X=Bz), and dibenzylacetophenone (β-benzoyl-α*γ*-diphenylpropane), m. p. 78°. The phenyl compounds (R′=Ph) give ketones, viz., αα-diphenylacetone, m. p. 45—46° (oxime, m. p. 164°), from X=NH_2·CH_2·CO or NHBz·CH_2·CO and R=Me, and diphenylacetophenone, m. p. 135—136° (R=Ph). β-Glycylamino-αα-diphenylethyl alcohol with hydrochloric acid gives diphenylacetaldehyde, but with 40% sulphuric acid at 120—128° deoxybenzoin. During the hydrolysis of the acylamino-alcohols with 8% or 15% sodium hydroxide, there are obtained, in addition to the corresponding amino-alcohols, from γ-hippurylamino-α-phenyl-β-benzylbutan-β-ol, a *substance*, m. p. 163° (impure), together with an unisolated *compound* which is hydrolysed by acid to γ-amino-α-phenyl-β-benzylbutan-β-ol, benzoic acid, and glycine, and from γ-hippurylamino-α*γ*-diphenyl-β-benzylbutan-β-ol, a *substance*, m. p. 173°. In the case of the benzyl (but not the phenyl) compounds containing the hippurylamino-group, a glycylamino-derivative is isolable. No dibenzyl ketone is identified where R′=CH_2Ph, but benzophenone is isolated where R′=Ph, except in the case of β-glycylamino-αα-diphenylpropyl alcohol. C. HOLLINS.

Formation of chrysene by the dehydrogenation of cholesterol. O. DIELS and W. GADKE (Ber., 1927, **60**, [*B*], 140—147; cf. A., 1925, i, 1062).—The hydrocarbon, m. p. 246—248°, obtained by the dehydrogenation of cholesterol by palladised charcoal is identified as chrysene. In addition, a hydrocarbon, m. p. about 180°, which is unsaturated towards bromine, and a hydrocarbon, m. p. about 325°, stable towards bromine, are also produced. H. WREN.

Yeast ergosterol. I. F. REINDEL, E. WALTER, and H. RAUCH (Annalen, 1927, **452**, 34—46).—The ergosterol used had m. p. 160—161°, $[\alpha]_D$ −117° (all rotations in chloroform); acetate, m. p. 172—173°

(cf. Windaus and Grosskopf, A., 1923, i, 75); benzoate, m. p. 163—165°. Attempts to obtain the corresponding ketone by oxidation led to breakdown products, whether chromic acid, potassium permanganate, lead tetra-acetate, or fuming nitric acid at —20°, each in acetic acid, was used. Attempts to obtain ergosteryl chloride also failed, owing to an isomerisation which readily occurs. Thus when ergosteryl acetate was dissolved in chloroform and treated at 0° with hydrogen chloride, *isoergosteryl acetate*, m. p. 129—131°, $[\alpha]_D$ −62·5°, was obtained, which was hydrolysed by potassium methoxide to *isoergosterol*, $C_{27}H_{41}\cdot OH$, m. p. 135—136°, $[\alpha]_D$ −86·9° (*benzoate*, m. p. 135°). This is presumably a valency isomerism, since catalytic hydrogenation of the original and of the *iso*ergosteryl acetates gave the same α-ergostanyl acetate, $C_{27}H_{47}\cdot OAc$, m. p. 110°, $[\alpha]_D$ +5·18° in chloroform, hydrolysed to α-ergostanol, m. p. 130—131°, $[\alpha]_D$ +17·86° (*benzoate*, m. p. 130—131°), from which ergostanyl chloride, $C_{27}H_{47}Cl$, was obtained crystalline, m. p. 104—105°, by the action of phosphorus pentachloride. The α-ergostanyl acetate is further capable of isomerisation to *β-ergostanyl acetate*, m. p. 94—95°, $[\alpha]_D$ +3·0°, 95%, with 5% of a new *acetate*, m. p. 110—111°, of a *sterol*, m. p. 141—142°. Hydrolysis of the β-acetate gave *β-ergostanol*, m. p. 114—118°, also obtained by isomerisation of α-ergostanol. Either ergostanol gave with chloroacetyl chloride a *β-ergostanyl chloroacetate*, m. p. 166—167°. When β-ergostanyl acetate was subjected to catalytic hydrogenation, a small amount of hydrogen only was absorbed, and a *γ-ergostanyl acetate*, m. p. 144—145°, $[\alpha]_D$ +5·95°, was formed in 80% yield, with an acetate, m. p. 109°, possibly α-ergostanyl acetate. *γ-Ergostanol* obtained by hydrolysis has m. p. 144—145°, $[\alpha]_D$ +15·94° (*benzoate*, m. p. 163—165°; *chloroacetate*, m. p. 200—201°). E. W. Wignall.

Organic molecular compounds with co-ordination centres. I. H. Rheinboldt [with H. Pieper and P. Zervas] (Annalen, 1927, **451**, 256—273).—Examination of a series of complex acids similar to those obtained by Wieland and Sorge (A., 1916, i, 710) from deoxycholic acid, and by Boedecker (*ibid.*, 1920, i, 848) from *apo*cholic acid, shows that the number of mols. of bile acid combined with the central fatty acid molecule depends on the number of carbon atoms in the latter, but not on saturation or on the presence of a free carboxyl group. Fatty acids containing 4 to 8 carbon atoms combine with 4 mols., those containing 9 to 14 with 6 mols., and those containing more than 15 with 8 mols. of bile acid. It is suggested, in accordance with the theoretical considerations of Hüttig (*ibid.*, 1921, ii, 193), that these compounds represent a new type of organic molecular compound, in which the whole fatty acid molecule acts as a co-ordination centre. New *choleic acids* have been prepared from the following compounds and deoxycholic acid, the number of mols. of the latter being given in parentheses: tiglic acid (4), m. p. 171·5—172°; sorbic acid (4), m. p. 171—172°; *n*-heptoic acid (4), m. p. 169°; *n*-octoic acid (4), m. p. 170°; pelargonic acid (6), m. p. 173°; *n*-decoic acid (6), m. p. 174—175°; *n*-undecoic acid (6), m. p. 176°; undecenoic acid (6), m. p. 176—177°; tridecoic acid (6), m. p. 177—178°; myristic acid (6), m. p. 181—182°; *n*-pentadecoic acid (8), m. p. 183·5—184°; cetyl palmitate (8), m. p. 195°; *n*-heptadecoic acid (8), m. p. 185·5—186·5°; stearolic acid (8), m. p. 174°; arachidic acid (8), m. p. 188—189°; behenic acid (8), m. p. 189—189·5°; ethyl behenate (8), m. p. 191·5°; brassidic acid (8), m. p. 184°; dibromobehenic acid (8), m. p. 177°; behenolic acid (8), m. p. 183—183·5°; lignoceric acid (8), m. p. 193—193·5°; cerotic acid (8), m. p. 193—194°; octylcetylacetic acid (8), m. p. 188—188·5°; cerylformic acid (8), m. p. 194·5°; montanic acid (?), m. p. 196°; ethyl montanate (8), m. p. 197—198°; and from the following compounds and *apo*cholic acid: tiglic acid (4), m. p. 168—168·5°; sorbic acid (4), m. p. 170—171°; ethyl behenate (8), m. p. 190°, and montanic acid, m. p. 190°. The great stability of the last-named compound is shown by means of a m.-p. curve. H. E. F. Notton.

Sulphonation of cinnamic acid: proof that the secondary product is *m*-sulphocinnamic acid; synthesis of *o*-sulphocinnamic acid; action of sodium hydrogen sulphite on cinnamic acid derivatives. F. J. Moore and G. R. Tucker (J. Amer. Chem. Soc., 1927, **49**, 258—266; cf. A., 1922, i, 454).—Contrary to the statement of van Duin (*ibid.*, 737), sulphonation of cinnamic acid with fuming sulphuric acid (18% free SO_3) at below 35° yields *p*- and *m*-sulphocinnamic acids, the *o*-isomeride not being produced. At higher temperatures, a disulphonic acid is formed, but the *o*-sulphocinnamic acid is again not produced. The *m*-sulphocinnamic acid was characterised by mixed m. p. of the following salts, obtained both from the sulphonation product and from synthetic *m*-sulphocinnamic acid: p-*toluidine hydrogen* salt, m. p. 227—230°; p-*anisidine hydrogen* salt, m. p. 238—239°. The o-*toluidine* (? hydrogen) salt was not obtained crystalline. *Barium hydrogen* o-*sulphocinnamate* was prepared by treating sodium *o*-bromocinnamate with sodium hydrogen sulphite in boiling aqueous solution until acidification caused no appreciable precipitation, and heating the product with sodium sulphite and a small proportion of copper sulphate for 40 hrs. at 170°. From it, the following salts of o-*sulphocinnamic acid* (+$2H_2O$) were prepared: *aniline hydrogen* salt, m. p. 208—209°; p-*toluidine hydrogen* salt (H_2O), m. p. 225—227°; o-*toluidine hydrogen* salt, m. p. 234—235°; and p-*anisidine hydrogen* salt, m. p. 205—207°. The *monochloride*, obtained by the action of phosphorus pentachloride on the sodium salt, has m. p. 179—182°. Oxidation of the potassium salt with aqueous permanganate affords salicylic acid. The action of aqueous sodium hydrogen sulphite on bromocinnamic acids yields products formed by addition of the sodium hydrogen sulphite to the double linking, which are transformed into sulphocinnamic acids under the conditions of Rosenmund's reaction (A., 1921, i, 370).

F. G. Willson.

***p*-Methylbenzylallylacetic acid and its cyclisation to tetrahydronaphthalene derivatives. A new dimethylnaphthalene.** G. Darzens and A. Heinz (Compt. rend., 1927, **184**, 33—35).—Ethyl sodiomalonate reacts with *p*-methylbenzyl chloride in

toluene to form *ethyl* p-*methylbenzylmalonate*, b. p. 179—180°/20 mm., and the sodium derivative of this forms with allyl bromide *ethyl* p-*methylbenzylallylmalonate*. The corresponding *acid*, on warming, gives p-*methylbenzylallylacetic acid*, b. p. 180°/20 mm., *methyl* ester, b. p. 146—150°/15 mm. This acid is converted by sulphuric acid into 1 : 7-*dimethyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*-3-*carboxylic acid*, m. p. 142—144° (*methyl* ester, b. p. 172°/15 mm.), and p-*methylbenzylvalerolactone*, b. p. 187°/15 mm. Dehydrogenation of the former by heating with sulphur gives rise to 1 : 7-*dimethylnaphthalene*-3-*carboxylic acid*, m. p. 217° (*methyl* ester, m. p. 68—69°, b. p. 199—201°/15 mm.), from which 1 : 7-*dimethylnaphthalene*, b. p. 147—149°/15 mm., *picrate*, m. p. 123—124°, is obtained (cf. J.C.S., 1907, **91**, 1149). B. W. ANDERSON.

Preparation and analysis of methylation products of thiosalicyclic (*o*-thiolbenzoic) acid. G. SACHS and M. OTT (Monatsh., 1926, **47**, 415—418).—*o*-Methylthiolbenzoic acid (Meister, Lucius, & Brüning, E.P. 593/07; B., 1907, 1003) when treated with an aqueous or alcoholic solution of mercuric acetate yields a *mercury* salt, m. p. 158—159°, which when heated with methyl iodide for 2 hrs. at 150° yields *o-carbomethoxyphenyldimethylsulphonium mercuric iodide*, $CO_2Me{\cdot}C_6H_4{\cdot}SMe_2I,HgI_2$, m. p. 123—124·5°, which is also obtained by the action of methyl sulphate on lead *o*-thiolbenzoate, $C_6H_4<\overset{CO_2}{S}>Pb$, and treatment of the product with potassium mercuric iodide. If a concentrated solution of iodine in potassium iodide is added instead of the potassium mercuric iodide, *o-carbomethoxyphenyldimethylsulphonium pentaiodide*, $CO_2Me{\cdot}C_6H_4{\cdot}SMe_2I_5$, is obtained. Determination of the methyl group by the method of Pollak and Spitzer (A., 1922, ii, 789) gives low results, but a value more nearly approaching the theoretical is obtained by the addition of mercuric iodide to the hydriodic acid, the silver iodide being converted into the chloride by a current of chlorine at the ordinary temperature before weighing. J. W. BAKER.

Bile acids. XXV. Degradation of [*cyclo*hexane]dicarboxylic acid. H. WIELAND, O. SCHLICHTING, and W. VON LANGSDORFF (Z. physiol. Chem., 1926, **161**, 74—79).—Three methods for the conversion of *cyclo*hexane-1 : 2-dicarboxylic acid into compounds which should be convertible into adipic acid were tried unsuccessfully. Magnesium methyl iodide reacts in warm ether with ethyl *cyclo*hexane-1 : 2-dicarboxylate to give the 2-*hydroxy*isopropylcyclo*hexanecarboxylic lactone*, m. p. 80° (*potassium* and *silver* salts of the hydroxy-acid are described), and oily *anhydro*-1 : 2-*di*(*hydroxy*isopropyl)cyclo*hexane* (1 : 1 : 3 : 3-*tetramethylhexahydrophthalan*), b. p. 80—83°/15 mm. In vigorously boiling ether, the product is 1 : 2-*di*(*hydroxy*isopropyl)cyclo*hexane*, m. p. 104°, which is converted by aqueous-alcoholic hydrochloric acid into the anhydro-compound. Reduction of ethyl *cyclo*hexane-1 : 2-dicarboxylate by Bouveault's method gives a small yield of *ωω-dihydroxy*-1 : 2-*dimethyl*cyclo*hexane* [1 : 2-*di*(*hydroxymethyl*)cyclo*hexane*], m. p. 57°, and the corresponding anhydro-compound (*hexahydrophthalan*), b. p. 170—175°/730 mm. The formation of the anhydro-compound in each case prevents oxidation of the two glycols to adipic acid.

Ethyl *cyclo*hexane-1 : 2-dicarboxylate is converted by way of the *dihydrazide*, m. p. 245°, *diazide*, and *diurethane*, m. p. 145°, into 1 : 2-diamino*cyclo*hexane dihydrochloride, m. p. 303°, but attempts to prepare from this the dihydroxy-compound failed. C. HOLLINS.

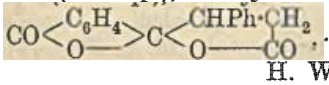
Dependence of rotatory power on chemical constitution. XXXI. Resolution of *m*-carboxyphenylmethylsulphine-*p*-toluenesulphonylimine. S. G. CLARKE, J. KENYON, and H. PHILLIPS (J.C.S., 1927, 188—194).—Chloramine-T and *m*-methylthiolbenzoic acid react, giving dl-m-*carboxyphenylmethylsulphine*-p-*toluenesulphonylimine*, $C_6H_4Me{\cdot}SO_2{\cdot}N{\cdot}SMe)C_6H_4{\cdot}CO_2H$, m. p. 173—175° (cf. Mann and Pope, *ibid.*, 1922, **121**, 1052). Treatment with brucine furnished the l-*brucine*-l-*acid* salt, m. p. 123—125°, $[\alpha]_{5461}$ −144°, $[\alpha]_{4359}$ −279° (in ethyl alcohol), which on decomposition gave l-m-*carboxyphenylmethylsulphine*-p-*toluenesulphonylimine*, m. p. 172—173°, $[\alpha]_{5461}$ (in ethyl alcohol) −338°. A table of specific rotatory powers of this substance in different solvents for different wave-lengths is given.

d-m-*Carboxyphenylmethylsulphine*-p-*toluenesulphonylimine*, m. p. 172—173°, $[\alpha]_{5461}$ +338°, $[\alpha]_{4359}$ +627° (in ethyl alcohol), was obtained from its l-*cinchonidine* salt, m. p. 204°, $[\alpha]^{17.5}_{5461}$ (in chloroform) +48·27° (other rotatory powers are given).

The sulphonylimine is decomposed by hydrogen peroxide into *m*-carboxyphenylmethylsulphone and *p*-toluenesulphonamide, and by hydrochloric acid into the sulphonamide together with *m*-carboxyphenyl methyl sulphoxide and *m*-methylthiolbenzoic acid. A review of the constitution of chloramine-T and its reactions with thioethers in the light of the electronic theory of valency is given. H. BURTON.

Persistence of optical activity in the elimination of water from optically active glycols. I. A. MCKENZIE and W. S. DENNLER (Ber., 1927, **60**, [*B*], 220—225).—*r*-α-Naphthylglycollic acid is resolved into its optical antipodes by crystallisation of the cinchonine salt from rectified spirit whereby d-α-*naphthylglycollic acid*, m. p. 124—125°, $[\alpha]_D^{14}$ +162° in water, $[\alpha]_D^{14}$ +194° in ethyl alcohol, is obtained. *Methyl* d-α-*naphthylglycollate*, b. p. 230—232°/36 mm., $[\alpha]_{5461}$ +115° in acetone, is converted by magnesium benzyl chloride into β-1-*naphthyl*-αα-*dibenzylethylene glycol*, m. p. 195—196°, $[\alpha]_D^{18}$ −78° in acetone, which is transformed by cold, concentrated sulphuric acid into r-benzyl β-phenyl-α-1-naphthylethyl ketone, m. p. 58·5—59·5° (cf. A., 1926, 834), and by boiling dilute sulphuric acid into a partly racemised product from which l-*benzyl* β-*phenyl*-α-1-*naphthylethyl ketone*, m. p. 78°, $[\alpha]_D$ −278° in acetone, is isolated by fractional crystallisation. The active ketone is completely racemised by alcoholic alkali, thus proving that the α-naphthyl group exerts an influence similar to that of the phenyl residue. H. WREN.

Smooth extension of the ring from indandione to dihydroxynaphthalene derivatives. I. D. RADULESCU and G. GHEORGIU (Ber., 1927, **60**, [*B*], 186—190).—Ethyl 2-phenylindan-1 : 3-dione-2-acet-

ate, m. p. 105—106° (corresponding *methyl* ester, m. p. 110—112°), is converted by zinc chloride, concentrated sulphuric acid, or, preferably, sodium ethoxide in the absence of air into *ethyl* 1 : 4-*dihydroxy*-2-*phenylnaphthalene*-3-*carboxylate*, m. p. 153—154°, the yield being almost quantitative. It is transformed by the action of air on its alkaline solution partly into *ethyl* 2-*phenyl*-1 : 4-*naphthaquinone*-3-*carboxylate* (+0·5H_2O), m. p. 112°, and partly into 3-hydroxy-2-phenyl-1 : 4-naphthaquinone, m. p. 145—146° [identified further by conversion into the corresponding methyl derivative, m. p. 122—123°, acetate, m. p. 112—113°, and monophenylhydrazone, m. p. 199—200° (decomp.)]. The ester is smoothly converted into 3-hydroxy-2-phenyl-1 : 4-naphthaquinone by boiling alkali in the presence of air. It is transformed by reductive acetylation into *ethyl* 1 : 4-*diacetoxy*-2-*phenylnaphthalene*-3-*carboxylate*, m. p. 134°. 1 : 3 : 4-*Triacetoxy*-2-*phenylnaphthalene*, m. p. 166—168°, is described. 2-*Phenylindan*-1 : 3-*dione*-2-*acetic acid*, m. p. 214—215° (*barium* and *sodium* salts), is prepared by hydrolysis of the corresponding ester by acid; the corresponding *chloride*, m. p. 198—200°, and *amide*, m. p. 255—256°, are described. Treatment with concentrated potassium hydroxide converts the acid into β-phthaloyl-β-phenylpropionic acid, m. p. 169—171° (decomp.), readily transformed into the *lactone*,  , m. p. 175—176°. H. WREN.

Parachor and chemical constitution. IV. Three- and four-membered rings. S. SUGDEN and H. WILKINS (J.C.S., 1927, 139—147).—From measurements of the densities and surface tensions of nine compounds containing a three-membered ring, it is deduced that the parachor for such rings is 17. The *normal* and *labile* esters of 3-methyl-Δ^2-*cyclo*propene-1 : 2-dicarboxylic acid give values indicating that each of these compounds contains a three-membered ring and a non-polar double linking. The value 11·6 obtained for four-membered rings from measurements made on three *cyclo*butane derivatives is in good agreement with the value previously obtained (A., 1924, ii, 662).

The hypothesis is put forward that the value of structural parachors depends on the intensity of unsaturation. Thus the ratio between the number of hydrogen atoms required to convert any ring structure into an open-chain saturated compound (latent valencies $=x$), and the number of octets sharing this unsaturation (n), gives the degree of unsaturation. From this value ($x/n=1$ for double linking), and the value for the parachor for the double linking (23·2), the value for ring structures can be calculated. These values are in good agreement with those found experimentally. H. BURTON.

Glutaconic acids. XXI. Non-formation of Δ^2-tetrahydro*iso*phthalic acid by reduction of *iso*phthalic acid. E. H. FARMER and H. L. RICHARDSON (J.C.S., 1927, 59—63; cf. A., 1926, 1039).—The main product of the reduction of *iso*phthalic acid (cf. Perkin and Pickles, J.C.S., 1905, 87, 293), is *cis*-Δ^4-tetrahydro*iso*phthalic acid (formerly described as Δ^2-acid). A small quantity of the Δ^3-tetrahydro*iso*phthalic acid, m. p. 244°, is also formed, probably not as a primary reduction product. The Δ^3-acid is also obtained by the action of boiling alkali on the *cis*-Δ^1-compound, and on oxidation with ozone gives β-carboxyadipic acid. Adipic (or glutaric) acid, the expected oxidation product of the true Δ^2-form, could not be detected when the reduction product, after removal of the Δ^3- and *cis*-Δ^4-acids, was oxidised with ozone. It is concluded that Perkin and Pickles' *cis*-Δ^4-acid (which should be either Δ^2- or *trans*-Δ^4-) is absent. The absence of the *trans*-Δ^4-acid is indicated only by its non-isolation, since the ozone oxidation product of *cis*- and *trans*-forms is the same, tricarballylic acid. H. BURTON.

Oxidation of nitrophenylcyanoacetates. A. FAIRBOURNE and H. R. FAWSON (J.C.S., 1927, 46—50).—Ethyl sodiocyanoacetate condensed with *p*-chloronitrobenzene, chloro-2 : 4-dinitrobenzene, and picryl chloride, yields *ethyl* p-*nitrophenylcyanoacetate* (I) (*sodium* derivative), *ethyl* 2 : 4-*dinitrophenylcyanoacetate*, (II), m. p. 66° (*sodium* and *silver* derivatives), and *ethyl* 2 : 4 : 6-*trinitrophenylcyanoacetate*, m. p. 95°. Hydrolysis of I and II with hot dilute hydrochloric acid gives *p*-nitrophenylacetonitrile and 2 : 4-*dinitrophenylacetonitrile*, m. p. 89°. *Ethyl* 2 : 4-*dinitrophenylethylcyanoacetate*, m. p. 98°, is obtained from the silver derivative of II and ethyl iodide.

Oxidation of I with chromic anhydride in boiling glacial acetic acid gives *ethyl* αβ-*di*-p-*nitrophenyl*-αβ-*dicyanosuccinate*, m. p. 209°, which is also obtained by treating the silver derivative of I with iodine. From II there is obtained by oxidation *ethyl* 2 : 4-*dinitrobenzoylformate*, m. p. 89° (*phenylhydrazone*, m. p. 170°), derived from the intermediate hydroxy-ester R·C(OH)(CN)·CO_2Et, by loss of hydrogen cyanide. The sodium derivative of II on treatment with bromine in moist ether gives *ethyl bromo*-2 : 4-*dinitrophenylcyanoacetate*, m. p. 98°, which on oxidation passes into *ethyl bromo*-2 : 4-*dinitrophenylhydroxycyanoacetate*, m. p. 157°, thus showing the bromine to be in the ring. The same sodium derivative when treated with chlorine in aqueous solution gives *ethyl chloro*-2 : 4-*dinitrophenylcyanoacetate*, m. p. 101°. No substituted anthracene derivative was obtained from any of the oxidations. H. BURTON.

3-Nitro-4-amino- and 3 : 4-dihalogeno-benzaldehydes. H. H. HODGSON and H. G. BEARD (J.C.S., 1927, 20—27).—*p*-Acetamidobenzaldehyde (p-*nitrophenylhydrazone*, m. p. 264—265°), on nitration with diacetylorthonitric acid in acetic anhydride solution, gives 3-*nitro*-4-*acetamidobenzylidene diacetate*, m. p. 114°, which on hydrolysis yields 3-nitro-4-acetamidobenzaldehyde (p-*nitrophenylhydrazone*, m. p. 289—290°) and 3-nitro-4-aminobenzaldehyde (p-*nitrophenylhydrazone*, m. p. 270—272°; *oxime*, m. p. 207°). The 4-halogeno-3-nitrobenzaldehydes were obtained in the usual way from the nitroaminoaldehyde, and also by nitration of the 4-halogenobenzaldehydes. 4-Chloro-3-nitrobenzaldehyde (p-*nitrophenylhydrazone*, m. p. 278—279°; *oxime*, m. p. 146°), 4-bromo-3-nitrobenzaldehyde [p-*nitrophenylhydrazone*, m. p. 282—283°; oxime, m. p. 154° (Schöpff, A., 1892, i, 336, gives m. p. 145—146°)], and 4-*iodo*-3-*nitrobenz*-

aldehyde, m. p. 141° (p-*nitrophenylhydrazone*, m. p. 277—278°; *oxime*, m. p. 157°), are described and their structures proved by oxidation to the corresponding benzoic acids. Conversion of these aldehydes into the dihalogeno-compounds was carried out by the method previously described (B., 1926, 511). There were prepared in this way 3 : 4-dichlorobenzaldehyde [p-*nitrophenylhydrazone*, m. p. 276—277°; oxime, m. p. 118—119° (Erdmann and Schwechten, A., 1891, i, 450, give m. p. 114—115°)]; 4-*chloro*-3-*bromobenzaldehyde*, m. p. 70° (p-*nitrophenylhydrazone*, m. p. 273—274°; *oxime*, m. p. 131°); 4-*chloro*-3-*iodobenzaldehyde*, m. p. 117° (p-*nitrophenylhydrazone*, m. p. 277—278°; *oxime*, m. p. 115—116°); 3-*chloro*-4-*bromobenzaldehyde*, m. p. 52° (p-*nitrophenylhydrazone*, m. p. 272—273°; *oxime*, m. p. 104°); 3 : 4-*dibromobenzaldehyde*, m. p. 75° (p-*nitrophenylhydrazone*, m. p. 270—274°; *oxime*, m. p. 129°); 4-*bromo*-3-*iodobenzaldehyde*, m. p. 127° (p-*nitrophenylhydrazone*, m. p. 265°; *oxime*, m. p. 141°); 3-*chloro*-4-*iodobenzaldehyde*, m. p. 70·5° [p-*nitrophenylhydrazone*, m. p. 261—262° (decomp.); *oxime*, m. p. 129°]; 3-*bromo*-4-*iodobenzaldehyde*, m. p. 66° (p-*nitrophenylhydrazone*, m. p. 260—261°; *oxime*, m. p. 157—158°), and 3 : 4-*di*-*iodobenzaldehyde*, m. p. 118° [p-*nitrophenylhydrazone*, m. p. 245—247° (decomp.); *oxime*, m. p. 177—178°].

Oxidation of the aldehydes gives the corresponding acids, the following being described: 4-*chloro*-3-*iodobenzoic acid*, m. p. 216—217°; 4-*bromo*-3-*iodobenzoic acid*, m. p. 243—244°; 3-*chloro*-4-*iodobenzoic acid*, m. p. 219°; and 3-*bromo*-4-*iodobenzoic acid*, m. p. 242—243°. p-*Acetamidobenzylidene*-p-*toluidine* and 3-*nitrobenzaldehyde*-4-*azo*-β-*naphthol* have m. p. 187—188° and 271°, respectively. H. BURTON.

Action of phosphorus halide on alkylformanilides. Preparation of secondary and tertiary *p*-alkylaminobenzaldehydes. A. VILSMEIER and A. HAACK (Ber., 1927, 60, [*B*], 119—122; cf. Fischer, Muller, and Vilsmeier, A., 1925, i, 439).—Methylformanilide is converted by phosphoryl chloride in presence of benzene into the additive *compound*, $C_6H_5\cdot NMe\cdot CHCl\cdot O\cdot POCl_2$, which when heated at 70° (or preferably first converted by phosphorus pentachloride into methyldichloromethylaniline and then heated) yields *p*-methylaminobenzaldehyde, m. p. 56—57°. Treatment of methylformanilide with phosphoryl chloride and subsequently with a tertiary fatty-aromatic amine gives dialkylaminoaldehydes according to the scheme: $C_6H_5\cdot NMe\cdot CHCl_2 + C_6H_5\cdot NMe_2 \longrightarrow HCl + C_6H_5\cdot NMe\cdot CHCl\cdot C_6H_4\cdot NMe_2$ and $C_6H_5\cdot NMe\cdot CHCl\cdot C_6H_4\cdot NMe_2 + C_6H_5\cdot NMe\cdot CHCl_2 \longrightarrow CHCl_2\cdot C_6H_4\cdot NMe_2 + C_6H_5\cdot NMe\cdot CH{:}NMePhCl$. *p*-Dimethylaminobenzaldehyde, m. p. 73°, *p*-diethylaminobenzaldehyde, *p*-methylbenzylaminobenzaldehyde, m. p. 68°, and p-*dibenzylaminobenzaldehyde*, m. p. 88—90°, are thus prepared. Dimethyl-*m*-toluidine and α-dimethylaminonaphthalene give less satisfactory yields of aldehyde. H. WREN.

Reactions of nitrosyl chloride. II. Action on aromatic aldoximes. H. RHEINBOLDT, M. DEWALD, F. JANSEN, and O. SCHMITZ-DUMONT (Annalen, 1926, 451, 161—178; cf. A., 1925, i, 1131).—Nitrosyl chloride reacts with aromatic aldoximes, yielding chloro-oximes, a nitroso-derivative being probably formed as an intermediate product: $R\cdot CH{:}NOH \longrightarrow R\cdot CHCl\cdot NO \longrightarrow R\cdot CCl{:}NOH$. The formation of the nitroso-compound is indicated by the green colour developed in the reaction mixtures, but the intermediate compound could be isolated only in the case of piperonaloxime (*hydrochloride* described). When this oxime is treated with 3 mols. of nitrosyl chloride in ethereal solution, ω-*chloro*-ω-*nitroso*-3 : 4-*methylenedioxytoluene*, $(CH_2O_2{:}C_6H_2\cdot CHCl\cdot NO)_2$, colourless crystals melting at about 75° to a green liquid, which solidifies and then melts at 125—126°, is deposited. This substance dissolves in organic solvents to a green solution and readily passes into *chloropiperonaloxime*, yellow needles, m. p. 129°, when the solid or its solutions are warmed. With *p*-toluidine in ether solution, the chloro-oxime yields the p-*toluidino*-derivative, $CH_2O_2{:}C_6H_3\cdot C(:NOH)\cdot NH\cdot C_6H_4\cdot Me$, m. p. 150—151°.

By the action of nitrosyl chloride in ethereal solution on aromatic aldoximes, the following substances were prepared: ω-*p*-toluidinobenzaldoxime, m. p. 161—162° (decomp.); ω-*chlorofurfuraldoxime*, m. p. 103—104° [*anilino*-derivative, m. p. 126—127° (decomp.)], and *difurylfuroxan*, m. p. 113—114°; ω-*chloroanisaldoxime*, m. p. 120°; ω-*chloro*-p-*tolualdoxime*, m. p. 69—70° [p-*toluidino*-derivative, m. p. 134—135° (decomp.)]; ω-*chlorocuminaldoxime*, oil [*anilino*-derivative, m. p. 145—146° (decomp.)]; ωω′-*dichloroterephthaldialdoxime*, m. p. 188° (decomp.); ω-chloro-*o*-nitrobenzaldoxime, m. p. 99—100°; ω-chloro-*m*-nitrobenzaldoxime, m. p. 99·5—100°; ω-chloro-*p*-nitrobenzaldoxime, m. p. 123·5—124°; ω-*chloro*-o-*nitropiperonaloxime*, m. p. 116—117° (decomp.) [*piperidino*-derivative, m. p. 181—182° (decomp.)]; ω-*chloro*-p-*cyanobenzaldoxime*, m. p. 151—152°; ω-*chloro*-p-*carboxybenzaldoxime*, m. p. 198—199° (decomp.); ω-*chlorocinnamaldoxime*, m. p. 98°.

The *O*-methyl ethers of benzaldoxime and *m*-nitrobenzaldoxime do not react with nitrosyl chloride, as would be expected from the mechanism of the reaction given above. R. W. WEST.

Reducing action of a mixture of magnesium iodide (or bromide) and magnesium on aromatic ketones. Probable formation of magnesium subiodide (or sub-bromide). M. GOMBERG and W. E. BACHMANN (J. Amer. Chem. Soc., 1927, 49, 236—257).—When benzophenone is treated, according to the Grignard procedure, with magnesium and an aryl halide in ether–benzene in presence of iodine, and the product hydrolysed, benzopinacol is obtained in practically theoretical yield. The reduction depends on the simultaneous action of magnesium and magnesium iodide, and does not take place in absence of either of these. It is therefore concluded that the reaction is due to the intermediate formation of magnesium subiodide, MgI, which combines with the benzophenone with formation of a free radical, termed a "halomagnesium ketyl," $Ph_2C(OMgI)\cdot$, the bimolecular form of which is hydrolysed to benzopinacol. The reduction takes place in benzene solution in presence of a trace of ether, and small amounts of moisture do not inhibit the reaction. The latter proceeds at 0°, and is almost as rapid at 25° as

at the b. p. of the solvent, a few minutes sufficing for the complete reduction of 55 g. of ketone. When benzophenone is added to a solution of magnesium iodide in ether–benzene at 25°, the additive *compound* $(Ph_2CO)_3,MgI_2$ is precipitated, and if the amount of iodine present is insufficient for the quantitative formation of this product, the reduction will not proceed. The presence of the slightest excess of iodine over and above this proportion, however, brings about complete reduction, which supports the view that magnesium and magnesium iodide react under these conditions to form the subiodide, and also indicates that the bimolecular form of the above halomagnesium ketyl continuously loses magnesium iodide, with formation of the magnesium pinacolate. At 60°, a trace of iodine is sufficient to bring about the reduction, as the above additive compound is not precipitated, and is probably dissociated. Benzopinacol can also be obtained in 90—95% yield by the action of magnesium and magnesium bromide, and of beryllium and beryllium iodide, on benzophenone. Negative results were obtained with magnesium metal and chloride, with zinc and its halides, cadmium and its halides, silver and magnesium iodide, and with zinc and mercuric iodide, mercuric chloride, magnesium iodide, or magnesium bromide. Magnesium amalgam does not reduce benzophenone to the pinacol in ether–benzene. Rearrangement of benzopinacol to β-benzopinacolin is effected by warming the former in glacial acetic acid in presence of a trace of iodine. The dissociation of the iodomagnesium pinacolate with formation of the above "ketyl" is shown by the analogy of its behaviour with that of triphenylmethyl. The solid material is colourless, but gives intensely coloured solutions, the colour of which is discharged by a small amount of oxygen and reappears on keeping. The iodomagnesium pinacolate is obtained, together with methane, both in theoretical yield, by the action of magnesium methyl iodide on benzopinacol, and also from magnesium phenyl iodide and benzil. Treatment of the iodomagnesium pinacolate with iodine affords, quantitatively, benzophenone and magnesium iodide, whilst oxygen yields benzophenone and magnesium oxyiodide. The action of magnesium and magnesium iodide on 4-methylbenzophenone yields analogously 4 : 4'-dimethylbenzopinacol, m. p. 173—175°, which, when heated in acetic acid with a trace of iodine, affords a *product*, m. p. 114—116°, probably a pinacolin or a mixture of its structural isomerides. Di-*p*-tolyl ketone affords similarly 4 : 4' : 4'' : 4'''-tetramethylbenzopinacol, m. p. 183—184°, the additive *product*, $[(C_7H_7)_2CO]_2,MgI_2,Et_2O$, being formed intermediately. *4 : 4' : 4'' : 4'''-Tetramethylbenzopinacolin*, m. p. 137—138°, obtained from the pinacol as above, is described. *p*-Chlorobenzophenone is converted analogously into 4 : 4'-dichlorobenzopinacol, m. p. 172—178°, whilst phenyl diphenylyl ketone affords in the same way 4 : 4'-*diphenylbenzopinacol* (s-*dihydroxydiphenyldidiphenylylethane*), m. p. 198—199°, in 97% yield (cf. Schlenk, A., 1914, i, 396). When the latter is boiled with acetyl chloride and acetic acid in benzene solution, it yields 92% of the pinacolin *phenyl phenyldidiphenylylmethyl ketone*, $Bz{\cdot}CPh(C_6H_4Ph)_2$, m. p. 198°, and 8% of the pinacolin, $PhC_6H_4{\cdot}CO{\cdot}CPh_2{\cdot}C_6H_4Ph$. Didiphenylyl ketone affords similarly 4 : 4' : 4'' : 4'''-*tetraphenylbenzopinacol*, m. p. about 200° (decomp.). When heated, the latter decomposes into didiphenylyl ketone and didiphenylylcarbinol, whilst it yields 4 : 4' : 4'' : 4'''-*tetraphenylbenzopinacolin*, m. p. 204—207°, when boiled with acetyl chloride and acetic acid in benzene. Fluorenone yields analogously *fluorenopinacol*, m. p. 190—192° (decomp.), which, when heated with 70% sulphuric acid and acetic acid, yields the corresponding pinacolin, 9-diphenylenephenanthrone, m. p. 255°. An additive *product* of fluorenone and fluorenopinacol (1 : 1) is described. *Xanthopinacol*, m. p. 185—187° (decomp.), is obtained analogously, with intermediate formation of the additive *product* $(C_{13}H_8O_2)_2,MgI_2,Et_2O$. When heated with 70% sulphuric acid and acetic acid, xanthopinacol yields dixanthylene, m. p. 312—313°. Analogous preparations of the pinacols from anthrone and Michler's ketone are described. It is concluded that the formation of a subhalide may explain many reactions which are effected with "activated" magnesium. F. G. WILLSON.

Action of magnesium phenyl bromide on trisubstituted acetonitriles. (MME.) RAMART-LUCAS and F. SALMON-LEGAGNEUR (Compt. rend., 1927, **184**, 102—104).—By the action of magnesium phenyl bromide in benzene, toluene, or xylene on nitriles, $CR_3{\cdot}CN$, the ketones, $CR_3{\cdot}COPh$, are obtained, the hydrobromides of the ketimines, $CR_3{\cdot}CPh{:}NH,HBr$, being isolable when one or two of the substituent groups, R, are aromatic. Phenyl *tert.*-butyl ketone (oxime, m. p. 167°), *phenyl α-phenyl-α-methylpropyl ketone* (*β-benzoyl-β-phenylbutane*), b. p. 187—189°/16 mm., *phenyl α-phenyl-α-ethylpropyl ketone* (*γ-benzoyl-γ-phenylpentane*), m. p. 48—49°, b. p. 218°/35 mm. [*oxime*, m. p. 187—188°; *ketimine hydrobromide*, m. p. 208—210° (decomp.)], *phenyl α-phenyl-α-benzylpropyl ketone* (*β benzoyl-αβ-diphenylbutane*), m. p. 112—113° [*oxime*, m. p. 201—202°; *ketimine hydrobromide*, m. p. 227° (decomp.)], and *phenyl αα-diphenyl-β-methylpropyl ketone* (*α-benzoyl-αα-diphenylisobutane*), m. p. 98° (*ketimine hydrobromide* hydrolysed with difficulty), are described. C. HOLLINS.

Action of nitromethane and its homologues on benzil. I. KASIWAGI (Compt. rend., 1927, **184**, 35—37).—Benzil reacts readily with the sodium derivative of nitromethane, forming ethyl benzoate and a white powder, which, on treatment with acid, yields ω-nitrostyrene and β-nitro-α-phenylethyl alcohol. With the sodium derivative of nitroethane, benzil forms ethyl benzoate and a white powder containing nitrogen and 19% of sodium. This, on treatment with acid, is resolved into benzoic acid and acetaldoxime. Presumably in each case a complex intermediate compound is first formed. B. W. ANDERSON.

Preparation of α-diketones from αβ-unsaturated ketones. C. DUFRAISSE and H. MOUREU (Compt. rend., 1927, **184**, 99—101).—By the successive addition of bromine (1 mol.), piperidine (4 mols.), and excess of acid to a solution of an αβ-unsaturated ketone (1 mol.), the series of five reactions: $\cdot CO{\cdot}CH{:}CH{\cdot} \longrightarrow \cdot CO{\cdot}CHBr{\cdot}CHBr{\cdot} \longrightarrow \cdot CO{\cdot}CBr{:}CH{\cdot} \longrightarrow \cdot CO{\cdot}CBr(NC_5H_{10}){\cdot}CH_2 \longrightarrow \cdot CO{\cdot}C(NC_5H_{10}){:}CH{\cdot} \longrightarrow \cdot CO{\cdot}C(OH){:}CH$, may be induced to occur in a

single operation, giving 40—80% yields of α-diketones. The following diketones, R·CO·CO·Me, are synthesised: R=methyl, ethyl, *n*-propyl, *iso*propyl (poor yield), phenyl, and benzyl; also phenyl-*p*-methoxybenzylglyoxal, and, in poor yield, α-phenyl-β-ethylglyoxal. No experimental details are given.

C. Hollins.

New diketone from phenyl *p*-tolyl ketone. T. W. Jezierski (Rocz. Chem., 1926, **6**, 738—740).—The main product of the reaction between phenyl *p*-tolyl ketone and sulphur is *s-di-pp'-dibenzoyldiphenylethane*, $(Ph{\cdot}CO{\cdot}C_6H_4{\cdot}CH_2)_2$, m. p. 239—240°.

R. Truszkowski.

Condensations of unsaturated substances with diazomethane. II. Condensation of diazomethane with carbon disulphide and xyloquinone. R. Rotter (Monatsh., 1926, **47**, 493—495).—Diazomethane reacts with xyloquinone in ether solution at the temperature of a freezing mixture to yield a moderately stable condensation *product*, $C_{10}H_{12}O_2N_4$, which is more stable than the corresponding product obtained from benzoquinone (Pechmann and Seel, A., 1899, i, 947), but which, like the latter, can be converted into a stable secondary product. No pure product could be isolated by the interaction of diazomethane and carbon disulphide.

J. W. Baker.

Naphthazarin. P. Pfeiffer [with H. Oberlin and B. Segall] (Ber., 1926, **60**, [*B*], 111—115).—Confirmation of Dimroth and Ruck's conception (A., 1926, 297) of naphthazarin as 5 : 8-dihydroxy-1 : 4-naphthaquinone is found in the observation that it is converted by stannic chloride in presence of benzene into the *compound*, $C_2H_2<\overset{CO}{CO}>C_6H_2<\overset{O}{O}>SnCl_2,C_6H_6$, this behaviour being characteristic of hydroxy-ketones containing the hydroxyl group in the *ortho*-position to the carbonyl group (cf. Pfeiffer and others, A., 1913, i, 879); the corresponding *quinizarin* derivative, $C_6H_4<\overset{CO}{CO}>C_6H_2<\overset{O}{O}>SnCl_2$, is described. Further, naphthazarin is unable to add pyridine, which is in harmony with the presence of *ortho*- but not of *para*-hydroxy-groups.

The *compound*, $SnCl_3{\cdot}O{\cdot}C_6H_3(OMe){\cdot}COMe$, from pæonol and the $SnCl_3$ derivative of methyl salicylate (cf. Pfeiffer, *loc. cit.*) appear unimolecular in freezing naphthalene, whereas the mol. wts. of the benzylidene- and *p*-anisylidene-pæonol compounds could not be established. In both compounds, therefore, the tin atom has an unoccupied co-ordination position, unless it be assumed that this position is occupied by a naphthalene molecule. Steric considerations render a unimolecular structure in the usual sense very improbable for these compounds.

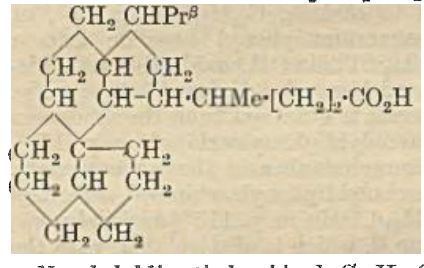
H. Wren.

Action of oxalyl chloride on homologues of naphthalene and 1 : 6-dimethoxynaphthalene. R. Lesser and G. Gad (Ber., 1927, **60**, [*B*], 242—245).—The action of oxalyl chloride on various methylnaphthalenes in presence of aluminium chloride gives acenaphthenequinones in satisfactory yield only in the case of 1 : 6-dimethylnaphthalene. *3-Methylacenaphthenequinone*, m. p. 198—199° (corr.), and 2 : 2'-*dimethylnaphthil*, m. p. 237—238° (corr.) [corresponding *azine*, $C_{30}H_{22}N_{21}$, m. p. 269° (corr.)], are derived from 2-methylnaphthalene. 1 : 6-Dimethylnaphthalene affords 5 : 8-*dimethylacenaphthenequinone*, m. p. 193—194° (corr.), yielding, with *o*-phenylenediamine, the *azine*, $C_{20}H_{14}N_2$, m. p. 198—199° (corr.), and with 3-hydroxythionaphthen the *compound*, $C_{22}H_{14}O_2S$. 3 : 7-*Dimethylacenaphthenequinone*, m. p. 207° (corr.) [*azine*, m. p. 194° (corr.)], and (?) 2 : 6-*dimethylnaphthoic acid* are derived from 2 : 6-dimethylnaphthalene. 2 : 7-Dimethylnaphthalene yields 2 : 7-*dimethyl*-1-*naphthoic acid*, m. p. 173° (corr.), and very little 3 : 8-*dimethylacenaphthenequinone*, m. p. 207—208° (corr.). 1 : 6-Dimethoxynaphthalene affords 13-*hydroxy*-4 : 5-*benzocoumaranone*-2 : 3-*dione* (5-*hydroxy*-1 : 2-*diketodihydro*-β-*naphthofuran*), m. p. 298—300° (corr. decomp.) after darkening at 275°, 3 : 6-*dimethoxyacenaphthenequinone*, m. p. 227° (corr.) [corresponding *azine*, m. p. 196—197° (corr.)], and a *substance*, m. p. 238—239° (corr.). 2 : 7-Dimethoxynaphthalene is converted into 3 : 8-dimethoxyacenaphthenequinone, m. p. 279° (corr.) [*azine*, m. p. 253° (corr.); *monophenylhydrazone*, m. p. 128° (corr.); *diphenylhydrazone*, m. p. 232—233° (corr.)], and 7-methoxy-1 : 2-diketodihydro-β-naphthofuran, m. p. 204° (corr.) [*quinoxaline* derivative, $C_{19}H_{14}O_3N_2,CH_3{\cdot}CO_2H$, m. p. 275—276° (corr.)] (cf. Staudinger and others, A., 1921, i, 432, 433).

H. Wren.

Bile acids. XXV. Degradation of [*cyclo*hexane]dicarboxylic acid. H. Wieland, O. Schlichting, and W. von Langsdorff.—See this vol., 243.

Bile acids. XXVI. Nature of the side-chain and of the fourth ring. H. Wieland, O. Schlichting, and R. Jacobi (Z. physiol. Chem., 1926, **161**, 80—115; cf. A., 1924, i, 857).—Degradation of cholanic acid by means of alternate Grignard reactions and oxidations shows the side-chain to be ·CHMe·CH_2·CH_2·CO_2H, and the annexed structure is suggested for cholanic acid. Five bisnorcholanic acids (side-chain ·CHMe·CO_2H) are described, and their isomerism is discussed.



Norcholyldimethylcarbinol, $C_{26}H_{46}O$, m. p. 96—97°, b. p. 220°/2 mm., prepared from ethyl cholanate, m. p. 92°, and magnesium methyl iodide, is oxidised by chromium trioxide in acetic acid to norcholanic acid, $C_{23}H_{38}O_2$, m. p. 177° (*methyl* ester, m. p. 74°; *ethyl* ester, m. p. 66—67°), the yield being much better than from norcholyldiphenylcarbinol, m. p. 106·5° (cf. Cerecedo, Diss., Munich, 1921; Lunde, Diss., Freiburg, 1925; Cerecedo prepared from the diphenylcarbinol a *hydrocarbon*, $C_{36}H_{48}$, m. p. 121°). Ethyl norcholanate gives with magnesium methyl iodide *bisnorcholyldimethylcarbinol*, m. p. 116°, which is oxidised to *α-bisnorcholanic acid*, m. p. 214°, $[\alpha]_D^{20}$ —7·5° (in alcohol). *Bisnorcholyldiphenylcarbinol*,

m. p. 122—123°, gives the same acid in twice the yield. *Ethyl bisnorcholanate*, m. p. 106—107°, reacts less easily with the Grignard agent, giving *trinorcholyldimethylcarbinol*, $C_{21}H_{35}\cdot CMe_2\cdot OH$, m. p. 159—160°, which is converted by oxidation into two stereoisomeric γ- and δ-*bisnorcholanic acids*. The γ-acid, m. p. 210—211° (*methyl* ester, m. p. 117°; *ethyl* ester, m. p. 82—83°), is optically inactive, whilst the δ-acid, m. p. 184° (*methyl* ester, m. p. 99°), has $[\alpha]_D$ +31·74° (in alcohol). β-*Bisnorcholanic acid*, m. p. 242°, $[\alpha]_D^{18}$ +23·33° (in alcohol) (oily *ethyl* ester), is recovered from unreacted ester which has been treated for a short time with magnesium phenyl bromide; the diphenylcarbinol obtained from the β-ester is oxidised by chromic-acetic acid to ætiocholanic acid, m. p. 218°. A fifth isomeride, ε-*bisnorcholanic acid*, m. p. 181°, $[\alpha]_D$ +14·30° (*methyl* ester, m. p. 123°), is isolated by means of its insoluble *sodium* salt from the oxidation product of the neutral portion in the preparation of the α-acid.

The diphenylcarbinol, $C_{21}H_{35}\cdot CPh_2\cdot OH$, from ethyl bisnorcholanate, is converted by crystallisation from acetic acid into an unsaturated *hydrocarbon*, $C_{19}H_{31}\cdot CMe{:}CPh_2$, m. p. 175—176°, which on oxidation (without isolation) yields *ætiocholanic acid*, m. p. 219° (*methyl* ester, m. p. 98—99°; *ethyl* ester, m. p. 78—79°). The unsaturated *hydrocarbon*, $C_{32}H_{40}$, m. p. 233°, obtained from ethyl ætiocholanate and magnesium phenyl bromide, is oxidised to *ætiobilianic acid*, $C_{19}H_{30}O_4$, m. p. 228° (*anhydride*, m. p. 206°).

From the neutral products of these various oxidations are isolated the following compounds: (1) From norcholyldimethylcarbinol, an α-*acetoxyketone*, $C_{22}H_{37}\cdot CO\cdot CMe_2\cdot OAc$, m. p. 147°, the corresponding α-*hydroxyketone*, m. p. 96—97°, and *norcholyl methyl ketone*, $C_{22}H_{37}\cdot COMe$, m. p. 113° [*oxime*, m. p. 151° (decomp.); *semicarbazone*, m. p. 232° (decomp.)], the last-mentioned ketone being reduced by Clemmensen's method to *homocholane*, m. p. 75°. (2) From bisnorcholyldimethylcarbinol, *bisnorcholyl methyl ketone*, m. p. 148° [*semicarbazone*, m. p. 223° (decomp.)], which is reduced to *cholane*, $C_{24}H_{42}$, m. p. 90°, or converted by magnesium phenyl bromide into a *carbinol*, $C_{21}H_{35}\cdot CH_2\cdot CPhMe\cdot OH$, oxidisable to α-bisnorcholanic acid and *bisnorcholyl phenyl ketone*, m. p. 140° (a *stereoisomeride* is obtained from the oxidation products of bisnorcholyldiphenylcarbmol, m. p. 130°, together with ε-bisnorcholanic acid above-mentioned). (3) From bisnorcholyldiphenylcarbinol, *ætiocholyl methyl ketone*, $C_{19}H_{31}\cdot COMe$, m. p. 115° [*semicarbazone*, m. p. 236° (decomp.)], which is also isolated, with the cyclic ketone *ætiocholanone*, $C_{19}H_{30}O$, m. p. 105° [*semicarbazone*, m. p. 263 (decomp.)], from the neutral products in the oxidation of norcholyldimethylcarbinol to norcholanic acid. C. HOLLINS.

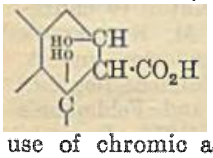
Two sterol-like substances from *Asclepius syriaca*. I. L. SCHMID and R. STOHR (Monatsh., 1926, 47, 433—436).—The sterol-like product $C_{27}H_{46}O$ isolated from *Asclepius syriaca* by the method of Klein and Pirschle (A., 1924, i, 355) in 0·5% yield has m. p. 176° (after sintering at 164°) and sublimes in a vacuum at 180°. When treated with acetic anhydride, it yields an *acetate*, m. p. 206°, which when treated in ethereal solution with a solution of bromine in acetic acid yields a *bromoacetate*, $C_{33}H_{53}O_2Br$, m. p. 265°, and a second *bromoacetate*, $C_{47}H_{75}O_3Br$, m. p. 201°, the latter corresponding with an alcohol, $C_{45}H_{74}O_2$. The second bromoacetate when heated with 10% alcoholic potassium hydroxide solution yields a *bromo-alcohol*, $C_{45}H_{75}O_2Br$, m. p. 170° (*propionate*, m. p. 214°). Phosphorus pentachloride has no action on the hydroxyl group present in the original sterol, and, since it yields no condensation product with digitonin, it is probably similar to amyrin. J. W. BAKER.

β-Amyrin from *Manila elemi* resin. IV. A. ROLLETT (Monatsh., 1926, 47, 437—445; cf. A., 1923, i, 588; 1925, i, 945).—Treatment of the crude amyrin with a slight excess of benzoic anhydride at 150° for 3—5 hrs. yields the mixed α- and β-benzoates in nearly quantitative yield, separation being subsequently effected by the method previously described. When the β-benzoate is heated with copper in an atmosphere of carbon dioxide or hydrogen under reduced pressure, a sublimate giving the reactions of benzoic acid is obtained, together with a small quantity of *di-β-amyrin ether*, m. p. 135—136°, probably contaminated with a little β-amyrilene. Treatment of the β-benzoate in a suspension of acetic acid and carbon disulphide with a solution of bromine in acetic acid yields a *substance*, $C_{37}H_{53}O_2Br$, which is obtained in three different crystalline forms (highest m. p. obtained, 202°, mixed m. p. with dibromo-β-amyrin benzoate, 190°), and in one case a *substance* of the same composition, m. p. 234—235°. Hydrolysis of these bromo-products yields only amorphous substances. β-Amyrenone on bromination in acetic acid solution yields *monobromo-β-amyrenone*, m. p. 198—199°, detailed crystallographic data for this compound being given. It is unattacked by heating with acetic anhydride. J. W. BAKER.

Scoparin. F. HEMMELMAYR and J. STREHLY (Monatsh., 1926, 47, 379—392; cf. A., 1893, i, 601; 1894, i, 542; 1918, i, 503).—Scoparin, heated in methyl-alcoholic solution, yields the same product as that previously obtained in ethyl alcohol. Attempts to replace all the hydroxylic hydrogen atoms by metals or acyl radicals were unsuccessful, but the results are consistent with the formulæ $C_{20}H_{20}O_{10}$ or $C_{22}H_{22}O_{11}$, of which the latter is preferred. The following are described: *heptapotassium* salt; *pentasodium* salt; *barium* salt, $C_{44}H_{36}O_{22}Ba_4$; *pentachloroacetyl* derivative, soluble in alkali with intense yellow colour, and *hexa-* (or *hepta-* ?)*anisoyl* derivative, m. p. 135°. When boiled with dilute sulphuric acid, scoparin is converted into an isomeric *substance* which slowly loses water. Dilute hydrochloric acid, on the other hand, causes the loss of 2 mols. of water to yield a brown *substance*, $C_{22}H_{18}O_9$, m. p. about 240° (*acetyl* derivative, m. p. 210°). G. M. BENNETT.

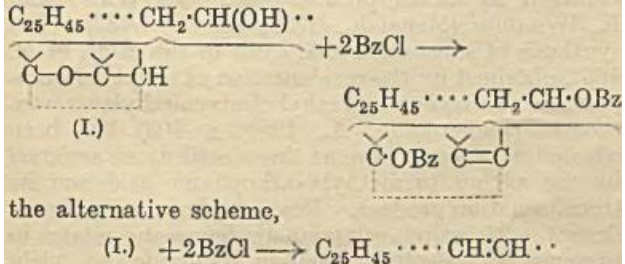
Saponins and related substances. XVI. Hederagenin. A. W. VAN DER HAAR (Rec. trav. chim., 1926, 46, 28—32; cf. A., 1925, i, 946; Jacobs, *ibid.*, 947, 948; 1926, i, 1250).—The author acknowledges that the so-called hederagenin chloride, methyl ester, and amide (A., 1922, i, 160) are identical with the neutral sulphites of these compounds described by Jacobs. *Hederagenin menthyl ester sulphite* has m. p. 265—266°. The non-recognition of the presence of

the sulphite residue was due to the fact that hederagenin methyl ester and its sulphite have the same m. p. Hederagenin monoacetate, m. p. 156—157°, supposed to be formed by the loss of one acetyl group from hederagenin diacetate on heating or in boiling alcohol, is shown to be the diacetate of the same m. p. described by Jacobs, the former description being the result of an analytical error. The view is maintained that the difference in ease of acetylation is best explained by the assumption that the hydroxyl groups are secondary and tertiary, and that the formation of hederagenolic acid and hederagenone requires their location on the β-carbon atoms with reference to the carboxyl group. The formation of the sulphite bridge and acetonyl derivative is possible if the hydroxyl groups are in the *cis*-position (annexed formula). Jacobs' use of chromic acid oxidation, sulphuric acid, and Clemmensen's reduction is criticised.

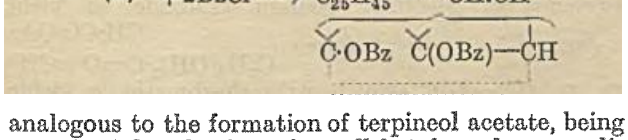


J. M. GULLAND.

Phytochemistry. IV. Betulin. III. O. DISCHENDORFER and H. GRILLMAYER (Monatsh., 1926, **47**, 419—425; cf. this vol., 59; Schulze and Pieroh, A., 1922, i, 1045).—*allo*Betulin on treatment with benzoyl or *p*-bromobenzoyl chloride at 150—180° for 8 hrs. yields, respectively, *heterobetulin dibenzoate*, m. p. 230°, $[\alpha]^{20}$ +35·49°, and the corresponding *di-p-bromobenzoate*, m. p. 253° (after sintering at 200°), $[\alpha]_D$ +40·16°, in which both the acyl groups are attached to oxygen. The former on hydrolysis yields *heterobetulin*, $C_{30}H_{50}O_2$, m. p. 267—268° (after sintering at 260°), $[\alpha]_D^{20}$ +11·59°, which is isomeric but not identical with *allo*betulin, and on re-esterification with benzoyl chloride and pyridine yields the original dibenzoate, and with acetic anhydride the *diacetate*, m. p. 248—249°, $[\alpha]_D^{20}$ +28·29°. When heated with 95% formic acid, heterobetulin yields a *monoformate*, m. p. 284—285° (decomp.), $[\alpha]_D^{19}$ +44·52°, which is isomeric with *allo*betulin formate, the ethereal oxygen linking being ruptured and re-formed in another position. These reactions show that the di-esters obtained from *allo*betulin are the enol esters of the unknown monoketone heterobetulone. The formation of heterobetulin dibenzoate from *allo*betulin is analogous to the formation of terpin diacetate by the acetolysis of cineole, and is represented by the scheme:



the alternative scheme,



analogous to the formation of terpineol acetate, being negatived by the fact that *allo*betulone forms a di- and not a tri-ester with benzoyl chloride.

J. W. BAKER.

Action of anhydrous formic acid on *d*-α-pinene. J. REISMAN (Bull. Soc. chim., 1927, [iv], **41**, 94—98).—Prolonged (2 months') action of anhydrous formic acid on *d*-α-pinene (Aleppo turpentine, α_D +42° per dm.) affords a mixture of limonene, dipentene, terpinene, terpinolene, and diterpilene, together with the formates of terpineol and terpinenol and traces of bornyl formate. R. BRIGHTMAN.

Determination of unsaturated hydrocarbons and formation of tricyclic rings by dehydration of alcohols. S. S. NAMETKIN and L. J. BRUSSOVA (J. Russ. Phys. Chem. Soc., 1926, **57**, 372—378).—The authors have used the reaction of perbenzoic acid, with compounds containing a double linking (cf. Prilischaev, A., 1910, i, 86), to determine the amount of such compounds when they are formed by the dehydration of alcohols, in cases when there is the possibility of a tricyclic compound being formed. The latter do not react with perbenzoic acid. The compound is treated with excess of perbenzoic acid, the mixture kept for 3 days at the ordinary temperature, and after adding potassium iodide and sulphuric acid, titrated with sodium thiosulphate. Tricyclene, formed by the oxidation of camphor semicarbazone (A., 1920, i, 855), contains 35% of non-tricyclic compound, probably camphene.

Pure cyclo*fenchene*, b. p. 143—143·5°/754 mm., d_4^{20} 0·86013, n^{20} 1·4515, is obtained in an analogous way from fenchone. α-Methylcamphene, obtained by the dehydration of tertiary methylfenchyl alcohol with potassium hydrogen sulphate, contains 2% of saturated hydrocarbon. The method confirms the structure given to this compound. Other terpene compounds have been examined with similar results.

E. ROTHSTEIN.

Optical superposition. VII. Bornyl dimethoxysuccinates. T. S. PATTERSON, J. D. FULTON, and (MRS.) J. M. MACCULLOCH [(MISS) J. M. SEMPLE] (J.C.S., 1926, 3224—3230; cf. *ibid.*, 1915, **107**, 142; A., 1924, i, 1041; 1925, i, 115).—The rotatory power of bornyl *i*-dimethoxysuccinate is nearly the same as the mean of the rotatory powers of the *d*- and *l*-esters. The results are not taken as confirming the principle of optical superposition, since the differences from the mean observed are dependent on the temperature, and cannot be due to experimental error. *Bornyl* l-*dimethoxysuccinate*, m. p. 70°, α_y^{14} (1 dm.) −2·28°, *bornyl* d-*dimethoxysuccinate*, m. p. 103°, α_y^{16} (1 dm.) +11·4°, and *bornyl* i-*dimethoxysuccinate*, m. p. 114°, $[\alpha]_y^{23\cdot5}$ +44·79°, are described, together with the rotatory powers of solutions of similar concentrations in different solvents over a range of temperature. H. BURTON.

True camphenone. S. S. NAMETKIN and A. S. ZABRODINA (J. Russ. Phys. Chem. Soc., 1926, **57**, 379—381).—From α-nitrocamphene (cf. A., 1925, i, 416), the authors obtain α-camphenone, to which they assign the structure $CMe_2{\cdot}CH{-}CH_2(\beta)$ / CH_2 / $CH_2{:}C{-}CH{-}CO(\alpha)$. The potassium salt of secondary α-nitrocamphene, freed from water, was slowly added to a vigorously shaken solution of tin in fuming hydrochloric acid, and the product purified by distillation in steam. By this

method 30 g. of nitrocamphene yielded 3 g. of the crude ketone. The residue of the steam distillation also yielded 3 g. of the hydrochloride of the amino-derivative previously described (*loc. cit.*). The *semicarbazone*, m. p. 205°, yields the pure *ketone*, m. p. 77—78°. The latter yields the *oxime*, m. p. 117—118°. E. ROTHSTEIN.

Constitution of the acid formed by the action of sulphuric acid on camphorquinone. M. B. BHAGVAT and J. L. SIMONSEN (J.C.S., 1927, 77—89).—The keto-acid, $C_{10}H_{16}O_3$, formed by the action of sulphuric acid on camphorquinone and previously described as *d*-2 : 2 : 4-trimethyl*cyclo*hexan-3-one-1-carboxylic acid (A., 1925, i, 919), is *d*-2 : 2 : 3-trimethyl*cyclo*hexan-4-one-1-carboxylic acid. Bromination of the methyl ester in acetic acid solution gives *methyl* 5 : 5-*dibromo*-2 : 2 : 3-*trimethyl*cyclo*hexan*-4-*one*-1-*carboxylate*, m. p. 57—58°, which, on treatment with barium hydroxide, yields a mixture of acids (I), (II), (III), and (IV) (below). 4-*Hydroxy*-2 : 2 : 3-*trimethyl*-Δ^3-cyclo*hexen*-5-*one*-1-*carboxylic acid* (I), m. p. 151—152° [*methyl* ester, m. p. 73—74° (*dioxime*, m. p. 138—139°; *disemicarbazone*, m. p. 206—207°); *acetyl* derivative (+0·5H_2O), m. p. 128°], is converted by digestion with 50% potassium hydroxide solution into 1-*hydroxy*-4 : 4 : 5-*trimethyl*cyclo*pentane*-1 : 3-*dicarboxylic acid* (II) (+0·5H_2O), m. p. 191—192° (*potassium* salt). The *acetyl* derivative of (II) decomposes at 207—208°, resolidifying to 4 : 4 : 5-*trimethyl*-Δ^5-cyclo*pentene*-1 : 3-*dicarboxylic* acid (III), m. p. 257—258° [*sodium* salt (inactive in aqueous solution); *dianilide*, m. p. 200—201°], which, on reduction with sodium and amyl alcohol, yields trans-4 : 4 : 5-*trimethyl*cyclo*pentane*-1 : 3-*dicarboxylic acid*, m. p. 182—183°. Oxidation of (III) or of l-4 : 4 : 5-*trimethyl*-Δ^5-cyclo*pentene*-1 : 3-*dicarboxylic acid* (IV), m. p. 215—216° (*sodium* salt has $[\alpha]_D^{25}$ —62° in water; *dianilide*, m. p. 208—209°), with nitric acid gives γ-methylbutane-$\alpha\beta\gamma$-tricarboxylic acid (V). Oxidation of (III) with potassium permanganate at 0° yields *γ-acetyl-γ-methylbutane-αβ-dicarboxylic acid* (VI), m. p. 125—126°, and a second *keto-dicarboxylic acid* (VII), $C_{10}H_{12}O_5$, m. p. 183—185° [*oxime* (+0·5H_2O), decomp. 214°; *semicarbazone*, decomp. 241°]. Further oxidation of (VI) with sodium hypobromite gives (V), also obtained on oxidation of (VII) with nitric acid.

The structure of the original keto-acid is established by these results, and the presence of a methylene group adjacent to the carbonyl group is confirmed by preparation of an *oximino*-ester by the action of *iso*amyl nitrite on the methyl ester in presence of sodium. Hydrolysis of this non-crystallising oil with formaldehyde and hydrochloric acid, followed by treatment with dilute potassium hydroxide solution, gives the acid (I) and thence the acid (III), identical with that prepared from the dibromo-ester. The suggestion that the keto-acid can exist in keto- and enolic forms (*loc. cit.*) is confirmed by the preparation of the *acetyl* derivative of the enolic form by treating camphorquinone with acetic anhydride and zinc chloride. l-4-*Acetyl*-2 : 2 : 3-*trimethyl*-Δ^3-cyclo*hexene*-1-*carboxylic acid* has m. p. 109—111°, $[\alpha]_D$ —66·3° in chloroform, and does not show mutarotation. Hydrolysis gives the ordinary ketonic form of the acid. Direct acetylation of the latter could not be effected. M. CLARK.

New terpene alcohol, $C_{10}H_{18}O$. O. ACHMATOWICZ (Rocz. Chem., 1926, 6, 804—814).—Bornyl acetate, prepared in presence of sulphuric acid or zinc chloride, yields on hydrolysis a new alcohol, apparently a space isomeride of borneol, termed *endoborncol*, m. p. 186°, b. p. 203—204°, which on oxidation yields camphor. Its *ethyl ether*, b. p. 83—87°/20 mm., 197—198°/751 mm., *phenylurethane*, m. p. 138—139°, and *benzoate*, b. p. 186—187°/15 mm., are described. R. TRUSZKOWSKI.

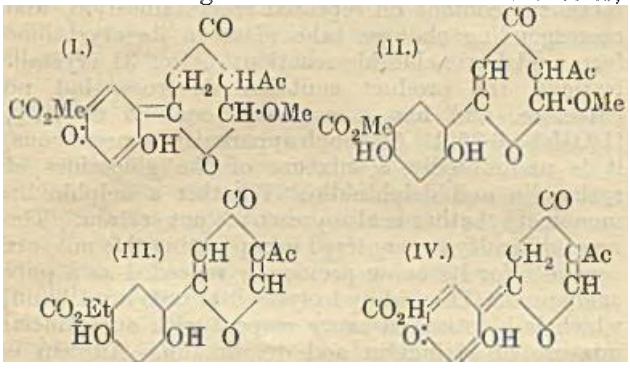
Cadinene. II. Compounds related to cadinene. G. G. HENDERSON and J. M. ROBERTSON (J.C.S., 1926, 2811—2816; cf. Henderson and A. Robertson, A., 1924, i, 1328).—*iso*Cadinene (*loc. cit.*) is probably identical with Tröger and Feldmann's sesquiterpene from cade oil (A., 1899, i, 376; Lepeschkin, *ibid.*, 1908, i, 278) and with Ruzicka and Capato's hexahydrocadalene (*ibid.*, 1925, i, 943). They differ from cadinene in the position of the double linkings. Oil of false cubebs yields on fractionation a mixture of dicyclic alcohols, $C_{15}H_{25}$·OH, consisting mainly of l-*cadinol*, b. p. 153—155°/10 mm., d_4^{16} 0·9727, n_D^{16} 1·508, $[\alpha]_{5461}$ —54° (cf. *d*-cadinol +22°, other properties identical), which is converted into cadinene dihydrochloride, m. p. 118°, $[\alpha]$ —43·7° (in chloroform). There is also isolated a new dicyclic sesquiterpene alcohol, *cubebol* (*phenylurethane*, m. p. 186°, $[\alpha]_{5461}^{19}$ +58·9°; *α-naphthylurethane*, m. p. 197—198·5°; *dibromide*, oily; *dibromide phenylurethane*, decomp. at 76—80°; no stable hydrochloride), which, regenerated from the phenylurethane by means of alcoholic potassium hydroxide, has m. p. 61—62°. C. HOLLINS.

Furfuraldehyde in industry. D. H. KILLEFFER.—See B., 1927, 92.

5-Hydroxymethylfurfuraldehyde. J. J. BLANKSMA (Helv. Chim. Acta, 1927, **10**, 67).—The properties of this compound (Reichstein, this vol., 61, there incorrectly described as 5-hydroxyfurfuraldehyde) had been previously described (Troje, A., 1925, ii, 1210; Middendorp, *ibid.*, 1919, i, 129). H. E. F. NOTTON.

Condensation of esters of ethoxymethylene-β-ketonic acids with resacetophenone and their relation to xanthophanic acid. R. WEISS and K. WOLDICH (Monatsh., 1926, 47, 427—432).—The synthesis of substances analogous to the ester, m. p. 165°, obtained by the condensation of ethyl resacetophenonecarboxylate and ethyl ethoxymethyleneacetoacetate (Liebermann, A., 1909, i, 403) has been effected in order to support the constitutions assigned by the author to methylxanthophanic acid and its transformation product. Resacetophenone itself condenses with ethyl ethoxymethyleneacetoacetate in presence of alcoholic sodium ethoxide to yield *2-resorcyl-5-acetyl*-1 : 4-*pyrone*, $C_6H_3(OH)_2\cdot C(=O)-CH=CH\cdot CO\cdot CAc$, m. p. 169—170° (which with diazomethane yields another *substance*, m. p. 168°); and with *ethyl ethoxymethylenebenzoylacetate* (prepared, mixed with ethyl benzoylacetate, from which it cannot be separated, by the action of this ester on ethyl orthoformate and

acetic anhydride) to yield 2-*resorcyl*-5-*benzoyl*-1 : 4-*pyrone*, m. p. 180°. Treatment of the transformation product obtained by the action of magnesium methoxide on ethylxanthophanic acid (*idem*, *ibid.*, 1908, i, 548) with sulphuric acid merely hydrolyses the ester group without eliminating a molecule of alcohol, a *substance*, m. p. 176°, to which the constitution $C_6H_2(OH)_2(CO_2H)\cdot C(CH{:}CO\cdot CHAc)\cdot O\cdot CH\cdot OMe$ is being obtained. The following constitutions are therefore assigned to methylxanthophanic acid (I) and its transformation product (II), respectively, the action of magnesium methoxide merely bringing about a tautomeric change. The constitution of the ester,



m. p. 165°, obtained by Liebermann and the corresponding acid, m. p. 185°, are therefore represented by the formulæ (III) and (IV), respectively.

J. W. Baker.

Hydrogenation of xanthone and xanthen. V. Ipatiev and N. Orlov (Compt. rend., 1926, **183**, 973—975).—Xanthone when hydrogenated in presence of copper oxide yields xanthen, which on further hydrogenation in presence of nickel oxide gives 2-*hydroxydi*cyclo*hexylmethane*, m. p. 40—43°, d_0^{40} 0·9581; this further gives *di*cyclo*hexylmethane*, b. p. 250—252°/763 mm.

L. F. Hewitt.

Tannins and related substances. XXII. Passage from the flavone to the catechin series. K. Freudenberg and A. Kammüller (Annalen, 1927, **451**, 209—213; cf. A., 1926, 73).—Catalytic reduction of quercetin pentamethyl ether (3 : 5 : 7 : 3′ : 4′-pentamethoxyflavone) in presence of platinum-black affords 11% of *dl-epi*catechin pentamethyl ether (A., 1925, i, 1165). *Luteolin tetramethyl ether* (5 : 7 : 3′ : 4′-*tetramethoxyflavone*), m. p. 192°, obtained by simultaneous hydrolysis and methylation of luteolin tetraacetate, is hydrogenated under similar conditions, yielding 24% of deoxy*epi*catechin tetramethyl ether (*ibid.*, 419), identified as the *monobromo*-derivative, m. p. 155—156°.

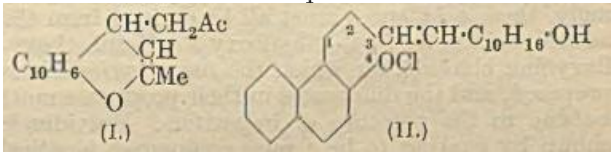
H. E. F. Notton.

Tannins and similar substances. XXIII. Syntheses of catechin derivatives. K. Freudenberg and M. Harder (Annalen, 1927, **451**, 213—222).—2 : 4 : 6-Trimethoxybenzaldehyde condenses with hippuric acid in presence of acetic anhydride and sodium acetate, forming 2-*phenyl*-4-*trimethoxybenzylideneoxazolone*, m. p. 172°. On hydrolysis with sodium hydroxide and oxidation of the resulting pyruvic acid with hydrogen peroxide, 2 : 4 : 6-*trimethoxyphenylacetic acid*, m. p. 183°, is obtained. The corresponding *acid chloride* condenses with veratrole in presence of aluminium chloride to give 3 : 4-*dimethoxyphenyl* 2 : 4 : 6-*trimethoxybenzyl ketone*, m. p. 144—145°. This is converted by magnesium methyl iodide into α-2 : 4 : 6-*trimethoxyphenyl*-β-3 : 4-*dimethoxyphenyl*-Δ^{α}-*propylene*, which exists in two stereoisomeric forms, m. p. 89—90° and 101°, respectively, both of which are reduced by sodium and alcohol to α-2 : 4 : 6-*trimethoxyphenyl*-β-3 : 4-*dimethoxyphenylpropane*, identical with the pentamethoxy-derivative, m. p. 104—105° (A., 1925, i, 692), obtained from the reduction product of anhydrocatechin tetramethyl ether. The formation of the latter compound from catechin must therefore have been accompanied by a migration of the 3 : 4-dimethoxyphenyl group from the 2- to the 3-position.

Attempts to isolate intermediate products of hydrogenation of cyanidin chloride (cf. *ibid.*, 1165) were unsuccessful. When, however, tetramethyl-luteolinidin chloride (*ibid.*, 825) is treated with 1 mol. of hydrogen in 96% alcoholic solution in presence of platinum-black and a little hydrochloric acid, α-3 : 4-dimethoxybenzoyl-β-2′-hydroxy-4′ : 6′-dimethoxyphenylethane is obtained. In absolute alcohol, ring-fission does not occur, the final and only isolable product being deoxy*epi*catechin tetramethyl ether (cf. preceding abstract). 2 : 4 : 6-Trimethoxybenzaldehyde is reduced by hydrogen and platinum-black to methylphloroglucinol trimethyl ether, b. p. 100—105°/1 mm., m. p. 27—28° (cf. Herzig, A., 1901, i, 205). When a nickel catalyst is used, a good yield of 2 : 4 : 6-*trimethoxybenzyl alcohol*, m. p. 63°, is obtained.

H. E. F. Notton.

Styrylpyrylium salts. VIII. 2-Styryl derivatives of β-naphthapyrylium chloride. R. Dickinson and I. M. Heilbron (J.C.S., 1927, 14—20; cf. *ibid.*, 1922, **121**, 1198; 1923, **123**, 2521).—Condensation of 2-naphthol-1-aldehyde with acetone in presence of alkali gives a poor yield of 1-*acetonyl*-3-*methyl*-1 : 4-β-*naphthapyran* (I), m. p. 152—153°. Condensation in presence of hydrogen chloride gives 3-(β-2′-*hydroxy*-1′-*naphthylvinyl*)-β-*naphthapyrylium chloride* (II). Addition of water to the warm alcoholic solution of this compound precipitates *di*-β-*naphtha*spiro*pyran* (cf. Lowenbein and Katz, A., 1926, 956; Dilthey and Wizinger, *ibid.*, 1163). Explanations are suggested for the colour-development in hot solutions of the spiran in nitrobenzene and



aqueous-alcoholic potassium hydroxide, respectively. The 2-styryl-β-naphthapyrylium salts are obtained in good yield by condensation of 2-naphthol-1-aldehyde with styryl methyl ketones in alcoholic solution in presence of dry hydrogen chloride. They show close resemblance to the 2-styrylbenzopyrylium salts. On treatment with aqueous sodium hydroxide, they give colourless solutions, slowly becoming intensely red. It is suggested that this may be due to fission of the pyrylium ring. The following are described: 3-*styryl*-β-*naphthapyrylium chloride* (+H·CO_2H);

3-p-*hydroxystyryl*-β-*naphthapyrylium chloride*, (+$2H_2O$); 3-3′-*methoxy*-4′-*hydroxystyryl*-β-*naphthapyrylium chloride* (+$2H_2O$); 3-p-*methoxystyryl*-β-*naphthapyrylium chloride* (+$H{\cdot}CO_2H,H_2O$); 3-3′ : 4′-*dimethoxystyryl*-β-*naphthapyrylium chloride* (+$H{\cdot}CO_2H,H_2O$); 3-3′ : 4′-*methylenedioxystyryl*-β-*naphthapyrylium chloride* (+$H{\cdot}CO_2H,H_2O$); 3-p-*dimethylaminostyryl*-β-*naphthapyrylium perchlorate*.

M. CLARK.

Synthesis of anthocyanins. II. Synthesis of 3- and 7-glucosidoxyflavylium salts. A. ROBERTSON and R. ROBINSON (J.C.S., 1927, 242—247; cf. A., 1926, 956).—ω-O-*Tetra-acetylglucosidoxyacetophenone*, m. p. 104—105°, prepared from benzoylcarbinol and *O*-tetra-acetyl-α-glucosidyl bromide in presence of silver carbonate, condenses with β-resorcylaldehyde in ethereal solution in presence of hydrogen chloride, giving a product which yields, on deacetylation with methyl-alcoholic ammonia, 3-β-*glucosidoxy*-7-*hydroxyflavylium chloride*. This compound shows ψ-base formation on addition of sodium acetate. Hydrolysis of the chloride yields dextrose and 3 : 7-dihydroxyflavylium chloride. The latter is also obtained by direct condensation of β-resorcylaldehyde and benzoylcarbinol or its acetate. β-Resorcylaldehyde reacts with *O*-tetra-acetylglucosidyl bromide in acetone solution in presence of aqueous potassium hydroxide, giving 4-*O*-*tetra-acetylglucosidoxy*-2-*hydroxybenzaldehyde*, m. p. 134—135°, which condenses with ω-methoxyacetoveratrone, in presence of hydrogen chloride, giving, after deacetylation, 7-*glucosidoxy*-3 : 3′ : 4′-*trimethoxyflavylium chloride* (*picrate*, decomp. 240—252°). Hydrolysis yields fisetinidin chloride trimethyl ether.

M. CLARK.

Vegetable colouring matters. I. Constitution of some anthocyanidins. P. KARRER and R. WIDMER [in part with H. HURLIMANN and O. NIEVERGELT] (Helv. Chim. Acta, 1927, **10**, 5—33).—Hydrolysis of anthocyanins with 10—15% sodium or barium hydroxide proceeds readily on boiling, and the acid product of fission, with methoxyl groups intact, may be isolated in the usual way. When œnin, myrtillin, althæin, ampelopsin, and malvin, or the corresponding anthocyanidins (cf. Willstatter, A., 1915, i, 282, 289), are treated in this way, pure syringic acid (4-hydroxy-3 : 5-dimethoxybenzoic acid) is obtained in each case in 10—35% yield. Accordingly, these substances must all be derived from the anthocyanidin, 5 : 7 : 4′-trihydroxy-3′ : 5′-dimethoxyflavylium chloride, for which the name *syringidin* is proposed, and the differences in their properties must be due to the presence of impurities. Malvidin is shown by analysis to be a pure compound, identical with syringidin. Œnin, which is conveniently purified by repeated recrystallisation of the picrate from boiling water, contains less than the theoretical amount of methoxyl, and is therefore not a pure compound. Œnidin chloride may be separated by fractional crystallisation from 7% sulphuric acid into more and less soluble fractions, of which the latter has a higher methoxyl content than the original material and a solubility of the same order as that of malvidin chloride. The dark red blooms of *Cyclamen persicum*, Mill., contain a monoglucoside, *cyclamin*, isolated as the *picrate*, $C_{29}H_{27}O_{19}N_3$, which yields œnidin on hydrolysis with acids and is probably identical with œnin. Pæonidin is hydrolysed by 16% sodium hydroxide, giving crystalline vanillic acid. This confirms the formula of Nolan, Pratt, and Robinson (A., 1926, 1043). Since cyanilidin (Kataoka, *ibid.*, 1150) also yields vanillic acid on hydrolysis, it must be identical and not isomeric with pæonidin. Myrtillin, regarded by Willstatter (*ibid.*, 1917, i, 47) as a galactoside of delphinidin monomethyl ether, is resolved by means of its picrate into two fractions. The more soluble one is methoxyl-free, and is hydrolysed by acids to delphinidin and a mixture of dextrose and galactose. The less soluble fraction increases in methoxyl content on repeated recrystallisation, and corresponding changes take place in its crystalline form and ferric chloride reaction. After 31 crystallisations, the product contains dextrose, but no galactose, and has a methoxyl content of 7·7% [1(OMe)=6·3%]. Although apparently homogeneous, it is undoubtedly a mixture of the glucosides of syringidin and delphinidin. Whether a delphinidin monomethyl ether is also present is not certain. The great difficulty encountered in separating this mixture accounts for its being previously regarded as a pure compound. On acid hydrolysis, it affords myrtillidin, which is identical in every respect with an artificial mixture of syringidin and delphinidin. Althæin is hydrolysed to dextrose and althæidin, which, although it corresponds in composition with a delphinidin monomethyl ether, is actually, like myrtillidin, a mixture or loose molecular compound of delphinidin and its dimethyl ether. When ampelopsin is purified through the picrate, its methoxyl content becomes much higher than that of the product described by Willstatter, and it is indistinguishable from œnin. The various reactions which these substances show with alcoholic ferric chloride may now be correlated with their syringidin content; thus malvin, a pure syringidin derivative, gives no reaction, œnin, cyclamin, and ampelopsin (80—90% pure) give a reddish-violet colour, whilst the different fractions of myrtillin (50% or less pure) give colours ranging from wine-red to pure blue as the methoxyl content decreases.

H. E. F. NOTTON.

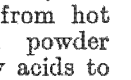
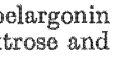
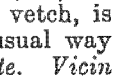
Vegetable colouring matters. II. P. KARRER and R. WIDMER (Helv. Chim. Acta, 1927, **10**, 67—86).—*Monardœin*, the colouring matter of the flowers of the golden balm, *Monarda didyma*, is extracted by 2% methyl-alcoholic hydrogen chloride and purified by reprecipitating its *picrate* from hot water. *Monardœin chloride* is a red, amorphous powder which gives a scarlet aqueous solution. The picrate, *sulphate*, and *picrolonate* are also amorphous. It is hydrolysed by cold 10% sodium hydroxide to 1 mol. of *p*-hydroxycinnamic acid and 1 mol. of *monardin*. The latter is identical in composition, appearance, m. p. (280°), and reactions with pelargonin, but its specific rotation is smaller: $[\alpha]_D$ −244°, $[\alpha]_{614}$ −133°. It is hydrolysed by acids to 1 mol. of pelargonidin and 2 mols. of dextrose. Thus although monardæin chloride contains 4—6% of methoxyl, it must be a *p*-hydroxycinnamoylpelargonidin diglucoside. Pure pelargonidin may be rapidly and conveniently obtained from these flowers.

About 0·1% of a pure anthocyanin (*gentianin*) may be extracted from the dried flowers of the blue gentian, *Gentiana acaulis*, by digestion with 2% methyl-alcoholic hydrogen chloride, fractional precipitation of the crude dye with lead acetate, and reprecipitation of the amorphous *picrate* from hot water. *Gentianin chloride*, a bluish-red powder containing 10% of water, is hydrolysed by acids to 1 mol. of *p*-hydroxycinnamic acid, 1 mol. of delphinidin, and 1 mol. of dextrose, and is therefore a *p*-hydroxycinnamoyldelphinidin monoglucoside.

Dried pomegranate flowers (*Punica granatum*) contain about 0·1% of an anthocyanin, *punicin*, which may be isolated in the usual way and purified by means of its crystalline *ferrichloride*. *Punicin chloride* has m. p. 293°, $[\alpha]_D$ −232° or −246°, but in all other respects it is identical with monardin and pelargonin chlorides. It is hydrolysed by acids to dextrose and pelargonidin.

Sambucin, the anthocyanin of the elderberry (*Sambucus nigra*), is extracted from the fresh skins in the usual way and purified by recrystallising its picrate. *Sambucin chloride*, a red powder, which gives a brownish-red aqueous solution, consists principally of cyanidin rhamnoglucoside, $C_{27}H_{31}O_{15}Cl$, but analyses and determination of its partition coefficient between amyl alcohol and water indicate that it also contains a small amount of a monoglucoside of cyanidin. Sambucin is thus analogous to keracyanin and prunicyanin (Willstatter and Zollinger, A., 1917, i, 45).

Vicin, the anthocyanin of the dark-red vetch, is extracted from the dried flower in the usual way and purified through the crystalline *picrate*. *Vicin chloride*, which corresponds with the formula $C_{21}H_{21}O_{12}Cl,2H_2O$, forms apparently homogeneous brownish-red needles, and is hydrolysed by acids to a mixture of delphinidin with dextrose and rhamnose. The relative quantities of these indicate that vicin is a mixture of delphinidin monoglucoside and monorhamnoside in roughly equal amounts. The flowers of the scarlet vetch appear to contain a different anthocyanin. H. E. F. NOTTON.

New transformations of oximes and phenylhydrazones. O. DIELS, O. BUDDENBERG, and S. WANG (Annalen, 1927, **451**, 223—241).—The perchlorates of α-phenyl-Δ^{α}-pentene-γδ-dione-δ-oxime and its methyl ether are decomposed into their components by water in the normal way. The *perchlorate*, m. p. 95°, of the corresponding *benzyl ether*, m. p. 80°, is, however, converted by a kind of Beckmann rearrangement into the isomeric 3-*keto*-5-*phenyl*-2-*methylpyrroline*-2-*benzyl ether*,  , m. p. 76°. This substance is highly reactive and readily absorbs atmospheric oxygen. With carboxyethylcarbimide, it gives a *compound*, $C_{22}H_{22}O_5N_2$, m. p. 95°. Alkali decomposes it into acetophenone and ammonia, whilst aniline, piperidine, and ammonia liberate benzyl alcohol, forming 2-*anilino*-, m. p. 192—194°, 2-*piperidino*-, m. p. 179°, and 2-*amino*-3-*keto*-5-*phenyl*-2-*methylpyrroline*, m. p. 201°, respectively. The last-named, for which the alternative formula $NH_2\cdot CPh{:}CH\cdot CO\cdot CMe{:}NH$ is suggested, is converted by nitrous acid into *αβγδ-tetraketo-α-phenylpentane-β-monoxime*, yellow, m. p. 56° (decomp.). This is readily and quantitatively decomposed, on warming in inert solvents, into benzoyl cyanide, carbon monoxide, and acetic acid. When a methyl-alcoholic solution of α-phenyl-Δ^{α}-pentene-γδ-dione-δ-phenylmethylhydrazone (A., 1911, i, 464) is boiled for a short time in absence of air, the isomeric 2-*phenylmethylamino*-3-*keto*-5-*phenyl*-2-*methylpyrroline* (I), m. p. 117—118°, is obtained. On shaking with oxygen, it gives a *dioxide*, decomp. 126—127°, which may be prepared in the same way from the original phenylmethylhydrazone in presence of formic or perchloric acid. When the dioxide is exposed to the air, or when (I) is treated with alkaline hydrogen peroxide, 2-*phenylmethylamino*-4-*hydroxy*-3-*keto*-5-*phenyl*-2-*methylpyrroline*, intense yellow, m. p. 151° [*semicarbazone*, m. p. 180°; *phenylhydrazone*, m. p. 99—111° (decomp.)], is formed. This gives a *quinoxaline* derivative, $C_{24}H_{22}N_4$, m. p. 158—159°, with *o*-phenylenediamine. When the pyrroline is heated with formic acid, nitrogen is eliminated from the ring, which then closes in a different way, yielding 3-*phenylmethylamino*-1:2-*diketo*-5-*phenyl*-Δ^3-cyclopentene,  , m. p. 200—201° (*quinoxaline* derivative, $C_{24}H_{19}N_3$, m. p. 182°). 2-*Phenylmethylamino*-3-*keto*-5-p-*anisyl*-2-*methylpyrroline dioxide*, decomp. 122°, is also described. When (I) is heated with formic acid in absence of air, methylaniline is eliminated, leaving the *compound*,  bright yellow, m. p. 220—221° (decomp.). H. E. F. NOTTON.

Catalytic hydrogenation of pyridine. W. S. SADIKOV and A. K. MIKHAILOV (J. Russ. Phys. Chem. Soc., 1926, **58**, 527—540).—Pyridine was hydrogenated in an open tube, and by Ipatiev's method under pressure in the presence of catalysts prepared by Zelinsky's method. In an open tube at 150°, with 40% platinised asbestos, the hydrogenation was very slow (300 hrs.) The product was fractionated and the refractive indices and densities were determined. No amylamine was isolated, but 60% of tetrahydropyridine, together with condensation products of higher b. p. With 20% platinised asbestos at 200°, hydrogenation by Ipatiev's method was very slow: after 6 hrs. 6·6%, after 24 hrs., 7·8%; at 250° after 16 hrs., about 20%. Palladised asbestos (20%), under the same conditions, gave a 70% yield after 19 hrs., whilst 20% iridised asbestos gave complete absorption of hydrogen after 12 hrs. With 20% osmised asbestos, absorption is complete after 6 hrs. at 240°, and a 30% yield of condensation products of higher b. p. is obtained; 5% and 1% osmium catalysts also give complete absorption. The theories of contact catalysis of Willstatter, Langmuir, and Bodenstein are discussed, and a mechanism is suggested. The efficiency of the catalysts is in the order of their oxidisability: a colloidal suspension of the metal in pyridine may be formed which adsorbs oxygen and causes the hydrogen molecule to dissociate into atoms, which then add on to the unsaturated compound. The possible influence of traces of water is also mentioned. M. ZVEGINTZOV.

Syntheses of tetrahydro*iso*quinoline and *as*-homotetrahydro*iso*quinoline bases according to the glycine–aluminium chloride method. II. J. VON BRAUN and K. WIRZ (Ber., 1927, 60, [*B*], 102—110; cf. A., 1924, i, 873).—The primary effect of the successive action of phosphorus pentachloride and aluminium chloride on glycine derivatives, $C_6H_5\cdot[CH_2]_n\cdot NR\cdot CH_2\cdot CO_2H$ (where n=2 or 3), is to cause loss of carbon monoxide; ring closure to tetrahydro*iso*quinoline or *as*-homotetrahydro*iso*quinoline derivatives occurs subsequently and appears to be independent of the nature of the substituent, R.

Methyl-β-phenylethylamine is converted by ethyl bromoacetate in ethereal solution into *ethyl methyl-β-phenylethylaminoacetate*, $Ph\cdot[CH_2]_2\cdot NMe\cdot CH_2\cdot CO_2Et$, b. p. 151—155°/12 mm. (non-crystalline *hydrochloride* and *picrate*; *methiodide*, m. p. 160°), from which *methyl-β-phenylethylaminoacetic acid*, m. p. 163° (*hydrochloride*, m. p. 155°), is prepared. The acid is converted by phosphorus pentachloride in presence of acetyl chloride into *methyl-β-phenylethylaminoacetyl chloride hydrochloride*, which, with aluminium chloride in benzene, affords *2-methyltetrahydro*iso*quinoline*, b. p. 213° (*hydrochloride*, m. p. 163°; *picrate*, m. p. 146°; *methiodide*, m. p. 189°).

p-Xylyl bromide is converted by potassium cyanide in aqueous acetone in 95% yield into the corresponding nitrile, which is catalytically hydrogenated to β-*p*-tolylethylamine. Alternatively, β-*p*-tolylethyl alcohol, from *p*-bromotoluene, magnesium, and ethylenechlorohydrin, is converted successively into β-p-*tolylethyl bromide*, b. p. 115°/14 mm., β-p-*tolylethylphthalimide*, m. p. 113°, and β-*p*-tolylethylamine. With ethyl bromoacetate, the base yields *ethyl* β-p-*tolylethylaminoacetate*, b. p. 176—177°/21 mm., transformed successively into β-p-*tolylethylaminoacetic acid hydrochloride*, m. p. 216°, and *benzenesulphonyl*-β-p-*tolylethylaminoacetic acid*, m. p. 89°. The latter substance with phosphorus pentachloride and aluminium chloride in nitrobenzene affords *2-benzenesulphonyl-7-methyltetrahydro*iso*quinoline*, m. p. 154°, hydrolysed to *7-methyltetrahydro*iso*quinoline*, b. p. 125°/18 mm., d_4^{24} 1·0176 (*hydrochloride*, m. p. 216°; *picrate*, m. p. 202°; *methiodide*, m. p. 133°; *nitroso*-compound, m. p. 87°; non-crystalline *benzoyl* derivative).

β-*p*-Tolylethyl bromide is converted by potassium cyanide into β-p-*tolylpropionitrile*, b. p. 137°/15 mm., which is reduced by Ladenburg's method to γ-p-*tolyl*-n-*propylamine*, b. p. 126°/23 mm. (*hydrochloride*, m. p. 225°; *picrate*, m. p. 154°; *benzoyl* derivative, m. p. 85°; *phenylthiocarbamide* compound, m. p. 82°). With ethyl bromoacetate, the amine affords *ethyl* γ-p-*tolylpropylaminoacetate*, b. p. 191°/22 mm., which yields γ-p-*tolylpropylaminoacetic acid hydrochloride*, m. p. 211°, and *benzenesulphonyl*-γ-p-*tolylpropylaminoacetic acid*, m. p. 116°. *2-Benzenesulphonyl-8-methyl*-as-*homotetrahydro*iso*quinoline*, m. p. 126°, is hydrolysed by hydrochloric acid at 130° to the free *base*, b. p. 137—139°/19 mm., m. p. 27°, d_4^{25} 1·0048 (*hydrochloride*, m. p. 223°; *benzoyl* derivative, m. p. 101°; *nitroso*-compound, m. p. 91°).

p-Bromocumene is converted by magnesium and ethylenechlorohydrin into β-p-iso*propylphenylethyl alcohol*, b. p. 147°/20 mm., and thence successively into β-p-iso*propylphenylethyl bromide*, b. p. 134—136°/20 mm., β-p-iso*propylphenylpropionitrile*, b. p. 150°/17 mm., and γ-p-iso*propylphenyl*-n-*propylamine*, b. p. 143°/20 mm. (*hydrochloride*, m. p. 196°; *picrate*, m. p. 122°; *benzoyl* derivative, m. p. 71°). The amine is converted successively into *ethyl* γ-p-iso*propylphenyl*-n-*propylaminoacetate*, b. p. 205—210°/20 mm., γ-p-iso*propylphenyl*-n-*propylaminoacetic acid hydrochloride*, m. p. 210°, *benzenesulphonyl*-γ-p-iso*propylphenyl*-n-*propylaminoacetic acid*, m. p. 101°, *2-benzenesulphonyl-8-isopropyl*-as-*homotetrahydro*iso*quinoline*, m. p. 92°, and *8-isopropyl*-as-*homotetrahydro*iso*quinoline*, b. p. 146°/13 mm., m. p. 31° (*hydrochloride*, m. p. 248°; *picrate*, m. p. 236°; *methiodide*, m. p. 214°; *benzoyl* derivative, m. p. 83°; *nitroso*-compound, m. p. 70°).

Piperonal is very smoothly hydrogenated in decahydronaphthalene in the presence of nickel to piperonyl alcohol, b. p. 157°/16 mm., m. p. 54°, which is converted through the corresponding chloride and cyanide into homopiperonylamine. The ester formed from the amine and ethyl bromoacetate is very readily hydrolysed to *β-methylenedioxyphenylethylaminoacetic acid hydrochloride*, m. p. 241°. *Benzenesulphonyl-β-methylenedioxyphenylethylaminoacetic acid*, m. p. 131°, does not suffer smooth ring closure when treated with phosphorus pentachloride and aluminium chloride.

H. WREN.

Preparation and properties of pyrrole-1-carboxylic acid, its amide, pyrrolide, and glycine derivative. W. TSCHELINZEV and B. MAXOROV (Ber., 1927, 60, [*B*], 194—199).—*Pyrrole-1-carboxylic acid*, m. p. 95° (decomp.), is obtained by cautious hydrolysis of ethyl pyrrole-1-carboxylate, b. p. 180°, or from the aqueous liquors derived from the action of ethyl chloroformate on sodium pyrrole. It decomposes slowly at the ordinary temperature, rapidly when heated, into carbon dioxide and pyrrole. The *ammonium* salt is described, but the sodium, potassium, barium, calcium, and silver compounds are too unstable to permit isolation. The acid is converted by phosphorus pentachloride in presence of chloroform into the corresponding chloride, and thence into the amide, m. p. 166°, pyrrolide, $C_4H_4N\cdot CO\cdot NC_4H_4$, m. p. 61°, and *ethyl 1-pyrroylaminoacetate*, m. p. 77—78° (whence *1-pyrroylglycine*, m. p. 156°).

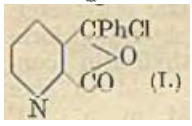
H. WREN.

Oxidation of pyridine and the pyridine nucleus with permanganate. M. DELÉPINE (Compt. rend., 1927, 184, 206—208).—When a solution of pyridine in a mixture of potassium permanganate solution and a quantity of sulphuric acid equivalent to the potassium present is warmed to 70°, the pyridine is rapidly oxidised to carbon dioxide and ammonia. A portion of the latter is oxidised to nitric acid, since the quantity of permanganate required for the complete oxidation of the pyridine is in excess of that given by the equation $2C_5H_5N+11O_2=10CO_2+2NH_3+2H_2O$. α-Picoline similarly yields a considerable quantity of acetic acid (and some formic acid), whilst acetic and butyric acids are isolated from the products obtained by the oxidation of 2 : 5-dimethyl-4-propylpyridine. Quinoline and *iso*quinoline are similarly oxidised with the production of ammonia.

J. W. BAKER.

Tautomerism of 2-aminopyridine. II, III, IV. A. E. Tschitschibabin (J. Russ. Phys. Chem. Soc., 1926, **57**, 399—425).—See A., 1924, i, 987; 1925, i, 158, 1328, respectively. E. Rothstein.

Chloride and ester of 3-benzoylpyridine-2-carboxylic acid. A. Kirpal and H. Kunze (Ber., 1927, **60**, [*B*], 138—140).—3-Benzoylpyridine-2-carboxylic acid is converted by thionyl chloride into a difficultly separable mixture of products; if, however, the reagent is saturated with hydrogen chloride, the



(I.)

hydrochloride of 3-*benzoylpyridine*-2-*carboxyl ψ-chloride*, m. p. 103°, separates, from which the *ψ-chloride* (I), m. p. 93°, is derived. Cautious treatment with methyl alcohol transforms the latter compound into the *methyl ψ-ester*, m. p. 89°, characterised by its ready hydrolysis by acids and rapid isomerisation to the normal ester by alkali. H. Wren.

Nitration of 2-, 3-, and 4-phenylpyridines. R. Forsyth and F. L. Pyman (J.C.S., 1926, 2912—2924; cf. Forsyth, Nimkar, and Pyman, A., 1926, 611).—By the action of acetyl chloride and acetic acid on sodium *p*-nitrobenzene*iso*diazotate dissolved in pyridine (Kühling, A., 1895, i, 290; 1896, i, 236) there is obtained a mixture of the three *p*-nitrophenylpyridines, separated by fractional crystallisation of the bases, hydrochlorides, and nitrates. 2-*p*-Nitrophenylpyridine, m. p. 130·5—131·5° (*hydrochloride*, m. p. 185—186°), is reduced by tin and hydrochloric acid to 2-p-*aminophenylpyridine*, m. p. 97—98° [*dihydrochloride* does not melt at 310°; *picrate*, m. p. 218—219° (decomp.)], which is converted by reduction of the diazo-compound into 2-p-*hydrazinophenylpyridine*, m. p. 117°. 2-Phenylpyridine [*nitrate*, m. p. 115—117°; picrate, m. p. 176—177°; chloroplatinate, m. p. 209° (decomp.)], obtained in poor yield, with much 2-p-*phenetylpyridine*, m. p. 74—75° (*picrate*, m. p. 168—170°), by the action of amyl nitrite and alcohol on 2-*p*-aminophenylpyridine dihydrochloride, and in good yield by oxidation of the hydrazine with cupric acetate, is volatile in steam. 3-p-*Nitrophenylpyridine*, m. p. 148—149° (*nitrate*, m. p. 198°), the corresponding *amine*, m. p. 102—104° (+H_2O) or 118—120° (anhyd.) [*dihydrochloride*, m. p. about 310° (decomp.); *picrate*, m. p. 185—188° (yellow form) or 219—220° (orange form)], and *hydrazine*, m. p. 156—157°, and 3-phenylpyridine (an oil, volatile in steam; picrate, m. p. 162—164°; *nitrate*, m. p. 78—80°), are described, and also 4-p-*nitrophenylpyridine*, m. p. 123—124° (*hydrochloride*, m. p. 255°); the corresponding *amine*, m. p. 232—234° [*dihydrochloride*, m. p. 312° (decomp.)], and *hydrazine*, m. p. 205—207° [*dihydrochloride*, m. p. 272° (decomp.)], and 4-phenylpyridine, m. p. 74°, b. p. 282—284°/762 mm. (*dinitrate*, m. p. 114—115°; *mononitrate*, m. p. 140°). 4-Phenylpyridine is also synthesised by the Hantzsch method from benzaldehyde, ethyl acetoacetate, and ammonia.

Nitration of the three phenylpyridines by addition of their nitrates to sulphuric acid gives mixtures of *o*-, *m*-, and *p*-nitrophenylpyridines, the yields being from 2-phenylpyridine, 6% *o*-, 34·9% *m*-, 42·3% *p*-; from 3-phenylpyridine, 64·3% *p*-; from 4-phenylpyridine, 12·7% *o*-, 28·5% *m*-, 38·0% *p*-. The following phenylpyridines are new: 2-m-*nitro*-, m. p. 73—74° (*nitrate*, m. p. 193°; *methosulphate*); 2-o-*nitro*-, m. p. 60—61°; 4-m-*nitro*-, m. p. 109—110° [*nitrate*, m. p. 222° (decomp.): *methosulphate*]: 4-o-*nitro*-, m. p. 51—52° (+H_2O) (*nitrate*, m. p. 178—179). All the above m. p. are corrected.

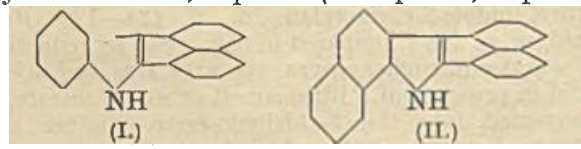
C. Hollins.

Indole group. I. H. Maurer and E. Moser (Z. physiol. Chem., 1926, **161**, 131—142).—The synthesis of β-3-indolinylpropionic acid (indole-3-propionic acid) from ethyl indole-2-carboxylate is described, and a synthesis of tryptophan is announced. Ethyl indole-2-carboxylate, m. p. 124—125° (free acid, m. p. 203°), prepared in 65% yield by reduction of ethyl *o*-nitrophenylpyruvate with zinc and acetic acid in presence of a little cobalt or nickel nitrate, is converted into the 3-aldehydo-ester (Fischer and Pistor, A., 1924, i, 86), which by condensation with ethyl malonate in presence of piperidine yields 3-*ethyl* 3-ββ-*dicarbethoxyvinylindole*-2-*carboxylate*, m. p. 141—142°. This is reduced by the Paal–Skita method to *ethyl* 3-ββ-*dicarbethoxyethylindole*-2-*carboxylate*, m. p. 77—78°, which is also prepared directly from ethyl indole-2-carboxylate and ethyl methoxymethylmalonate in alcoholic hydrochloric acid. The tricarboxylic *acid*, m. p. 198—199°, obtained by hydrolysis with aqueous-alcoholic alkali, is converted by heating at 200° into 2-carboxyindole-3-propionic acid (Kalb, Schweizer, and Schimpf, *ibid.*, 1926, 1151), m. p. 194° (ethyl ester, m. p. 94—85°), or at 215° into indole-3-propionic acid, m. p. 134°. Partial hydrolysis of the tricarboxylic ester gives 3-ββ-*dicarbethoxyethylindole*-2-*carboxylic acid*, m. p. 168—169°, which is decarboxylated at 190° to *ethyl* 3-*ethylindole*-ωω-*dicarboxylate*, m. p. 142° (free *acid*, m. p. 188—189°).

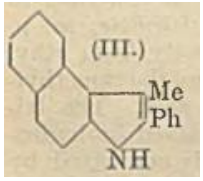
C. Hollins.

Indole condensation of phenylhydrazones. A. Korczyński, W. Brydowna, and L. Kierzek (Gazzetta, 1926, **56**, 903—914).—It has been shown (A., 1925, i, 973, 1097) that the condensation of phenylhydrazones to indoles is catalysed by small quantities of salts such as cupric or nickelous chloride. It is now found that the metallic ions are not catalysts: acetonephenylhydrazone heated in an alcoholic solution of cupric chloride did not condense, nor did acetophenonephenylhydrazone in benzene or chloroform with copper acetylacetone. Comparing methods of condensation, heating with a small quantity of nickel chloride is found to be more effective than the use of excess of zinc chloride, and even to succeed when hydrogen chloride in alcohol has no action. Indoles have been prepared from the phenylhydrazones of the following substances: Butaldehyde: hydrogen chloride in alcohol has no action, but nickel chloride gives 3-ethylindole, b. p. 146—151°/12 mm. (cf. Pictet and Duparc, A., 1888, 370). *n*-Octaldehyde: excess of zinc chloride gives a much smaller yield than a little nickel chloride of 3-n-*hexylindole*, a yellow liquid, b. p. 212—224°/14 mm. *n*-Nonaldehyde: nickel chloride yields 3-n-*heptylindole*, a red liquid, b. p. 179—182°/3 mm. [It is concluded from the character of these two substances that the solid "3-pentylindole" previously described (*loc. cit.*), is a polymeride]. Acetoveratrone: the *phenylhydrazone*, b. p. 120—130°/12 mm. (*hydro-*

chloride described), gives on distillation, alone or with nickel chloride, 2-*veratrylindole*, b. p. 210—215°/15 mm.; this substance gives a brown pine-shaving reaction. *p*-Phenoxyacetophenone: alcoholic hydrogen chloride has no effect, but nickel chloride gives 2-p-*phenoxyphenylindole*, yellow, m. p. 169°. Acenaphthenone: alcoholic hydrogen chloride gives 2 : 3-peri*naphthyleneindole* (I), orange, m. p. 200°, no pine-shaving reaction. Acenaphthenone α-naphthylhydrazone gives with hydrogen chloride or nickel chloride 2 : 3-peri*naphthylene*-α-*naphthindole* (II), yellowish-brown, m. p. 256° (black *picrate*, m. p. 260°).



Phenyl propyl ketone: nickel chloride gives 2-*phenyl*-3-*ethylindole*, yellow, m. p. 65° (*picryl* derivative hydrolysed by alcohol); this is anomalous in giving a reddish-violet pine-shaving reaction. *Dibenzyl ketone* α-*naphthylhydrazone*, m. p. 105°, treated with alcoholic hydrogen chloride gives 3-*phenyl*-2-*benzyl*-α-*naphthindole*, pale violet, m. p. 155—156°, no pine-shaving reaction. *Propiophenone* β-*naphthylhydrazone* gives 2-*phenyl*-1-*methyl*-β-*naphthindole* (III) with nickel chloride, yellow, m. p. 115°.



Attempts to prepare substituted indoles from phenylhydrazones substituted with negative groups in the nucleus of the phenylhydrazine have again failed.

When a phenylhydrazone condenses in two directions to give 2- and 2 : 3-substituted derivatives, the former can be determined by coupling with *p*-nitrobenzenediazonium chloride. This gives with 2-methyl- and 2-phenyl-indoles, respectively, 3-p-*nitrobenzeneazo*-2-*methylindole*, red, darkens at 210°, m. p. 219—220°, and 2-*phenyl*-3-p-*nitrobenzeneazoindole*, bluish-black, m. p. 280°, and when methyl ethyl ketone phenylhydrazone is heated with nickel chloride, the 2-ethylindole which forms 20% of the product is thus isolated as 3-p-*nitrobenzeneazo*-2-*ethylindole*, m. p. 60°.

E. W. WIGNALL.

Decomposition of β-3-indolylpropionic azide. R. H. F. MANSKE and R. ROBINSON (J.C.S., 1927, 240—242).—The *methyl* ester, m. p. 79—80°, of β-3-indolylpropionic acid (A., 1926, 1151) reacts with hydrazine hydrate to give β-3-*indolylpropionhydrazide*, m. p. 129—130°, converted by the action of nitrous acid into the corresponding azide. The latter is decomposed in boiling benzene solution, in presence of hydrogen chloride, giving 3-*keto*-3 : 4 : 5 : 6-*tetrahydro*-4-*carboline*, m. p. 173—174°. The constitution is established by distillation with zinc dust in a stream of hydrogen, when indole, accompanied by a small amount of norharman, is obtained. M. CLARK.

Relative stability of quinoline and indolinone rings. J. A. AESCHLIMANN (J.C.S., 1926, 2902—2912).—Gränacher and Mahal's "oxindole-3-acetic acid" (A., 1923, i, 713) is shown to be 2-ketotetrahydroquinolone-4-carboxylic acid; the quinoline ring is formed in preference to the indolinone ring.

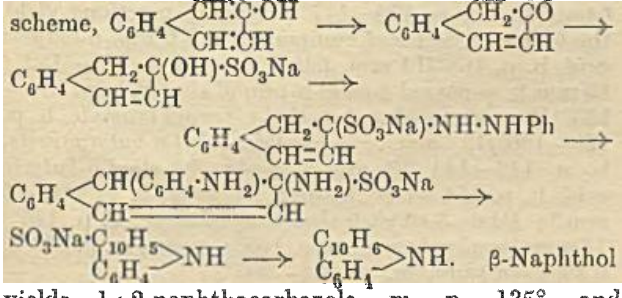
2-Quinolone-4-carboxylic acid, m. p. 343° (methyl ester, m. p. 241°; ethyl ester, m. p. 205°), prepared (*a*) from isatin and malonic acid in presence of sodium acetate and acetic acid (Borsche and Jacobs, A., 1914, i, 322), (*b*) from acetylisatin and sodium hydroxide (Camps, *ibid.*, 1900, i, 115, 310), (*c*) from acetylisatin or acetylisatic acid and sodium acetate crystals, is reduced by sodium amalgam, by zinc and acetic acid, by hydriodic acid and phosphorus, or by aluminium amalgam, to 2-ketotetrahydroquinoline-4-carboxylic acid, m. p. 220° (methyl ester, m. p. 164°; ethyl ester, m. p. 146°), also obtained in the monohydrated form (*o*-aminophenylsuccinic acid). 1-Methylisatin condenses with malonic acid in acetic acid to give 1-methyl-2-quinolone-4-carboxylic acid, m. p. 250° (*methyl* ester, m. p. 120°; ethyl ester, m. p. 134—135°), together with *o*-methylamino-β-carboxycinnamic acid, m. p. 163°. Reduction of the former yields 2-*keto*-1-*methyltetrahydroquinoline*-4-*carboxylic acid*, m. p. 171° (*methyl* ester, m. p. 80°), also obtained by methylation of ketotetrahydroquinolinecarboxylic acid. 1-*Phenylacetylisatin*, m. p. 188°, prepared from sodioisatin and phenylacetyl chloride, is converted by hot sodium hydroxide solution into 3-phenyl-2-quinolone-4-carboxylic acid, m. p. 295° (Gysae, A., 1894, i, 27; Hübner, *ibid.*, 1908, i, 288; Borsche and Jacobs, *loc. cit.*). 3-Thiol-2-quinolone-4-carboxylic acid (Granacher and Mahal's "oxindole-3-thiolacetic acid") condenses with *o*-phenylenediamine to give a *quinoxaline* derivative (+1MeOH or EtOH, not removable without decomp.). 2-Chlorocinchoninic acid, m. p. 196—200° (decomp.), and its ethyl ester, m. p. 63°, are obtained by the action of phosphorus pentachloride on 2-quinolone-4-carboxylic acid and ethyl ester, respectively. 6-Iodo-2-quinolone-4-carboxylic acid, unmelted at 300° (*methyl* ester, m. p. 261°; *ethyl* ester, m. p. 223°), is prepared by iodination and also from 5-iodoisatin and from 5-*iodo*-1-*acetylisatin*, m. p. 195°. Iodination of 2-ketotetrahydroquinoline-4-carboxylic acid at the ordinary temperature yields the 6(?)-*iodo*-derivative, m. p. 208° [*ethyl* ester, m. p. 169°; 5-*iodo*-2-*aminophenylsuccinic acid*, m. p. 180° (rapidly heated)]; the 6(?)-*bromo*-compound has m. p. 197°. 6-*Iodo*-3-*phenyl*-2-*quinolone*-4-*carboxylic acid*, obtained from 5-iodoisatin and phenylacetic acid, is reduced by sodium amalgam to 2-keto-3-phenyltetrahydroquinoline-4-carboxylic acid, m. p. 202° (Gysae's "dihydroisaphenic acid"). C. HOLLINS.

Synthesis of some substituted 3-methylquinolines. S. G. WILLIMOTT and I. A. SIMPSON (J.C.S., 1926, 2807—2811).—*o*-Nitroaldehydes are condensed with propaldehyde at the ordinary temperature in presence of pyridine to form an aldol which is reduced directly to the quinoline by zinc dust and acetic acid, or is converted by acetic anhydride into a cinnamaldehyde and thence by reduction with stannous chloride into the quinoline. *o*-Nitrobenzaldehyde gives in 64% yield 3-methylquinoline [chloroplatinate, m. p. 249°; *ethiodide*, m. p. 220° (decomp.); *dichromate*, m. p. 134°; *silver nitrate* double salt, m. p. 180°]. 6-Nitropiperonal gives an 18% yield of 6 : 7-*methylenedioxy*-3-*methylquinoline*, m. p. 74° (+2H_2O) or 105—106° (anhyd.) (*chloroplatinate*; *chloroaurate*; *picrate*, m. p. 259°; *methiodide*, m. p.

240°; *ethiodide*, m. p. 195°). From 6-nitroveratraldehyde are obtained β-*hydroxy*-β-6-*nitro*-3 : 4-*dimethoxyphenylisobutaldehyde*, 6-*nitro*-3 : 4-*dimethoxy*-α-*methylcinnamaldehyde*, m. p. 165—166°, and 6 : 7-*dimethoxy*-3-*methylquinoline*, m. p. 81—83° [*hydrochloride*, m. p. 220—223° (decomp.); *methiodide*, m. p. 245° (decomp.)]; and from 6-nitro-3-methoxybenzaldehyde, 6-*nitro*-3-*methoxy*-α-*methylcinnamaldehyde*, m. p. 115—116°, and 6-*methoxy*-3-*methylquinoline* [*hydrochloride*, m. p. 213—215°; *methiodide*, m. p. 280—283° (decomp.); *chloroplatinate*]. C. HOLLINS.

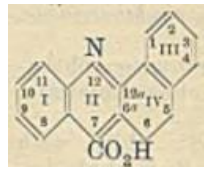
Condensation of 2-methylquinoline with *m*-nitrobenzaldehyde. T. W. J. TAYLOR and C. P. WOODHOUSE (J.C.S., 1926, 2971).—The sole product of the interaction of 2-methylquinoline and *m*-nitrobenzaldehyde at 100°, with or without zinc chloride, is 2-*m*-nitrostyrylquinoline, m. p. 156° [picrate, m. p. 261° (decomp.); dibromide, m. p. 170—171°]. No 2-β-hydroxy-β-*m*-nitrophenylethylquinoline is formed (cf. Wartanian, A., 1890, 329). C. HOLLINS.

Tautomerism of phenols. IX. Formation of naphthacarbazoles from naphthols. W. FUCHS and F. NISZEL (Ber., 1927, **60**, [*B*], 209—217; cf. this vol., 53).—The interaction of naphthols, phenylhydrazine, and sulphurous acid has been followed analytically by determination of excess of phenylhydrazine, ammonia, and aniline. Quantitative production of hydrazo-compounds involves the complete disappearance of phenylhydrazine, whereas subsequent formation of carbazoles requires the production of 1 mol. of ammonia for each mol. of phenylhydrazine used. Oxidation of the hydrazine produces equivalent amounts of ammonia and aniline. Smooth utilisation of phenylhydrazine with exclusive production of ammonia is observed with derivatives of β-naphthol, whereby naphthacarbazoles are formed and the intermediate *oo'*-diamines can be isolated. The course of the change is given in the



yields 1 : 2-naphthacarbazole, m. p. 135°, and 1-o'-*aminophenyl*-2-*naphthylamine*, m. p. 154°, which passes into the carbazole derivative when heated with sulphurous acid. 2 : 7-Dihydroxynaphthalene affords 7-*hydroxy*-1 : 2-*naphthacarbazole*, m. p. 178° (*benzoyl* derivative, m. p. 190°), and 7-*hydroxy*-1-o-*aminophenyl*-2-*naphthylamine* (*hydrochloride*); under modified conditions, 1 : 2 : 7 : 8-*naphthadicarbazole*, m. p. 338°, is produced. The formation of an additive *compound*, $C_{21}H_{21}O_4N_3S$, m. p. 193° (decomp.), from 2 : 7-dihydroxynaphthalene, sulphurous acid, and phenylhydrazine, is described. 2 : 7-Dihydroxynaphthalene methyl ether affords 7-*methoxy*-1 : 2-*naphthacarbazole*, m. p. 191° (also obtained from the hydroxy-compound and methyl sulphate), and 7-*methoxy*-1-o-*aminophenyl*-2-*naphthylamine*. 2 : 3-Dihydroxynaphthalene is converted by protracted treatment with phenylhydrazine hydrogen sulphite into a resin from which 3-*hydroxy*-1 : 2-*naphthacarbazole* and 3-*hydroxy*-1-o-*aminophenyl*-2-*naphthylamine*, m. p. 109—110° (*hydrochloride*), can be extracted with alkali hydroxide; the main product of the action appears to be 3-benzeneazo-1 : 2-naphthacarbazole. H. WREN.

Tetrophan. J. VON BRAUN (Annalen, 1926, **451**, 1—54; cf. A., 1923, i, 143, 947).—The physiological properties of a number of derivatives of tetrophan (annexed formula) have been examined with a view to determine the relationship between the structures and physiological actions of tetrophan and atophan (2-phenylquinoline-4-carboxylic acid). The presence of the carboxyl group appears essential, its elimination, substitution by other groups, or movement to one of the side rings causing the tetrophanic action to be lost. Removal of one of the rings I or III destroys the action, whilst the action is weakened by fusion of either another benzene ring in the 2 : 3-position or a saturated hydrocarbon ring in the 2 : 3- or 9 : 10-positions. Substitution in rings I, III, and IV does not affect the qualitative nature of the action, but the nature and position of the substituent have a quantitative effect. Rings II and III must be joined by a ring, IV, the length or degree of saturation of the carbon bridge having no qualitative although considerable quantitative effect on the action.



[With A. ROHMER.]—When 5 : 6-dihydro-α-naphthacridine is treated with nitric acid in acetic acid solution, it yields a *nitrate*, m. p. 158°, which is converted by sulphuric acid into a mixture of 8 : 10(?)-*dinitro*-5 : 6-*dihydro*-α-*naphthacridine*, m. p. 237°, and 8-*nitro*-5 : 6-*dihydro*-α-*naphthacridine*, m. p. 142° (*hydrochloride*, m. p. 220°; *nitrate*, m. p. 163°; *picrate*, m. p. 226°), which is oxidised by chromic acid in acetic acid solution to 8-*nitro*-5 : 6-*diketo*-α-*naphthacridine*, m. p. 250—270° (decomp.), and is readily hydrogenated to 8-*amino*-5 : 6-*dihydro*-α-*naphthacridine*, yellow needles, m. p. 94—95° [*dihydrochloride*, m. p. 280°; *dipicrate*, m. p. 202°; *methiodide* of *dimethyl* derivative, m. p. 176°; *acetyl* derivative, m. p. 197° (*hydrochloride*, m. p. 281°)]. The amino-compound is reduced by tin and hydrochloric acid to 8-*amino*-5 : 6 : 6*a* : 7 : 12 : 12*a*-*hexahydro*-α-*naphthacridine*, m. p. 103° (*diacetyl* derivative, m. p. 208°), and by Sandmeyer's reaction yields 8-*cyano*-5 : 6-*dihydro*-α-*naphthacridine*, m. p. 167°, which with alkalis yields 5 : 6-*dihydro*-α-*naphthacridine*-8-*carboxylic acid*, m. p. 237°.

[With H. JUNGMANN.]—Phosphorus pentachloride reacts with sodium 5 : 6-dihydro-α-naphthacridine-7-carboxylate, and treatment of the product with aqueous ammonia yields 5 : 6-*dihydro*-α-*naphthacridine*-7-*carboxylamide*, m. p. 220—222°, which by the Hofmann reaction in methyl-alcoholic solution gives the *methylurethane* derivative, m. p. 232—234°; this with hydrochloric acid yields 7-*amino*-5 : 6-*dihydro*-α-*naphthacridine*, m. p. 94—98° (*hydrochloride* described).

The silver salt of tetrophan reacts with acetobromoglucose in toluene solution, yielding the *acetylglucoside*, $C_{26}H_{31}O_{11}N$, m. p. 156°, $[\alpha]_D^{22}$ +21·5° in pyridine, which with methyl-alcoholic ammonia solution gives *tetrophanglucoside*, m. p. 78—80°. The physiological action of this substance is equal to that of tetrophan, probably due to the ready hydrolysis of the glucoside.

ω-Phthalimido-*o*-aminoacetophenone condenses with 1-ketotetrahydronaphthalene, yielding *7-phthalimidomethyl-5 : 6-dihydro-α-naphthacridine*, m. p. 300°, which with hydrochloric acid gives *7-aminomethyl-5 : 6-dihydro-α-naphthacridine*, m. p. 113° (*dihydrochloride*, m. p. 188—190°; *acetyl* derivative, m. p. 183°). Nitrous acid converts the amino-compound into *7-hydroxymethyl-5 : 6-dihydro-α-naphthacridine*, m. p. 140° (*hydrochloride*, m. p. 190°).

[With F. Zobel.]—*ar*-β-Aminotetrahydronaphthalene reacts with hydroxylamine and chloral hydrate, yielding the iso*nitroso*-compound, $C_{10}H_{11}$·NH·CO·CH:NOH, m. p. 166°, which with sulphuric acid gives a mixture of 4 : 5 : 6 : 7-*tetrahydro*-ang-β-*naphthisatin*, m. p. 189—190° (*phenylhydrazone*, m. p. 221°; *bromo*-derivative, m. p. 223°; *quinoxaline* derivative described), and 5 : 6 : 7 : 8-*tetrahydro*-lin-β-*naphthisatin*, m. p. 195° (*phenylhydrazone*, m. p. 255°; *bromo*-derivative, m. p. 236°; *quinoxaline* derivative described). The *lin*-β-compound yields the following substances: with hydrogen peroxide, *2-amino-5 : 6 : 7 : 8-tetrahydronaphthalene-3-carboxylic acid*, m. p. 183°, which by elimination of the amino-group gives 5 : 6 : 7 : 8-*tetrahydro*-β-*naphthoic acid*, m. p. 153°; with *cyclo*hexanone, 1 : 2 : 3 : 4 : 7 : 8 : 9 : 10-*octahydrobenzacridine-5-carboxylic acid*, which on distillation yields 1 : 2 : 3 : 4 : 7 : 8 : 9 : 10-*octahydrobenzacridine*, m. p. 146° (*picrate*, m. p. 208°; *methiodide*, m. p. 231°), and this, when distilled over lead oxide, gives *benzacridine*, m. p. 223° [*chloroplatinate*, m. p. 242° (decomp.)]; with 1-ketotetrahydronaphthalene, 9 : 10-*tetramethylenetetrophan*, m. p. 308°. *ar*-Tetrahydro-α-naphthylamine reacts with hydroxylamine and chloral hydrate, yielding an iso*nitroso*-compound, m. p. 179°, which with sulphuric acid gives 6 : 7 : 8 : 9-*tetrahydro*-α-*naphthisatin*, m. p. 228° (*phenylimide*, m. p. 245°; *oxime*, m. p. above 300°; 6 : 7 : 8 : 9-*tetrahydro*-α-*naphthoxindole*, m. p. 161°). The naphthisatin condenses with acetophenone, yielding tetramethyleneatophan (cf. A., 1923, i, 144) (*methyl* ester, m. p. 66°).

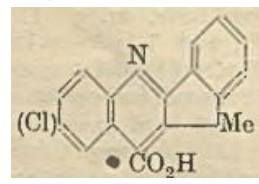
[With (Frl.) L. Brauns.]—Methylene di-isatin, during the preparation of which *methylene disalicylformic acid* and *di-isatylbenzophenone*, $CO\left(C_6H_3<\begin{matrix}NH\\CO-\end{matrix}>CO\right)$, both melting above 360°, were isolated, condenses with 1-ketotetrahydronaphthalene, yielding *ditetrophanylmethane*, $CH_2(C_{18}H_{13}O_2N)_2$, m. p. 305—308° (decomp.). As this substance contains two tetrophan complexes, it should be very active, but the insolubility of its salts made it difficult to test its physiological action.

[With O. Bayer.]—1-*Ketotetrahydroanthracene*, m. p. 95—96° [*oxime*, m. p. 170°; *semicarbazone*, m. p. 250° (decomp.); *phenylhydrazone*, m. p. 116°; *picrate*, m. p. 118°], condenses with isatin, yielding 2 : 3-*benztetrophan*, m. p. 300° (decomp.), which gives 2 : 3-*benz*-5 : 6-*dihydro*-α-*naphthacridine*, m. p. 160°.

[With H. Jungmann.]—7-*Nitro*-1-*ketotetrahydronaphthalene*, m. p. 72°, yields the following series of compounds: 7-*amino*-1-*ketotetrahydronaphthalene*, m. p. 136° (*hydrochloride*, m. p. 181°; *picrate*, m. p. 165°; *acetyl* derivative, m. p. 166°; *o-hydroxybenzylidene* derivative, m. p. 139°); 7-*dimethylamino*-1-*ketotetrahydronaphthalene* (*picrate*, m. p. 153°; *methiodide*, m. p. 202—203°); 7-*hydroxyethylamino*-1-*ketotetrahydronaphthalene* (*picrate*, m. p. 126°); 7-*hydroxy*-1-*ketotetrahydronaphthalene*, m. p. 159° (*acetyl* derivative, m. p. 82°); 7-*chloro*-1-*ketotetrahydronaphthalene*, m. p. 94° (*semicarbazone*, m. p. 226°). These ketones when condensed with isatin yield the following substances: 2-*chlorotetrophan*, m. p. 207—208° (decomp.); 2-*chloro*-5 : 6-*dihydro*-α-*naphthacridine*, m. p. 124°; 2-*aminotetrophan*, m. p. 297° (*dihydrochloride*, yellow needles; *acetyl* derivative, m. p. 315°); 2-*dimethylaminotetrophan*, m. p. 278°; 2-*hydroxyethylaminotetrophan*, m. p. 295°; 2-*hydroxytetrophan*, m. p. above 300° (*acetyl* derivative, m. p. 102°); 2-*methoxytetrophan*, m. p. 123°.

[With A. Stuckenschmidt.]—Acetophenone and ethyl α-bromopropionate react with zinc in benzene solution, yielding *ethyl αβ-dimethylcinnamate*, b. p. 133°/13 mm. (*αβ-dimethylcinnamic acid*, m. p. 101°), which is hydrogenated to *ethyl* β-*phenyl*-α-*methyl*-n-*butyrate*, b. p. 133°/13 mm. Reduction of this ester with alcohol and sodium yields *γ-phenyl*-β-*methyl*-n-*butyl alcohol*, b. p. 132—133°/13 mm., which with hydrobromic acid gives *γ-phenyl*-β-*methyl*-n-*butyl bromide*, b. p. 132—133°/13 mm. Potassium cyanide converts the bromide into *γ-phenyl*-β-*methyl*-n-*valeronitrile*, b. p. 148—149°/15 mm., which yields *γ-phenyl*-β-*methyl*-n-*valeric acid*, b. p. 175°/13 mm., on hydrolysis. By the Friedel-Crafts reaction, the *acid chloride*, b. p. 134°/13 mm., yields 1-*keto*-3 : 4-*dimethyltetrahydronaphthalene*, b. p. 142—143°/13 mm., n^{15} 1·5524, d_4^{15} 1·0513 (*semicarbazone*, m. p. 177°), which condenses with isatin to give 5 : 6-*dimethyltetrophan*, m. p. 175—177°. Similar reactions yield the following series of compounds: α-*benzyl*-n-*butyric acid*, b. p. 168°/14 mm. (*ethyl* ester, b. p. 131—132°/13 mm.); *γ-phenyl*-β-*ethyl*-n-*propyl alcohol*, b. p. 134—135°/13 mm.; *γ-phenyl*-β-*ethyl*-n-*propyl bromide*, b. p. 125—126°/13 mm.; *γ-phenyl*-β-*ethyl*-n-*butyronitrile*, b. p. 142—143°/13 mm.; *γ-phenyl*-β-*ethyl*-n-*butyric acid*, b. p. 174—175°/13 mm. (*chloride*, b. p. 146°/13 mm.); 1-*keto*-3-*ethyltetrahydronaphthalene*, b. p. 145°/13 mm. (*semicarbazone*, m. p. 165°; *oxime*, m. p. 188°); 6-*ethyltetrophan*, m. p. 204—205°.

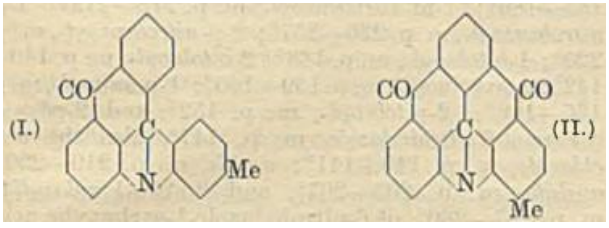
[With J. Reutter.]—Condensation of isatin with the appropriate ketones yields 4 : 5-*ethylenetetrophan*, m. p. 300° (decomp.), and 4 : 5-*trimethylenetetrophan*, m. p. 262—264° (decomp.).



α-Methylhydrindone yields, with isatin, iso*tetrophan* (annexed formula), m. p. 310° (decomp.), and with 5-chloroisatin, *chloroisotetrophan*, m. p. 292° (decomp.). The preparation of 2-*phenyl*-3-*γ-phenylpropylcinchoninic acid*, m. p. 244—246° (decomp.), is described. R. W. West.

Triphenylmethane compounds with linked benzene nuclei. III. Derivatives of diketo-5-

phenylacridine. R. WEISS and W. KNAPP (Monatsh., 1926, **47**, 485—491).—By the condensation of 1-chloroanthraquinone with *m*-toluidine, *m*-5-xylidine, *p*-xylidine, and *m*-aminobenzoic acid are obtained, respectively, 1-*anthraquinonyl*-m-*toluidine*, m. p. 154°; 1-*anthraquinonyl*-m-5-*xylidine*, m. p. 210°; 1-*anthraquinonyl*-p-*xylidine*, m. p. 210°; and 1-*anthraquinonyl*-m-*aminobenzoic acid*, m. p. 282—285°. On heating the first three with 75% sulphuric acid at 160°, dehydration occurs, yielding, respectively, 2-*methylketomethylene*-ɔ-*phenylacridine* (I) (3-*methylcœramidonine*), m. p. 206°, the corresponding 2 : 4-*dimethyl*-, m. p. 180°, and 1 : 4-*dimethyl*-compounds, m. p. 160°, whilst the substituted benzoic acid is unattacked.



1 : 4-Dimethylcœramidonine, on heating with yellow mercuric oxide at 180°, yields 1-*methyldiketomethylene*-5-*phenylacridine* (II), amorphous. The 1 : 3-dimethylcœramidonine, similarly treated, yields the substance $(C_{22}H_{10}O_2N)_2O$, 1 mol. of water being eliminated from 2 mols. after oxidation. The monomethyl compound is unattacked. J. W. BAKER.

***iso*Dialuric acid.** H. BILTZ and H. PAETZOLD [with P. NACHTWEY] (Annalen, 1927, **452**, 67—89; cf. A., 1923, i, 1233).—*iso*Dialuric acid can be regarded as $\frac{NH\cdot CO-C(OH)_2}{CO\cdot NH\cdot CH\cdot OH},H_2O$(I) $\frac{NH\cdot CO-CO}{CO\cdot NH\cdot CH\cdot OH},2H_2O$ (II) By treatment of *iso*dialuric acid (monohydrate, m. p. 133°, decomp., resolidifying at 180° and decomposing further at 250°; anhydrous, decomposes about 170°) with methyl alcohol and hydrochloric acid, a methyl ether, 5 : 6-*dihydroxy*-5-*methoxy*-5 : 6-*dihydrouracil*, $C_4H_5O_4N_2\cdot OMe,H_2O$, decomp. slowly at 180°, vigorously at 215°, and with ethyl alcohol an ethyl ether, the -5-*ethoxy*-analogue, decomp. 210°, anhydrous decomp. 160°, resolidifying to the same product as is given by an *iso*dialuric acid melt, have been obtained. The ethyl ether is hydrolysed by water, and with hydroxylamine hydrochloride gives slowly *iso*dialuric acid oxime, indicating that ether-formation occurs on one of the 5-hydroxyl groups of the structure (I); it reacts with diazomethane to give a syrup. *iso*Barbituric acid treated in methyl alcohol with chlorine gives a dimethyl ether of *iso*dialuric acid, 6-(or 5-)*hydroxy*-5 : 5-(or 5 : 6-)*dimethoxy*-5 : 6-*dihydrouracil* (III), decomp. 215° (corr.). This is more probably the 5 : 5-dimethoxy-derivative, since *iso*dialuric acid oxime is easily obtained from it, and since it is stable to water. Uric acid and *iso*barbituric acid can be obtained from (III), which is converted by diazomethane into a syrupy substance, the 1 : 3-*dimethyl* derivative. In ethyl alcohol, the corresponding diethyl ether, 6-(or 5-)*hydroxy*-5 : 5-(or 5 : 6-)*diethoxy*-5 : 6-*dihydrouracil* (IV), decomp. about 210°, is obtained, from which uric acid, *iso*barbituric acid, and, by diazomethane, the 1 : 3-*dimethyl* derivative, m. p. 115° (corr.), which with carbamide gives 1 : 3-dimethyluric acid, are derived. The third hydroxyl group cannot by any means be methylated.

From 5-methoxy-1 : 3-dimethyluracil, now prepared by the action of methyl sulphate on *iso*barbituric acid (new m. p. 198°, corr.), are obtained 6-*chloro*- (V) and 6-*bromo*-5 : 5-*dimethoxy*-1 : 3-*dimethyl*-5 : 6-*dihydrouracil* (VI), m. p. 86° (corr.) and 125° (corr.), respectively; attempts to replace halogen in these by hydroxyl have failed, silver oxide giving the original methoxydimethyluracil. The latter when treated with concentrated nitric acid gives 5-*hydroxy*-5-*methoxy*-1 : 3-*dimethyl*-5 : 6-*dihydrouracyl* 6-*nitrite*, decomp. 145° (corr.), which is converted by carbamide into 1 : 3-dimethyluric acid, and thus belongs to the *iso*dialuric acid series.

When treated with sodium and methyl alcohol, (V) and (VI) give 5 : 5 : 6-*trihydroxy*-1 : 3-*dimethyl*-5 : 6-*dihydrouracil*, m. p. 132° (corr.), reduced by hydriodic acid to 1 : 3-*dimethyliso barbituric acid*, and converted by carbamide into 1 : 3-dimethyluric acid.

*iso*Barbituric acid fails to react with phenylhydrazine, semicarbazide, or hydroxylamine (cf. Behrend and Roosen, A., 1888, 581; Annalen, 1889, **251**, 240). *iso*Dialuric acid gives the following derivatives: an oxime anhydride, m. p. 295° (corr.) after turning brown at 175° (cf. Behrend and Roosen, *loc. cit.*; the substance is shown not to be keto*iso*barbituric acid oxime monohydrate, which might be expected); *phenylhydrazone*, sinters at 240°, decomp. 260° (corr.), and p-*nitrophenylhydrazone*, decomp. 278°, both also obtainable from (III); *semicarbazone*, which darkens from 180°, but does not melt or decompose below 290°; from (V), 1 : 3-*dimethyliso dialuric acid phenylhydrazone*, decomp. 148° (corr.).

Acetyl chloride reacts with (III) or with *iso*dialuric acid to give 6-*chloro*-ɔ-*acetoxyuracil* (VII), decomp. 260° (corr.), hydrolysed by alkali to *iso*barbituric acid, by acid to 6-*chloro*-5-*hydroxyuracil* (VIII), which reddens from 270° and decomposes at 300°. Bromine converts (VII) and (VIII) into alloxan; (VII) is reduced by zinc and acetic acid to *iso*barbituric acid, and converted by chlorine and methyl alcohol into 6-*chloro*-5-*hydroxy*-5 : 6-*dimethoxy*-5 : 6-*dihydrouracil*, which turns yellow from 140°, decomposes from 160° to 260°, and is hydrolysed by water to alloxan.

*iso*Barbituric acid, when treated with acetic acid, acetic anhydride, and chlorine, gives *diacetyliso dialuric acid*, decomposed at 118° or by water, converted by carbamide into uric acid; with acetic anhydride alone, *diacetyliso barbituric acid*, m. p. 161° (corr.), which is hydrolysed by water to the monoacetyl derivative. The latter is oxidised by chlorine to *iso*dialuric acid, or in presence of methyl alcohol to the 5 : 5-dimethyl ether. The diacetyl compound is unaffected by chlorine in acetic acid.

From these results, it is concluded that *iso*dialuric acid has the formula (I), and, since 5 : 6-methylenedioxy- and 5 : 6-dimethoxy-uracil do not condense with carbamide, that in the Behrend synthesis of uric acid, the 5- and 6-hydroxyl groups of *iso*dialuric acid are first eliminated with hydrogen atoms of carbamide to give a compound which then loses water to give the double linking of uric acid.

E. W. WIGNALL.

Catalytic hydrogenation of azines. K. A. TAIPALE (J. Russ. Phys. Chem. Soc., 1926, **57**, 487—548).—A fuller description of work already published (cf. A., 1923, i, 547). E. ROTHSTEIN.

Anilopyrine and antipyrine. P. K. DUTT (Proc. Leeds Phil. Lit. Soc., 1926, **1**, 113—115).—Theoretical. The relative merits of the Michaelis and the Stolz formula for anilopyrine are discussed. The behaviour of anilopyrine alkohydroxides indicates a further resemblance between anilopyrine and antipyrine, since the quaternary hydroxides, in the absence of water, decompose spontaneously, giving anilopyrine methohydroxide, antipyrine, and methylaniline. This result proves that, in the successive alkylation of 5-anilino-1-phenylpyrazoles, the first alkyl group attaches itself to the nitrogen in position 2 and the second one to the amino-nitrogen. The nature of the groups attached to the nitrogen atom appears greatly to affect the relative yields of the products of decomposition. M. S. BURR.

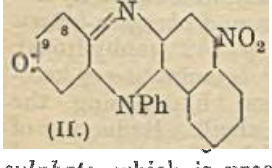
Opening of the glyoxaline ring. B. ODDO and Q. MINGOIA (Gazzetta, 1926, **56**, 958—960).—The long-accepted observation of Bamberger and Berlé (A., 1893, i, 437) that Schotten–Baumann benzoylation opens the ring of glyoxaline to give formic acid and dibenzamidoethylene is incorrect. The actual product from either glyoxaline or magnesyl-glyoxaline is a benzoylglyoxaline; any excess of benzoyl chloride appears as benzoic acid, and very little formic acid is detected. Traces of a *by-product*, m. p. 246—247°, are formed. E. W. WIGNALL.

Wandering of acyl groups in indazole derivatives. K. VON AUWERS and W. DEMUTH (Annalen, 1927, **451**, 282—307).—A large number of new acylindazoles have been prepared in order to determine the factors which condition the mobility of the acyl groups in these compounds. The new facts are in agreement with previous conclusions (cf. A., 1920, i, 638; 1924, i, 878, 1347; 1925, i, 1460; 1926, 306, 529). The mobility of the acyl radical in 2-acylindazoles is affected by the following factors: (*a*) the nature of the acyl radical; the mobility of any given group does not, however, run parallel with its ease of removal by hydrolysis, or with the strength of the corresponding acid; (*b*) the position of other substituents, their nature being comparatively unimportant; for instance, 2-acyl derivatives of 3-substituted indazoles can rarely be prepared, whilst those with a 5- or 7-substituent are unusually stable; the stability of the last-named may be due to the steric effect of the 7-substituent; (*c*) the relative basicity of the 1- and 2-nitrogen atoms, and (*d*) the tendency of the indazole nucleus to pass into a more saturated form, thus: $C_6H_4\langle^{CH}_{N}\rangle NAc \longrightarrow C_6H_4\langle^{CH}_{NA}\rangle N$. Indazoles having a nitro-group in the benzene nucleus are unexpectedly difficult to halogenate; in absence of a carrier, only the 3-position is attacked. 4-*Chloroindazole*, m. p. 156° (1-*acetyl*-, m. p. 66·5—67·5°; 2-*acetyl*-, m. p. 93—94°; 1-o-*nitrobenzoyl*-, m. p. 174°; 2-o-*nitrobenzoyl*-, m. p. 192—194°; 1-p-*nitrobenzoyl*-, m. p. 181—182°, and 2-p-*nitrobenzoyl*-, m. p. 154°, derivatives); 3-*chloro*-4-*nitroindazole*, m. p. 215°; 3-*bromo*-4-*nitroindazole*, m. p. 220—221°; 3-*bromo*-5-*nitroindazole*, m. p. 223—224°; 3-*chloro*-5-*nitroindazole*, m. p. 209—215°; 3-*chloro*-6-*nitroindazole*, m. p. 200°; 3-*bromo*-6-*nitroindazole*, m. p. 228—230° (1-*acetyl* derivative, m. p. 168°), and 3-*iodo*-6-*nitroindazole*, m. p. 259—261°, are described. The stability of the 2-acyl-6-nitroindazoles is, in general, closely similar to, but slightly less than, that of the corresponding indazole derivatives. Halogenated acetic acids and *m*-substituted benzoic acids again failed to give 2-acyl derivatives. The following are mentioned: 1-*chloroacetyl*-, m. p. 149°; 1-*dichloroacetyl*-, m. p. 137—138°; 1-*trichloroacetyl*-, m. p. 101—102°; 1-o-*nitrobenzoyl*-, m. p. 206—207°; 2-o-*nitrobenzoyl*-, m. p. 185—186°; 1-m-*nitrobenzoyl*-, m. p. 212—213°; 1-p-*nitrobenzoyl*-, m. p. 236—237°; 2-p-*nitrobenzoyl*-, m. p. 220°; 1-o-*toluoyl*-, m. p. 188°; 2-o-*toluoyl*-, m. p. 140—142°; 1-m-*toluoyl*-, m. p. 159—160°; 1-p-*toluoyl*-, m. p. 165—166°; 2-p-*toluoyl*-, m. p. 152°, and 2-*phenylcarbamyl*-6-*nitroindazole*, m. p. 147°, also the *acid chloride*, m. p. 140—141°; *amide*, m. p. 219—220°; *anilide*, m. p. 205—207°, and 6-*nitro*-1-*indazylide*, m. p. 257—260°, of 6-nitroindazole-1-carboxylic acid. 3-*Bromo*-7-*nitroindazole* has m. p. 177—178°. 7-*Nitro*-1-*acetylindazole*, m. p. 147°, has now been obtained by treating the 7-nitroacetylindazole of m. p. 135—136° (*ibid.*, 1920, i, 642) with bromine; the latter is therefore an unexpectedly stable 2-acetyl derivative. The 1-acetyl and also the 1-*benzoyl* derivative, m. p. 132—133°, unlike most 1-acylindazoles, are hydrolysed by hydrogen chloride in indifferent solvents. 2-*Benzoyl*-, m. p. 185°; 1-o-*nitrobenzoyl*-, m. p. 173—175°; 2-o-*nitrobenzoyl*-, m. p. 111—113°; 1-p-*nitrobenzoyl*-, m. p. 155—157°, and 2-p-*nitrobenzoyl*-7-*nitroindazole*, m. p. 205°, are described. Methylation of 6-nitroindazole with methyl sulphate in alkaline solution yields a mixture of 6-nitro-1- and 6-nitro-2-methylindazole, not the -2-derivative only, as previously stated. *Methyl* 6-*nitroindazole*-1-*carboxylate*, m. p. 169°, is converted by boiling absolute alcohol into the corresponding *ethyl* ester, m. p. 147—148°, from which N-*ethyl*-6-*nitroindazole*, m. p. 61—62°, is prepared by heating at 210°. An isomeric N-*ethyl*-6-*nitroindazole*, m. p. 91—93°, is formed when the ethyl ester is heated with ethyl iodide in a sealed tube. 6-Aminoindazole, conveniently prepared by reducing 6-nitroindazole with sodium sulphide in alkaline solution, gave the following derivatives: 6-*benzylideneaminoindazole*, m. p. 79—80°; 6-o-*hydroxybenzylideneaminoindazole*, m. p. 200—201° (1-*acetyl* derivative, m. p. 144—146°); 6-p-*anisylideneaminoindazole*, m. p. 155—156°; 6-p-*hydroxybenzeneazoindazole*, red, m. p. 253° (1-*acetyl* derivative, m. p. 228—230°); 6-*amino*-1-*methylindazole*, m. p. 172—173°; 6-*hydroxy*-1-*methylindazole*, m. p. 215—216°, and 6-*hydroxy*-2-*methylindazole*, m. p. 167—169°. H. E. F. NOTTON.

Synthesis of phenazine and some derivatives. F. KEHRMANN and C. MERMOD (Helv. Chim. Acta, 1927, **10**, 62—66).—The synthesis of the simpler phenazines from *o*-diamines and *o*-quinones is possible only in the absence of water. *o*-Benzoquinone and *o*-phenylenediamine react in dry ether in presence of anhydrous sodium sulphate to give 35% of phenazine. 2-Methylphenazine (50%) is obtained by the same

method from *o*-phenylenediamine and 4-methyl-*o*-benzoquinone and 88% of naphthaphenazine from *o*-phenylenediamine and 1 : 2-naphthaquinone. When 4-nitro-*m*-phenylenediamine is boiled with glacial acetic acid and acetic anhydride, *4-nitro-3-amino-acetanilide*, m. p. 178°, is formed. It is reduced by iron powder and water to 3 : 4-*diaminoacetanilide*. 4-Acetamido-*o*-benzoquinone (A., 1925, i, 560) and *o*-phenylenediamine yield, in absence of water, 68% of 2-acetamidophenazine (Fischer and Hepp, *ibid.*, 1889, 499). 2-Hydroxyphenazine could not be prepared by diazotising and boiling a solution of 2-aminophenazine, but it is formed when this substance is heated at 180° with 15% hydrochloric acid. 1 : 2 : 4-Triaminobenzene and 1 : 2-naphthaquinone condense in presence of acetic acid to 3-aminonaphthaphenazine (Nietzki and Otto, *ibid.*, 1888, 843). *3-Hydroxynaphthaphenazine*, decomp. 290°, is prepared by heating this with 25% hydrochloric acid in a sealed tube. H. E. F. NOTTON.

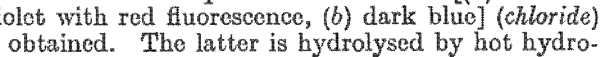
New azine colouring matters from naphthalene. F. KEHRMANN and B. PERROT (Helv. Chim. Acta, 1927, **10**, 53—61).—Phenyl-2 : 4-diamino-α-naphthylamine (Ullmann and Bruck, A., 1909, i, 21) condenses with benzil to give *6-amino*-1 : 2 : 3-*triphenyl*-7 : 8-*benzoquinoxalinium chloride* [colour of alcoholic solution (*a*) Ponceau-red, colour with concentrated sulphuric acid (*b*) reddish-violet], but not with other α-diketones. The corresponding *perchlorate* and *chloroplatinate*, and the *chloride* [(*a*) lemon-yellow, (*b*) reddish-violet] and *perchlorate* of its *acetyl* derivative are described. Phenyl-2 : 4-dinitro-α-naphthylamine is reduced by alcoholic ammonium sulphide to *phenyl-4-nitro-2-amino-α-naphthylamine* (I), m. p. 160—161°. This condenses with 4-acetamido-1 : 2-naphthaquinone, and on addition of nitric acid, *2-nitro-7-acetamido-5-phenyl*-3 : 4-8 : 9-*dibenzo-5-phenazonium nitrate* [(*a*) reddish-violet with red fluorescence, (*b*) dark blue] (*chloride*) is obtained. The latter is hydrolysed by hot hydrochloric acid to the corresponding 7-*amino*-derivative [(*a*) violet-red, (*b*) bluish-green], and reduced by stannous chloride to *2-amino-7-acetamido-5-phenyl*-3 : 4-8 : 9-*dibenzo-5-phenazonium chloride* [(*a*) greenish-blue, (*b*) dark blue] (*chloroplatinate*), which gives on acetylation the corresponding *diacetamido*-derivative [(*a*) reddish-violet, (*b*) dark blue], and, on hydrolysis, the 2 : 7-*diamino*-derivative [(*a*) greenish-blue, (*b*) bluish-green]. When 2-hydroxy-1 : 4-naphthaquinone and (I) are heated with hydrochloric acid in alcoholic solution, the 8 : 9-*benzo*-derivative of the *nitronaphthindone* (II) [(*a*) dark red, (*b*) bluish-green], which is reduced by stannous chloride to a violet *amino*-derivative, remains dissolved, whilst 2-(4-*nitro*-1-*anilino*-2-*naphthylamino*)-1 : 4-*naphthaquinone* [(*a*) brownish-orange] and 4-(4-*nitro*-1-*anilino*-2-*naphthylimino*)-2-*hydroxy*-1 : 4-*naphthaquinone* [(*a*) yellow, (*b*) bluish-violet] crystallise out. The solution of the second substance in concentrated sulphuric acid is red, immediately changing to blue owing to the formation of *8-nitro-2-hydroxy-9-phenyl*-3 : 4-6 : 7-*dibenzophenazonium sulphate*, which is precipitated when the solution is diluted. The third product is recovered unchanged from its sulphuric acid solution. 2 : 5-Dihydroxy-*p*-benzoquinone and (I) afford the *8-hydroxy*-derivative of (II) [(*a*) yellowish-red, (*b*) reddish-violet], which gives an *acetyl* derivative [(*a*) red, (*b*) red]; (I) also condenses with phenanthraquinone, but not with benzil. H. E. F. NOTTON.



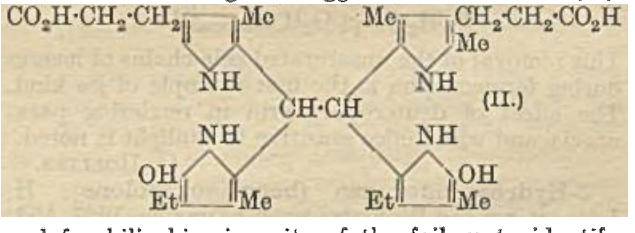
(II.)

Action of hydrazine hydrate on uridine. P. A. LEVENE and L. W. BASS (J. Biol. Chem., 1926, **71**, 167—172).—The action of hydrazine hydrate on uridine yields pyrazolone (isolated as dixanthyl derivative), but no free carbamide; in view of the results of Fosse and others (A., 1924, i, 428), this affords additional evidence in favour of the authors' previous conclusion (*ibid.*, 1926, 1260) that, in uridine, the ribose is attached to the 3-position of the pyrimidine nucleus. Carbamide glucoside yields a *xanthyl* derivative, m. p. 216—219° (decomp.); after heating the glucoside with hydrazine for 1 hr. at 65°, no unchanged glucoside and no free carbamide were detected. C. R. HARINGTON.

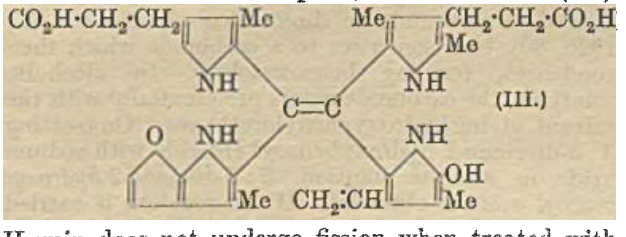
Bile pigment. X. (Porphyrin syntheses V.) Conversion of bile pigment and bilirubic acid into mesoporphyrin. Hæmopyrrole from mesobilirubinogen. H. FISCHER and F. LINDNER (Z. physiol. Chem., 1926, **161**, 1—16).—When bilirubic acid (I) is heated at 145° for 1·5 hrs. with hydrobromic–acetic acid, the hydroxyl is replaced by bromine and condensation to mesoporphyrin occurs; bilirubin itself requires 6 hrs. at 180° for the same change; mesobilirubinogen, 1·5 hrs. at 165°. In each case there is also formed a porphyrin or porphyrins with the same spectra, but giving a more soluble sodium salt; the corresponding methyl ester melts indefinitely at about 160° (mesobilirubinogen experiment).


(I.)

The Küster formula for hæmin involving neighbouring ethyl groups is rendered untenable by this synthesis. For mesobilirubinogen is suggested the structure (II),

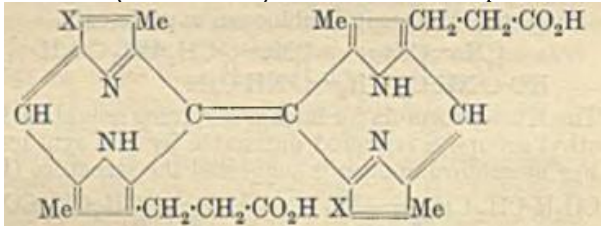

(II.)

and for bilirubin, in spite of the failure to identify opsopyrrolecarboxylic acid (see A., 1926, 1256) in the bilirubic acid mother-liquors, the structure (III).


(III.)

Hæmin does not undergo fission when treated with hydrobromic–acetic acid at 145° or 180°, but mesoporphyrin (methyl ester, m. p. 208—209°) is formed quantitatively at 180°. C. HOLLINS.

Natural porphyrins. XXI. Deuterohæmin and deuteroporphyrin. H. FISCHER and F. LINDNER (Z. physiol. Chem., 1926, **161**, 17—36).—Fresh ox-blood is fermented with yeast or spontaneously at 37°, alkalinity being maintained by successive additions of sodium carbonate and the progress of reaction followed by measurements of the hæmochromogen spectrum in pyridine. The diluted liquid is acidified and the precipitate is separated by decantation, pressed, washed with methyl alcohol, pressed again, and extracted with methyl alcohol containing 1% of sulphuric acid. After concentration of the extract, crude *deuterohæmin* crystallises on addition of concentrated hydrochloric acid, and is purified as the *methyl* ester, $C_{32}H_{30}O_4N_4ClFe$, m. p. 233°. The crude hæmin is converted by sodium amalgam, by hydrobromic- or hydriodic-acetic acid, or by hydrazine and acetic acid, into *deuteroporphyrin* (crystallographic data by STEINMETZ) (*methyl* ester, $C_{30}H_{32\text{ or }34}O_4N_4$, m. p. 218°; *copper* salt, m. p. 335°; *iron* salt; *copper* salt of the methyl ester, m. p. 230°; *iron* salt of the methyl ester, m. p. 250°). When heated in a vacuum for 3 hrs. at 200°, deuteroporphyrin is practically unchanged, whilst hæmatoporphyrin under the same conditions gives protohæmin. Deuteroporphyrin is converted by bromine in acetic acid into a *bromo*-compound, which with aqueous acetone loses only half its bromine and gives *dibromodeuteroporphyrin*, $C_{30}H_{26}O_4N_4Br_2$ (*methyl* ester, m. p. 261°). The oxidation of dibromodeuteroporphyrin with chromic acid to bromocitraconimide and hæmatic acid, and of deuteroporphyrin to citraconimide and hæmatic acid leads to the annexed structure (X=Br or H) for these two compounds.



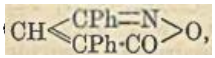
This removal of the unsaturated side-chains of hæmin during fermentation is the first example of its kind. The effect of deuteroporphyrin in rendering paramæciæ and white mice sensitive to sunlight is noted.

C. HOLLINS.

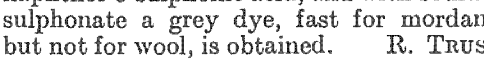
2-Hydroxyindoxazen (benzisooxazolone). H. LINDEMANN and W. SCHULTHEIS (Annalen, 1927, **451**, 241—255).—When *o*-hydroxybenzoyl azide is heated in solvents, nitrogen is evolved, an intermediate compound of the type $OH\cdot C_6H_4\cdot CO\cdot N:$ being formed. This does not undergo direct ring closure (cf. A., 1926, 80), but isomerises to a carbimide which then condenses, forming benzoxazolone. In alcoholic solutions, the carbimide reacts preferentially with the solvent, giving hydroxyphenylurethanes. On treating 3 : 5-dibromo-2-hydroxybenzoyl chloride with sodium azide in acetone solution, 3 : 5-*dibromo-2-hydroxybenzoyl azide* is obtained. If the reaction is carried out in glacial acetic acid, part of the acid chloride is converted into the quinonoid substance, (*o*) $O{:}C_6H_4{:}CO$ (cf. *loc. cit.*), which then combines with the solvent, yielding 3 : 5-dibromo-2-acetoxybenzoic acid. The azide melts at 114°, with loss of nitrogen, being converted into 4 : 6-dibromobenzoxazolone. 3 : 5-Dibromo-2-acetoxybenzoic acid affords successively the *acid chloride*, m. p. 68—69°, b. p. 184°/20 mm., and 3 : 5-*dibromo-2-acetoxybenzoyl azide*, m. p. 70—73°. When boiled in glacial acetic acid, the latter is converted into 3 : 5-dibromo-2-hydroxyacetanilide, m. p. 178° (cf. Holz, *ibid.*, 1885, 1211). In boiling benzene, it loses nitrogen, forming 3 : 5-*dibromo-2-acetoxyphenylcarbimide*, m. p. 76°, which further condenses to 4 : 6-dibromo-2-acetylbenzoxazolone when heated at 140°. Both azide and carbimide react with methyl alcohol, giving *methyl* 3 : 5-*dibromo-2-acetoxyphenylcarbamate*, m. p. 178° (decomp.). The corresponding *ethyl* ester, m. p. 163°, is hydrolysed by alcoholic potassium hydroxide to *ethyl* 3 : 5-*dibromo-2-hydroxyphenylcarbamate*, m. p. 122°. *o*-Acetoxybenzoyl chloride, m. p. 49—50°, prepared by an improved method, yields successively o-*acetoxybenzoyl azide*, m. p. 64—65° (decomp.); o-*acetoxyphenylcarbimide*, b. p. 112°/12 mm.; *methyl* o-*acetoxyphenylcarbamate*, m. p. 100—101°, and the corresponding *ethyl* ester, m. p. 75—76°. The *acetate*, $OH\cdot C_6H_4\cdot C(OH){:}N\cdot OAc$, m. p. 141—142°, of salicylhydroxamic acid (*ibid.*, 1889, 870) loses the elements of acetic acid when heated above its m. p. or treated with alkali, but instead of the expected 2-hydroxybenzisooxazole (cf. *ibid.*, 1926, 1047), benzoxazolone was again obtained. When, however, the isomeric o-*acetoxybenzhydroxamic acid*, m. p. 102—103°, is boiled with ammonia solution, 2-*hydroxybenziso-oxazole*, $C_6H_4<\overset{C(OH)}{\underset{O}{\diagdown\diagup}}>N$, m. p. 139° (*acetyl* derivative, m. p. 149°; *methyl ether*, m. p. 127·5°), is produced. This dissolves unchanged in dilute alkali; with more concentrated solutions, salicylic acid is obtained. The compound, m. p. 133—134°, of this formula described by Ransom and Nelson (*ibid.*, 1914, i, 269) was probably benzoxazolone.

H. E. F. NOTTON.

[So-called] *iso*oxazoline oxides. E. P. KOHLER and R. C. GOODWIN (J. Amer. Chem. Soc., 1927, **49**, 219—227; cf. A., 1926, 1140).—The action of methyl-alcoholic potassium acetate on α-bromo-γ-nitro-β-phenylpropiophenone (A., 1924, i, 571) has been re-examined in view of more recent results obtained in an analogous reaction (*ibid.*, 1926, 1140). The product, first reported as 2-hydroxy-3-methoxy-5-benzoyl-4-phenyl*iso*oxazolidine, has now been identified as *methyl* β-*hydroxy-γ-oximino-αγ-diphenyl*-n-*butyrate* (I), and it becomes the sole product of the above reaction if this is carried out in presence of acetic acid. Controlled hydrolysis with dilute aqueous potassium hydroxide affords β-*hydroxy-γ-oximino-αγ-diphenyl*-n-*butyric acid*, m. p. 168° (decomp.), which, with methyl-alcoholic hydrochloric acid, affords *methyl* β-*hydroxy-γ-keto-αγ-diphenyl*-n-*butyrate*, m. p. 78°; this yields the above oximino-ester when treated with hydroxylamine, and, on alkaline hydrolysis, affords β-*hydroxy-γ-keto-αγ-diphenyl*-n-*butyric acid*, m. p. 115° ($0{\cdot}5H_2O$), m. p. 142° (anhydrous). The latter was synthesised by brominating γ-keto-αγ-diphenyl-*n*-butyric acid and hydrolysing the *product*, m. p. 207—208°, with alkali Reduction of the hydroxyketonic acid with phosphorus and

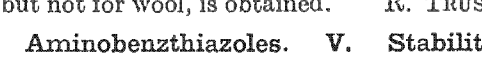
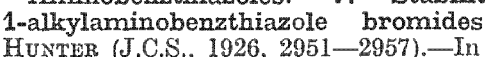
hydriodic acid affords the ketodiphenylbutyric acid, whilst hydroxylamine yields the above oximino-acid. The N-*acetyl* (m. p. 126°), ON-*diacetyl* (m. p. 98°), O-*acetyl* (m. p. 142°), N-*benzoyl* (m. p. 114°), and ON-*dibenzoyl* derivatives (m. p. 113°) of (I) are described. Treatment of the diacetate with aqueous potassium hydroxide affords *γ-keto-αγ-diphenylcrotonic acid*, m. p. 124°, identified by treatment with ozone, and by synthesis effected by brominating methyl γ-keto-αγ-diphenyl-*n*-butyrate and hydrolysis with alkali of the resulting stereoisomeric *bromo*-derivatives, m. p. 78° and 108°, respectively. A by-product in the preparation of (I) has now been identified as 6-*keto*-3 : 5-*diphenyl*-1 : 2-*oxazine*,  , m. p. It is obtained by the action of hydroxylamine on the above crotonic acid or on methyl β-bromo-γ-keto-αγ-diphenyl-*n*-butyrate. When heated with acetyl chloride, or, in strong alkaline solution, with silver nitrate, it is converted into 3 : 5-*diphenyl*isooxazole. F. G. Willson.

Oxazinesulphonic acids. J. S. Turski, J. Bojanowski, K. Moniuszko, and J. Vogelgarn (Rocz. Chem., 1926, **6**, 747—755).—An acid dye, staining wool indigo-blue, 6-naphthylphenoxazinesulphonic acid, is prepared by the action of Schaeffer's salt on nitrosodimethylaniline hydrochloride, whilst a pure blue dye with similar properties is obtained by condensation of the latter substance with β-naphthol-8-sulphonic acid, and with sodium *p*-phenylsulphonate a grey dye, fast for mordanted cotton, but not for wool, is obtained. R. Truszkowski.

Aminobenzthiazoles. V. Stability of the 1-alkylaminobenzthiazole bromides. R. F. Hunter (J.C.S., 1926, 2951—2957).—In the system  , increase in atomic volume of R should, according to Ingold's modified strain theory (*ibid.*, 1921, **119**, 305), enhance the aminothiazole phase, with consequent increased stability of the bromides. A stability curve for homologous series could not be obtained for the simple 1-alkylaminobenzthiazoles, but the prediction is verified for the 5-bromo-derivatives (see following abstract).

1-Methylaminobenzthiazole dibromide, decomp. 144—146°, prepared from bromine and *s*-phenylmethylthiocarbamide, is almost unchanged after 46 hrs.' exposure to air at 17°. The 1-ethylaminodibromide, m. p. 76—78° (decomp.), loses one third of its labile bromine in 44 hrs. 1-n-*Propylaminobenzthiazole tetrabromide*, m. p. 54—56°, loses nearly half its bromine in 44 hrs., and in 5 days a thin layer is converted completely into *dibromide*, m. p. 80—82° (decomp.). *s-Phenyl-n-butylthiocarbamide*, m. p. 65°, is converted by bromine into 1-n-*butylaminobenzthiazole dibromide*, m. p. 86° (decomp.), practically unaltered by 44 hrs.' exposure; 1-n-*butylaminobenzthiazole* melts at 87°. 1-iso*Butylaminobenzthiazole dibromide hydrobromide*, m. p. 66—68° (decomp.), loses nearly half its labile bromine in 48 hrs.; 1-iso*butylaminobenzthiazole* has m. p. 103—104°. The following 1-alkylaminobenzthiazoles are also described : n-*amyl*, m. p. 68—69° [*dibromide hydrobromide*, m. p. 90° (decomp.)]; iso*amyl*, m. p. 69—71° (*dibromide hydrobromide*); n-*hexyl*, m. p. 57° [*dibromide*, m. p. 100—102° (decomp.)]; n-*heptyl*, m. p. 55° (*dibromide hydrobromide*, m. p. 79—81°); and the following new *s*-phenylalkylthiocarbamides : n-*amyl*, m. p. 69—71°; n-*hexyl*, m. p. 103—104°; n-*heptyl*, m. p. 70—71°.

C. Hollins.

Aminobenzthiazoles. VI. Stability of the 5-bromo-1-alkylaminobenzthiazole bromides. R. F. Hunter and C. Soyka (J.C.S., 1926, 2958—2964; cf. preceding abstract and this vol., 236).—*s*-Di-*p*-bromophenylthiocarbamide, m. p. 184—185°, is converted by means of acetic anhydride into *p*-bromophenylthiocarbimide, which is condensed with alkylamines to give the following *s*-*p*-bromophenylalkylthiocarbamides : *methyl*, m. p. 148°; *ethyl*, m. p. 129°; n-*propyl*, m. p. 120°; n-*butyl*, m. p. 111°; iso*butyl*, m. p. 119°; n-*amyl*, m. p. 115°; iso*amyl*, m. p. 120°; n-*hexyl*, m. p. 106°; n-*heptyl*, m. p. 100°. Treatment of the ethyl, *n*-propyl, *n*- and *iso*-butyl compounds with bromine in hot chloroform yields 5-*bromo*-1-*alkylaminobenzthiazole dibromides*, melting at 140° (decomp.), 146° (decomp.), 149° (decomp.), and 127° (decomp.), respectively, which are reduced by hydriodic acid to the corresponding 5-*bromo*-1-*alkylaminobenzthiazoles*, m. p. 256—258°, 130°, 118°, and 137°, respectively. The dibromides show increasing stability as the alkyl group increases in atomic volume, the proportion of the labile bromine removed by dilute hydriodic acid under comparable conditions being respectively 98·9, 42·4, 37·3, and 19·0%. In the case of the ethyl compound, both forms of dibromide,  and  , are isolated, the latter (labile) form being converted into the former under special conditions. The following 5-bromo-1-alkylaminobenzthiazoles are also described : *methyl*, m. p. 225° [*hexabromide*, m. p. 122—124° (decomp.)]; n-*amyl*, m. p. 105° [*tetrabromide*, m. p. 86° (decomp.)]; iso*amyl*, m. p. 171° [impure; *dibromide*, m. p. 95° (decomp.)]; n-*hexyl*, m. p. 156° (*dibromide*); n-*heptyl*, m. p. 86° [impure; *dibromide*, m. p. 118—120° (decomp.)].

C. Hollins.

Aminobenzthiazoles. VII. The 2-alkylamino-β-naphthathiazole system. G. M. Dyson, R. F. Hunter, and C. Soyka (J.C.S., 1926, 2964—2969; cf. preceding abstracts).—Treatment of *s*-α-naphthylalkylthiocarbamides with bromine in hot chloroform yields a series of 2-alkylamino-β-naphthathiazole bromides, reducible by hydriodic or sulphurous acid to the bases. A tetrabromide is probably the normal product, but this may add on up to ten more bromine atoms, and a stability curve cannot be obtained. The following *s*-α-naphthylalkylthiocarbamides are new : n-*propyl*, m. p. 67°; n-*butyl*, m. p. 98°; iso*butyl*, m. p. 106°; n-*amyl*, m. p. 103°; iso*amyl*, m. p. 92°; n-*hexyl*, m. p. 89°; n-*heptyl*, m. p. 62°. The 2-alkylamino-β-naphthathiazoles described are : *methyl*, m. p. 193° [*hexabromide*, m. p. 163° (decomp.)]; *ethyl*, m. p. 218° [*tetrabromide*, m. p. 203° (decomp.)]; n-*propyl*, m. p. 242° (*hexabromide* sinters at 153°); n-*butyl*, m. p. 177° [*tetrabromide*, m. p. 134° (decomp.)]; iso*butyl*, m. p. 242°

[*hexabromide hydrobromide*, m. p. 103° (decomp.)]; n-*amyl*, m. p. 107° [*tetrabromide hydrobromide*, m. p. 123° (decomp.)]; iso*amyl*, m. p. 117° (*hexabromide hydrobromide* sinters at 135°); n-*hexyl*, m. p. 111° [*tetrabromide hydrobromide*, m. p. 127° (decomp.)]; n-*heptyl*, m. p. 97° (decomp.; *tetradecabromide*, $C_{18}H_{22}N_2Br_{14}S$, chars at 220°). C. HOLLINS.

[Phosphonitrilic chlorides and their transformations.] R. SCHENCK (Ber., 1927, **60**, [*B*], 160—161; cf. Schenck and Römer, A., 1924, ii, 752).—Revision of the determination of the mol. wts. of the anilide, piperidide, and phenylhydrazide derived from triphosphonitrilic chloride shows them to be termolecular. The quadrimolecular structure of tetraphosphonitrilic chloride persists in the anilide derived therefrom. H. WREN.

Derivatives of 10-chloro-5 : 10-dihydrophenarsazine. IV. Carboxy-derivatives. H. BURTON and C. S. GIBSON (J.C.S., 1927, 247—250).—Anthranilic acid condenses with *o*-bromophenylarsinic acid in boiling nitrobenzene in presence of anhydrous potassium carbonate and a trace of copper powder, forming 2-*carboxydiphenylamine*-6′-*arsinic acid*, m. p. 243° (decomp.). Reduction with sulphur dioxide in alcoholic hydrochloric acid solution containing a trace of iodine gives 2-*carboxydiphenylamine*-6′-*arsenic dichloride*, which immediately undergoes partial elimination of hydrogen chloride. Complete conversion into 10-*chloro*-5 : 10-*dihydrophenarsazine*-4-*carboxylic acid*, m. p. 243° (decomp.), is effected by boiling in acetic acid or sodium hydroxide solution. Reduction of the carboxylic acid with hypophosphorous acid yields 10 : 10′-*bis*-4-*carboxy*-5 : 10-*dihydrophenarsazine*, m. p. 253° (decomp.). *m*-Aminobenzoic acid yields, by a similar series of reactions, 3-*carboxydiphenylamine*-6′-*arsinic acid*, m. p. 238—239°, and 10-*chloro*-5 : 10-*dihydrophenarsazine*-3-*carboxylic acid*, m. p. above 300°. M. CLARK.

Spermine. V. F. WREDE, H. FANSELOW, and E. STRACK (Z. physiol. Chem., 1926, **161**, 66—73; cf. A., 1926, 751; Dudley and others, *ibid.*, 1925, i, 294; 1926, 308).—The base "$C_4H_{12}N_2$" obtained by oxidation of spermine (*loc. cit.*) is shown to be actually trimethylenediamine, $C_3H_{10}N_2$. The second base, $C_7H_{14}N_2$, gives a dihydro-derivative, $CH_2{\cdot}CH_2{>}N{\cdot}[CH_2]_3{\cdot}NH_2$, which is synthesised. This leads to the structure $NH_2{\cdot}[CH_2]_3{\cdot}NH{-}[CH_2]_4{\cdot}NH{\cdot}[CH_2]_3{\cdot}NH_2$ for spermine, $C_{10}H_{26}N_4$. The oxidation with copper and oxygen probably produces hydrolysis at the position marked, with oxidation of the amino-alcohol so produced to aminoaldehyde, which then condenses to $\begin{matrix}CH{=}CH\\ |\\ CH_2{\cdot}CH_2\end{matrix}{>}N{\cdot}[CH_2]_3{\cdot}NH_2$ or $\begin{matrix}CH{\cdot}CH_2\\ |\\ CH{\cdot}CH_2\end{matrix}{>}N{\cdot}[CH_2]_3{\cdot}NH_2$.

Trimethylenediamine, prepared by Fischer and Koch's method (A., 1884, 1289), gives a chloroplatinate, m. p. 240° (decomp.), and a *di*-m-*nitrobenzoyl* derivative, m. p. 212—213°, identical with those from the base, $C_3H_{10}N_2$, from spermine.

N-γ-Bromopropylphthalimide, condensed with pyrrolidine and subsequently hydrolysed with hydrochloric acid, yields *N*-γ-aminopropylpyrrolidine (chloroaurate, m. p. 206°; picrate, m. p. 216°), identical with the dihydro-compound of the base, $C_7H_{14}N_2$, from spermine. C. HOLLINS.

Rapid determination of opium in stomach contents. E. R. DOVEY (Analyst, 1927, **52**, 26—27).—The coloration produced by adding hydrochloric acid, mercuric chloride solution, and ferric chloride solution to the filtered liquid is compared with that of a similarly treated standard solution of the kind of opium most likely to have been taken. D. G. HEWER.

ψ-Morphine. Separation and determination of morphine, ψ-morphine, and related substances. A. K. BALLS (J. Biol. Chem., 1927, **71**, 537—542, 543—558).—ψ-Morphine was prepared by oxidation of morphine with hydrogen peroxide in presence of potassium cuprous cyanide, and was purified through the hydrochloride. It differs from morphine chiefly in its more acidic character and in the greater insolubility of its acidic salts. If a mixture of morphine with ψ-morphine and other higher oxidation products in alkaline solution be treated with silicotungstic acid, and the reaction be adjusted to p_H 7·8, the ψ-morphine is completely precipitated; on further acidification of the filtrate, the morphine is precipitated together with the other oxidation products. Alternatively, the filtrate may be adjusted to p_H 9·0 and the morphine alone then removed by extraction with amyl alcohol. On the above basis, a method has been elaborated by which morphine and ψ-morphine in concentrations of the order of 0·01% may be determined in muscle-tissue with an error of about 30%. C. R. HARINGTON.

Dependence of the degree of hydrolysis of cocaine on hydrogen-ion concentration. E. SADOLIN (Dansk Tidss. Farm., 1927, **1**, 223—233).—The degree of hydrolysis corresponding with the first stage of the hydrolysis of cocaine ($\cdot CO_2Me \longrightarrow \cdot CO_2H$) has been investigated by boiling 2% solutions of cocaine hydrochloride for 1 hr. under reflux, the p_H values of the solutions being previously adjusted to a known figure by employing Sorensen's buffer solutions. The extent of hydrolysis was found by determining the methyl alcohol formed, using Pregl's micro-modification of Zeisel's apparatus, the values obtained being corrected for the dilution and the effect due to the presence of cocaine hydrochloride. A 2% solution of cocaine hydrochloride is practically completely hydrolysed by boiling for 1 hr. when the p_H value exceeds 7·5, whilst for p_H values between 1 and 5 the hydrolysis shows a minimum of about 10%. The extent to which the second stage of hydrolysis of cocaine (benzoylecgonine $\longrightarrow$ ecgonine) takes place was investigated by boiling 2% cocaine hydrochloride solutions for 1 hr. as above and determining the benzoic acid formed; this was done either by acidifying the liquid and boiling it almost to dryness, the benzoic acid which passed over being titrated with 0·04*N*-sodium hydroxide, or, more exactly, by extracting the acidified solution twice with ether, evaporating this off, and titrating the residual benzoic acid as before. The values obtained show that the hydrolysis is minimal for p_H values between 2 and 7, where it amounts to

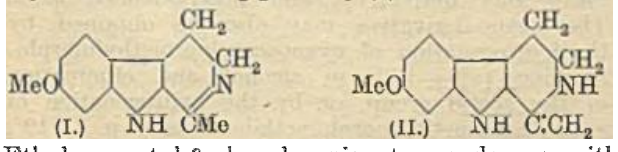
approximately 3% for 1 hr.'s boiling of the solution; with p_H values greater than 13, hydrolysis is complete. It is recommended to utilise this reaction for the determination of cocaine, the material being boiled for 1 hr. under reflux with sodium hydroxide solution of at least 0·1*N*; the solution is then acidified, extracted twice with ether, and the benzoic acid in the ether extract determined as above.

H. F. HARWOOD.

Double salt crystals of cocaine with rare metals. E. PACE (Arch. farm. sperim., 1926, 42, 35—41).—Crystalline double salts are described of cocaine with the following: *rubidium chloride*, m. p. 158° (decomp.); *beryllium chloride*, $Cn,BeCl_2$ (writing Cn for 1 mol. of cocaine, $C_{17}H_{21}O_4N$); *thallic chloride*, $Cn_2,TlCl_3$, m. p. 112°; *titanic acid*, Cn_2,H_4TiO_4, m. p. 106°; *zirconium sulphate*, $Cn_2,Zr(SO_4)_2$, m. p. 132°; *thorium chloride*, $Cn_2,ThCl_4$, m. p. 200°; *orthovanadic acid*, Cn,H_3VO_4, m. p. 139°; *tungstic acid*, Cn_2,H_2WO_5, m. p. 109°; *uranyl nitrate*, $Cn,UO_2(NO_3)_2$, m. p. 226°; *palladous chloride*, $Cn,PdCl_2$, m. p. 185°; *chloroplatinic acid*, Cn_2,H_2PtCl_6, m. p. 205°; *cerous nitrate*, $Cn,Ce(NO_3)_3$, m. p. 98°; *neodymium nitrate*, m. p. 82°; *yttrium nitrate*, $Cn,Yt(NO_3)_3$, m. p. 115°; *erbium sulphate*, m. p. 121°. Cocaine forms with selenium chloride a colourless *compound*, m. p. 42°, which changes on exposure to air into a red *compound*, Cn_2,Se_2Cl_2, m. p. 151°; this is suggested as a test for cocaine.

E. W. WIGNALL.

Harmine and harmaline. IX. Synthesis of harmaline. R. H. F. MANSKE, W. H. PERKIN, jun., and R. ROBINSON (J.C.S., 1927, 1—14).—The formulæ (I) and (II) are the only representations of the harmaline molecule consistent with its synthesis. The reactions of the base are satisfactorily interpreted on the hypothesis that these are tautomerides, the crystalline base being probably (I).



Ethyl α-acetyl-β-phenylpropionate condenses with benzenediazonium chloride in alkaline–alcoholic solution, and the product, after hydrolysis and treatment with alcoholic hydrogen chloride, yields the *ethyl* ester, m. p. 137—138°, of *3-phenylindole-2-carboxylic acid*, m. p. 186°. Sodium α-acetyl-β-phenylpropionate and benzenediazonium chloride react in alkaline solution to give *α-phenylbutane-βγ-dione-β-phenylhydrazone*, m. p. 108°. (Analogous reactions give the β-m-*nitrophenylhydrazone*, m. p. 146°, and the β-2 : 5-*dimethoxyphenylhydrazone*, m. p. 107°.) The β-phenylhydrazone is converted by boiling concentrated hydrochloric acid into *2-acetyl-3-phenylindole*, m. p. 151°, which yields 3-phenylindole on fusion with sodium hydroxide. Hydrolysis of ethyl δ-phthalimido-α-acetylvalerate with cold aqueous-alcoholic sodium hydroxide gives sodium *δ-o*-carboxybenzamido-α-acetylvalerate, which couples in alkaline solution with benzenediazonium chloride, yielding, after acidification, *ζ-o-carboxybenzamidohexane-βγ-dione-γ-phenylhydrazone*, m. p. 156—157°. Treatment with acetic anhydride gives *ζ-phthalimidohexane-βγ-dione γ-phenylhydrazone*, m. p. 172°, converted by boiling alcoholic hydrochloric acid into *2-acetyl-3-β-phthalimidoethylindole*, m. p. 214°. The action of hydrazine hydrate in hot alcoholic solution, followed by treatment of the product with hydrochloric acid (cf. A., 1926, 1132), yields phthalylhydrazide and the hydrochloride of *harmalan* (demethoxyharmaline). The free base ($+10H_2O$) has m. p. 182—183° and, on oxidation with chromic acid, yields harman. A similar series of reactions with sodium δ-*o*-carboxybenzamido-α-acetylvalerate and *m*-methoxybenzenediazonium chloride yields *ζ-o-carboxybenzamidohexane-βγ-dione-γ-m-methoxyphenylhydrazone*, m. p. 208° (decomp.); *ζ-phthalimidohexane-βγ-dione-γ-m-methoxyphenylhydrazone*, m. p. 167—168°; *6-methoxy-2-acetyl-3-β-phthalimidoethylindole*, m. p. 218°, and harmaline, yielding, on oxidation with chromic acid, harmine. In the indole cyclisation, effected in this case with *n*-butyl-alcoholic hydrogen chloride, closure takes place in the *p*-position to the methoxy-group (cf. J.C.S., 1921, 119, 1614).

ζ-o-Carboxybenzamidohexane-βγ-dione-γ-phenylhydrazone is converted by the action of hydrogen chloride in hot acetic acid solution into the *hydrochloride*, m. p. 286° (decomp.), of *5-keto-6-methyl-2 : 3 : 4 : 5-tetrahydropyridine-5-phenylhydrazone* ($+0·5C_6H_6$), m. p. 134—135°. The following are also described: *ζ-o-carboxybenzamidohexane-βγ-dione-γ-m-chlorophenylhydrazone*, m. p. 210° (decomp.), and *5-keto-6-methyl-2 : 3 : 4 : 5-tetrahydropyridine-5-m-chlorophenylhydrazone*, m. p. 161° (*hydrochloride*); *5-keto-6-phenyl-2 : 3 : 4 : 5-tetrahydropyridine-5-phenylhydrazone*, m. p. 146—147° (*hydrochloride*).

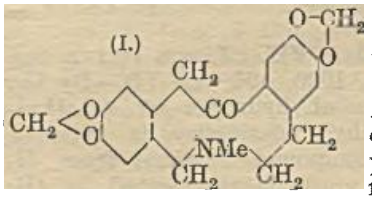
Preparation of γ-phthalimidobutyronitrile by direct replacement of bromine by the cyano-group in γ-bromopropylphthalimide can be effected by the use of anhydrous methyl-alcoholic sodium cyanide. The experimental details described must be closely followed.

M. CLARK.

Chloroarsinosoquinine. II. F. X. ERBEN and E. PHILIPPI (Ber., 1927, 60, [*B*], 122—124; cf. Erben and others, A., 1926, 188).—Chloroarsinosoquinine, m. p. 207—209° after darkening at 199—200° and softening at 204°, is most conveniently prepared by heating dehydroquinine with arsenic trichloride at 130—135° in the absence of a solvent. Neither the base nor its salts could be caused to crystallise.

H. WREN.

Synthesis of protopine and allied alkaloids. I. T. S. STEVENS (J.C.S., 1927, 178—187).—Attempts were made to synthesise the protopine isomeride

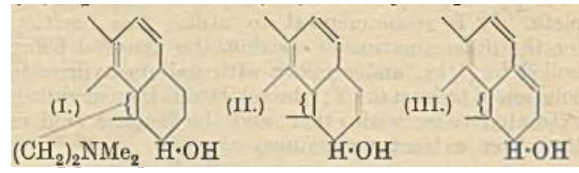


(I) without previous formation of a structure of the tetrahydroberberine type (cf. A., 1926, 964). Condensation of homopiperonylic acid with formaldehyde yields the *lactone* of *6-hydroxymethylhomopiperonylic acid* (II), m. p. 137°, the constitution of which is established by oxidation with permanganate to 4 : 5-methylenedioxyhomophthalic acid. The corresponding *6-hydroxymethylhomopiperonylamide*,

m. p. 164—167°, reacts with phosphorus trichloride, giving 6-*chloromethylhomopiperonylonitrile* (III), m. p. 83—85°, which condenses with *N*-methyl-β-piperonylethylamine to give N-*methyl*-N-β-*piperonylethyl*-6-*aminomethylhomopiperonylonitrile*, m. p. 74—76° [*nitrate*, m. p. about 150° (decomp.)]. Attempted conversion into (I) by an intramolecular Hoesch reaction gives N-*methyl*-N-β-*piperonylethyl*-6-*aminomethylhomopiperonylamide*, m. p. 140° [*picrate*, m. p. 210° (decomp.)]. Bromination of *N*-methyl-β-piperonylethylamine yields N-*methyl*-6-*bromo*-β-*piperonylethylamine* (IV) (*hydriodide*, m. p. 175°; *hydrochloride*, m. p. 162—164°; *benzoyl* derivative, m. p. 98—100°); this substance is alternatively obtained [together with a *compound*, m. p. 260° (*picrate*, m. p. 151—153°), probably trimethyl-6-bromo-β-piperonylethylammonium iodide] by successive treatment with methyl iodide and alcohol of the *piperonylidene* derivative, m. p. 108—112°, of 6-*bromo*-β-*piperonylethylamine* [*hydrochloride* ($+H_2O$), m. p. 208—210°; *hydriodide*, m. p. 221°; *benzoyl* derivative, m. p. 138—140°]. The last-named compound is obtained by the action of sodium hypochlorite on 6-bromo-β-piperonylpropionamide (*ibid.*, 952). The nitrile (III) reacts with (IV), giving N-*methyl*-N-6′-*bromo*-β-*piperonylethyl*-6-*aminomethylhomopiperonylonitrile* (*hydrochloride*, m. p. 205°; *nitrate*, decomp. 160°). Attempts to obtain (I) by an internal Grignard reaction involving the bromine atom and the nitrile group were unsuccessful. Successive treatment of the lactone (II) with phosphorus trichloride and methyl alcohol gives the *methyl* ester, m. p. 41—43°, of 6-*methoxymethylhomopiperonylic acid*, m. p. 93—95° (*silver* salt), which loses the methoxy-group, with regeneration of the lactone, on treatment with hot dilute hydrochloric acid. (Homopiperonyl methyl ether passes similarly into 2 : 3 : 6 : 7-bismethylenedioxy-9 : 10-dihydroanthracene.) Treatment of (II) with hydrogen bromide gives 6-*bromomethylhomopiperonylic acid*, m. p. 146—149°, reconverted into the lactone by primary or secondary bases or attempted condensation with β-piperonylethylamine or its *N*-methyl derivative. The *methyl* ester, m. p. 68—70°, obtained by the action of diazomethane, condenses with *N*-methyl-β-piperonylethylamine, giving, after hydrolysis, N-*methyl*-N-β-*piperonylethyl*-6-*aminomethylhomopiperonylic acid*, m. p. 136—140° [*oxalate* ($+C_2H_2O_4$), m. p. 178° (decomp.)]. Ring-closure to the compound (I) by conversion into the acid chloride and treatment with aluminium chloride could not be effected.

An improved method for the preparation of homopiperonylic acid is described. M. CLARK.

Morphine alkaloids. VII. J. VON BRAUN and R. S. CAHN (Annalen, 1926, **451**, 55—74).—By the action of two atoms of hydrogen on α-methylmorphimethine, a dihydro-derivative is obtained identical with the compound obtained from dihydrocodeine, which must be represented by (I). The action of two atoms of hydrogen on β-methylmorphimethine yields an isomeric dihydro-derivative, in which the double linking in the 9 : 10-position must have been reduced. The conclusion is reached that the facts are best explained by the 7 : 8-position of the double linking in codeine. Thus formula (II) represents α- and (III) β-methylmorphimethine.



Since when the hydroxyl group is replaced by chlorine in the tetrahydronormethylmorphimethines obtained from α-, β-, or γ-derivatives there is no tendency for the chlorine atom to combine with the hydrogen atom of the ·NHMe group with evolution of hydrogen chloride and ring closure, it is considered that the side-chain including the nitrogen atom is probably not attached to position 5. This suggests that the Wieland and Kotake (A., 1925, i, 1090) formula for codeine may be more nearly correct than that of Robinson.

Hydrogenation of α-methylmorphimethine in alcoholic solution using nickel as catalyst gives (III) dihydro-α-methylmorphimethine (I) (methiodide, m. p. 223—225°), but when either α- or β-methylmorphimethine is reduced using sodium and alcohol, (II) dihydro-β-methylmorphimethine (methiodide of acetyl derivative, $[\alpha]_D$ +75°) is obtained.

When cyanogen bromide reacts with acetyltetrahydromethyhnorphimethine, it yields the *methobromide* of the base, m. p. 225—226°, and *cyanoacetyltetrahydronormethylmorphimethine*, m. p. 100—101°, $[\alpha]^{20}$ —58° in chloroform. The cyanoacetyl derivative dissolves in a solution of sodium methoxide and the non-acetylated *cyano*-derivative separates as plates, m. p. 140°, $[\alpha]_D^{20}$ —51·4° in chloroform. This substance is slowly hydrolysed by dilute hydrochloric acid to tetrahydronormorphimethine, an oil which yields oily derivatives and poorly-defined salts. The cyano-derivative may also be obtained by the hydrogenation of cyanoacetylnormethylmorphimethine, $[\alpha]^{16}$ —106° in alcohol, and elimination of the acetyl group, or by the hydrogenation of cyano-α-normethylmorphimethine, m. p. 119°, $[\alpha]_D^{20}$ —196°.

Acetyl-β-methyhnorphimethine (*methobromide*, indefinite m. p.) reacts with cyanogen bromide, yielding *cyanoacetyl*-β-*methylmorphimethine* as an oil, which, on keeping with sodium methoxide solution, is hydrolysed to the *carbamide* derivative, β-$C_{17}H_{16}O_2$(OH)·NMe·CO·NH_2, m. p. 130—131°, $[\alpha]_D^1$ +364° in chloroform. This carbamide is readily hydrogenated to yield the *tetrahydro*-derivative as an oil, which is hydrolysed to tetrahydronormorphimethine. When treated in chloroform solution with phosphorus pentachloride, the tetrahydrobase yields the *chloro*-base, $C_{17}H_{20}O_2Cl$·NHMe, an oil stable towards sodium carbonate solution, as the *hydrochloride*, m. p. 267° (decomp.) [*chloroplatinate*, m. p. 223° (decomp.)].

Similarly, the following substances are derived from acetyltetrahydro-γ-methylmorphimethine (*methobromide* $+3H_2O$, m. p. 100—102°): *cyanoacetyltetrahydro*-γ-*normethylmorphimethine*, m. p 102°, $[\alpha]_D^{18}$ —104·5° in chloroform; *cyanotetrahydro*-γ-*normethylmorphimethine*, m. p. 117°, $[\alpha]_D^{17}$ —90·7° in

chloroform; *tetrahydro-γ-normethylmorphimethine*, a vitreous substance yielding no well-defined salts, which with phosphorus pentachloride yields a mixture of the chloro-derivative with a chlorine-free substance, probably the unchanged base. The chlorine in the mixture is stable towards sodium carbonate solution. R. W. WEST.

Organic derivatives of silicon. XXXII. Carbon-silicon binding. F. S. KIPPING (J.C.S., 1927, 104—107).—There is no authentic evidence for the formation of an ethylenic linking between carbon and silicon. The reactions leading to olefine formation are inapplicable, and it is exceedingly doubtful whether this linking is a possible one. Schlenk and Renning (A., 1913, i, 34) claim to have prepared the compound $SiPh_2{:}CH_2$ by distillation of crude diphenylmethylsilicol. This silicol is, however, only very slowly decomposed at its b. p., giving *diphenylmethylsilicyl oxide*, m. p. 51—52°. No evidence for the formation of an unsaturated compound could be obtained. *Diphenyldimethylsilicane*, obtained by the action of an excess of magnesium methyl iodide on dichlorodiphenylsilicane, has b. p. 176—178°/45 mm. M. CLARK.

Preparation of *m*-nitro-*p*-hydroxyphenylarsinic acid. I. OSTROMISSLENSKY.—See B., 1927, 93.

Production of arsinic acids of aromatic [heterocyclic] compounds [dihydrobenzoxazolones]. L. CASSELLA & Co.—See B., 1927, 125.

Dicyanates and dibenzoates of triphenylbismuthine and triphenylstibine. F. CHALLENGER and V. K. WILSON (J.C.S., 1927, 209—213).—*Triphenylbismuthine dicyanate*, m. p. 128·5—129°, is stable at the ordinary temperature, whereas triphenylbismuthine dithiocyanate and diselenocyanate immediately revert to derivatives of tervalent bismuth, yielding phenyl thiocyanate and selenocyanate. Comparative experiments indicate that the dithiocyanate is slightly more stable than the di-iodide, hence iodine is, apparently, more positive than thiocyanogen. This is in agreement with Birckenbach and Kellermann's electrochemical series (A., 1925, ii, 568; 1926, 965). *Triphenylstibine dieyanate* has m. p. 111—112°. Triphenylbismuthine and triphenylstibine react with benzoyl peroxide, giving *triphenylbismuthine dibenzoate*, m. p. 172—173·5°, and *triphenylstibine dibenzoate*, m. p. 171·5°, whilst triphenylphosphine gives benzoic anhydride and triphenylphosphine oxide. M. CLARK.

Arylseleninic acids. W. H. PORRITT (J.C.S., 1927, 27—29).—Arylseleninic acids are obtained by oxidation of the corresponding arylselenoglycollic acids with hydrogen peroxide (cf. A., 1925, i, 1196). If the temperature is allowed to rise during the first stage of this reaction, diaryl diselenides are also formed. The following are described: o-*tolylselenoglycollic acid*, m. p. 70—71°; m-*xylyl*-4-*selenoglycollic acid*, m. p. 90·5°; o-*xylyl*-4-*selenoglycollic acid*, m. p. 88°; toluene-*o*-seleninic acid, m. p. 126—127°, and toluene-*p*-seleninic acid, m. p. 171° (cf. Doughty and Elder, *ibid.*, 1913, i, 962); *toluene*-m-*seleninic acid*, m. p. 119—120°; *bromobenzene*-p-*seleninic acid*, m. p. 187°; m-*xylene*-4-*seleninic acid*, decomp. 146—147°; o-*xylene*-4-*seleninic acid*, decomp. 125°. *Di-o-tolyl selenide*, m. p. 64°, is obtained as a by-product in the preparation of the selenomercaptan from magnesium *o*-tolyl bromide and selenium. M. CLARK.

Preparation of organo-selenium compounds by means of the Friedel–Crafts reaction. R. E. LYONS and W. E. BRADT (Ber., 1927, **60**, [*B*], 60—63).—The action of anhydrous aluminium chloride on selenium dioxide and benzene yields diphenylselenium dichloride, m. p. 183—183·5° (cf. Lyons and Bush, A., 1908, i, 417), diphenyl selenide, diphenyl diselenide, and dichlorodiphenyl selenide, m. p. 96·5—97°. The *compound*, $Ph_2SeCl_2{,}2CH_3{\cdot}CO{\cdot}CH_3$, m. p. 127·8—127·9°, is incidentally described. H. WREN.

Cyclic organo-metallic compounds. III. Nitro- and amino-derivatives of phenoxtellurine. H. D. K. DREW and R. W. THOMASON (J.C.S., 1927, 116—125).—Phenoxtellurine (see this vol., 164) on treatment with nitric acid is first oxidised to the 10 : 10-dinitrate and afterwards undergoes nitration of the nucleus. The colourless nitro-dinitrates or basic nitrates thus produced are readily reduced by alkali hydrogen sulphite to the nitro-derivatives. Nitration with concentrated nitric acid thus yields 2-*nitrophenoxtellurine*, m. p. 129°, and a lesser yield of 4-*nitrophenoxtellurine*, m. p. 104°, accompanied by a small quantity of the 2 : 8-dinitro-derivative. Nitration with fuming nitric acid gives 2 : 8-*dinitrophenoxtellurine*, m. p. 228°, and a lesser yield of 4 : 8-*dinitrophenoxtellurine*, m. p. 197—198°. The $>Te(NO_3)_2$ grouping is therefore either *meta*-directive or its influence is negligible compared with that of the ether oxygen atom.

Additive *compounds* of indefinite m. p., containing one and two mol. proportions of the 2 : 8-dinitro-derivative, respectively, with one of the 2-nitro-derivatives are described. A similar but more stable additive *compound*, m. p. 59°, containing 1 mol. of phenoxtellurine and 1 mol. of 2(?)-chloro-8(?)-methylphenoxtellurine is obtained as a by-product in the preparation of phenoxtellurine from tellurium tetrachloride and solid diphenyl ether, its formation being ascribed to the presence of phenyl *p*-tolyl ether as an impurity in the last-named substance. These additive compounds are capable of recrystallisation from certain organic solvents, whilst other solvents effect their complete or partial separation into the constituent substances. Union of the bivalent tellurium atoms of the associated molecules does not occur, since the corresponding complex 10 : 10-dichlorides and dinitrates, containing only quadrivalent tellurium, may also, in some cases, be recrystallised unchanged.

Reduction of the corresponding nitro-derivatives gives: 2-*aminophenoxtellurine*, m. p. 157° (*hydrochloride*); 2 : 8-*diaminophenoxtellurine*, m. p. 198° (*hydrochloride*); 4 : 8-*diaminophenoxtellurine*, m. p. 156° (*hydrochloride*).

The constitutions of the nitro- and amino-derivatives were established by conversion of their 10 : 10-dichlorides, dinitrates, or similar salts into the corresponding diphenyl ethers by means of aqueous potassium hydroxide, which detaches the tellurium atom, replacing it by two atoms of hydrogen. M. CLARK.

Phenylgermanium derivatives. C. A. KRAUS and L. S. FOSTER (J. Amer. Chem. Soc., 1927, 49, 457—467).—Germanium tetraphenyl is obtained in 93% yield by a method analogous to that applied by Chambers and Scherer (A., 1926, 629) to the preparation of tin tetraphenyl. It has m. p. 235·7°, and is white when pure (cf. Morgan and Drew, *ibid.*, 1925, i, 1197). When boiled with bromine in carbon tetrachloride, it affords triphenylgermanium bromide, m. p. 138·7°, which yields triphenylgermanium oxide on hydrolysis with water or alkalis, and is converted by liquid ammonia into *triphenylgermanylamine*, $(GePh_3)_3N$. Hexaphenyldigermane (cf. Morgan and Drew, *loc. cit.*) is converted into sodium triphenylgermanide by sodium in liquid ammonia, and yields triphenylgermanium bromide when treated with bromine in carbon tetrachloride. *Triphenylgermanium fluoride*, m. p. 76·6°, obtained by evaporating the above oxide with hydrofluoric acid, is the most stable of the triphenylgermanium halides. *Triphenylgermanium iodide*, m. p. 157°, obtained by agitating a chloroform solution of the oxide with aqueous hydriodic acid, is unstable in air and in light petroleum solution. *Sodium triphenylgermanide*, obtained as above, crystallises with $3NH_3$, and is strongly ionised in liquid ammonia solution, in which it is readily oxidised to *sodium triphenylgermanolate*, $NaO{\cdot}GePh_3$, m. p. not below 250° (from liquid ammonia) or m. p. about 100° (from light petroleum). Treatment of the latter with water affords *triphenylgermanol*, m. p. 134·2°, above which it loses water with formation of the oxide. Ammonium bromide in liquid ammonia converts sodium triphenylgermanide into *triphenylgermane*, $GeHPh_3$. This exists in two forms, (α) m. p. 47°, and (β) m. p. 27° (monotropic relationship), and is stable at 250°. It gradually oxidises in air, and reacts with halogens or with strong halogen acids to form triphenylgermanium halides. It is reduced by sodium in liquid ammonia, with formation of sodium triphenylgermanide and disodium diphenylgermanide. Treatment of sodium triphenylgermanide in liquid ammonia with trimethylstannyl bromide affords *trimethylstannyltriphenylgermane*, $Me_3Sn{\cdot}GePh_3$, m. p. 88°. This reacts quantitatively with bromine to form the corresponding substituted tin and germanium bromides, but does not appear to dissociate in boiling benzene. F. G. WILLSON.

Mercuration in the aromatic series. VI. Mercurated derivatives of *o*-cresol. E. MAMELI (Gazzetta, 1926, 56, 948—958; cf. A., 1922, i, 695, 1080—1083).—Mercuration of *o*-cresol is most satisfactory in aqueous acetic acid, and gives 50·3—62·3% of o-*cresol*-4-*mercuriacetate* (I), m. p. 153—155°, decomp. 186—190°, 13·4—20·7% of o-*cresol*-6-*mercuriacetate* (II), m. p. 123—125°, decomp. 191°, and 2·6—7·0% of o-*cresol*-4 : 6-*dimercuriacetate* (III), m. p. 192—195° (decomp.), which is obtained in larger quantities by raising the temperature, and in good yield when 2 mols. of mercuric acetate are employed. Benzenediazonium chloride reacts with (I) to give phenyldisazo-*o*-cresol (Nolting and Kohn, A., 1884, 902). Treatment of (I) with bromine gives 4-bromo-*o*-cresol; of (II), 6-bromo-*o*-cresol. All three compounds on nitration yield 4 : 6-dinitro-*o*-cresol. o-*Cresol*-4-*mercurichloride*, m. p. 200—202° (decomp.), -6-*mercurichloride*, m. p. 160—162° (decomp.), and -4 : 6-*dimercurichloride*, m. p. 210—212° (decomp.), and the corresponding *mercurinitrates*, m. p. 212—213°, 208—210°, and 222°, respectively (decomp.), and *mercurisulphates* have been obtained. E. W. WIGNALL.

Nuclein metabolism. XV. Hydrolysis of thymus-nucleic acid with methyl-alcoholic hydrogen chloride. XVI. Action of human intestinal juices on thymus-nucleic acid. S. J. THANNHAUSER and G. BLANCO (Z. physiol. Chem., 1921, **161**, 116—125, 126—130; cf. Thannhauser and Ottenstein, A., 1921, i, 521).—XV. With the view of stabilising as a methylglucoside any carbohydrate present, dry thymus-nucleic acid is heated with hydrogen chloride in absolute methyl alcohol for 48 hrs. at 100°. Hydrochlorides of guanine and adenine separate out on cooling, and the diluted filtrate, after removal of phosphoric and hydrochloric acids as silver salts (together with a non-carbohydrate which gives the orcinol test), contains a mixture of pyrimidine nucleotides. Brucine salts of a cytosine–hexosediphosphoric acid, m. p. 220—222° (*brucine* salt), a cytosine–hexosephosphoric acid, m. p. 215—216°, a thymine–hexosediphosphoric acid, m. p. 195—196°, all previously prepared by hydrolysis with picric acid (*loc. cit.*) are obtained from the mixture (the higher m. p. are confirmed by purification of the earlier products). Cytosine, but no carbohydrate or methylglucoside, could be detected after removal of these nucleotides, and it is concluded that the purines of animal nucleic acid are not attacked in the molecule by means of a nucleotide linking.

XVI. Thymus-nucleic acid, fermented with human intestinal juices under a thick toluene layer at 37° for 3 days with hourly shaking, yields cytosine- and thymine–hexosediphosphoric acids (brucine salts, m. p. 120—121° and 250°, respectively) and adenine, charring at 206°. C. HOLLINS.

Proteins. IV. Preparation of rice-glutelin. V. Point of optimum flocculation of rice glutelin. K. KONDO and T. HAYASHI (Mem. Coll. Agric., Kyoto Imp. Univ., 1926, 37—53, 55—69).—IV. The molecule of rice-glutelin having been found susceptible to change in 0·2% sodium hydroxide solution, the authors have modified the usual technique of isolating proteins; 0·5*N*- instead of 10% (2*N*-) sodium chloride is used to extract the globulin, albumins, etc., 0·05*N*-sodium hydroxide to dissolve the glutelin, and 0·0o*N*-acetic acid to flocculate it. The nitrogen distribution figures for the anhydrous protein so prepared are tabulated.

V. Maximum flocculation and precipitation of rice-glutelin (cf. *supra*) occurs in dilute sodium acetate solution, the reaction of which is near absolute neutrality. The reaction of the solution, in which maximum flocculation of the protein takes place, changes after the addition of the protein. Examining the factors that may be responsible for this, the conclusion is reached that the protein cannot completely take the form $NH_2{\cdot}R{\cdot}CO_2H$

in the presence of salt in the solution, *i.e.*, the protein cannot behave as an isoelectric ion in presence of salt. Applying these considerations to the theory, it is further concluded that it is impossible to determine the isoelectric point of a protein difficult of solution, *e.g.*, casein or rice-glutelin, by the usual method. Determination by this customary method gives an apparent isoelectric point, which must be differentiated from the theoretical value. W. Robson.

Proteins. VI. Influence of salts on the point of optimum flocculation of rice-glutelin. K. Kondo, T. Hayashi, and T. Matsushita (Mem. Coll. Agric., Kyoto Imp. Univ., 1926, 71—81).—Results of the study of the influence of sodium acetate, sodium chloride, potassium chloride, and lithium chloride on solutions of rice-glutelin, made according to the procedure described above, show that these salts carry the optimum point of flocculation to the acidic side, and that the apparent isoelectric reaction of a protein difficult of solution is variable according to the salt used and its concentration. W. Robson.

Proteins. VII. Refractive indices of protein solution. I. K. Kondo and T. Hayashi (Mem. Coll. Agric., Kyoto Imp. Univ., 1926, 83—94).—In contradistinction to the theory propounded by Robertson and by Wington, the authors conclude, from their results, that the refractive indices of solutions of sodium rice-glutelinate or sodium caseinate are not linearly related to their concentrations. The authors, moreover, maintain that the determination of the nitrogen-equivalent-refractivity of the protein indicates the degree of dissociation of the protein salt, and conclude that to an ampholyte such as protein belong different nitrogen-equivalent-refractivities, according as the protein behaves as a cation or an anion. W. Robson.

Rate of hydrolysis of solutions of proteins in acids as measured by the formation of amino-nitrogen. D. M. Greenberg and M. F. Burk.—See this vol., 213.

Analysis of proteins. VIII. Determination of cystine in the modified Van Slyke method. R. H. A. Plimmer and J. Lowndes (Biochem. J., 1927, **21**, 247—253).—97% of pure cystine is precipitated by phosphotungstic acid. On boiling with acids it loses 7% of its nitrogen and only 40% is then precipitated by phosphotungstic acid. The amounts of cystine sulphur in the egg-proteins and caseinogen have been determined. The presence of another sulphur compound is indicated. A crystalline precipitate consisting in part of arginine, possibly racemic, was formed in the monoamino-fractions of egg-proteins and caseinogen on keeping for more than 15 months. The sulphur of cystine can be determined in the presence of phosphotungstic acid by a modification of the Benedict method of sulphur determination. S. S. Zilva.

Separation and determination of 2 : 5-diketopiperazines in presence of amino-acids and peptides. A. Blanchetiere (Bull. Soc. chim., 1927, [iv], **41**, 101—110).—Siegfried's carbamate reaction (A., 1905, ii, 332; 1906, i, 144) can be utilised for the determination of diketopiperazines in presence of amino-acids and peptides, with an experimental error of up to 10%. The amino-acids are precipitated quantitatively and the peptides almost quantitatively, acetone in both cases giving better results than 70% alcohol as used by Schryver (*ibid.*, 1921, i, 182; 1925, i, 89). Acetone, however, causes difficulties in the Kjeldahl determination of the nitrogen remaining in solution (from which figure the proportion of diketopiperazines is calculated). Details of the determination are given. The maximum experimental error (10%) is obtained with diketopiperazines such as *cyclo*glutamylglutamic acid which are more readily hydrolysed by barium hydroxide. Proteins such as egg-albumin are not appreciably hydrolysed by barium hydroxide under these conditions. R. Brightman.

Determination of arginine in pure proteins and tissues by a modification of Jansen's method. A. Bonot and T. Cahn (Compt. rend., 1927, **184**, 246—247).—Arginine may be accurately determined by a modification of the method of Jansen (A., 1917, ii, 184), the arginine being decomposed by arginase in a medium of exactly p_H 9·9, the carbamide formed being precipitated by means of a 10% methyl-alcoholic solution of xanthydrol, and weighed as dixanthylcarbamide. Full details are given, the method giving results accurate within 2%. J. W. Baker.

Sources of error in organic elementary analysis. III. Rubber, cork, and tap lubricants. J. Lindner (Ber., 1927, **60**, [*B*], 124—129; cf. this vol., 66, 166).—In three cases investigated, the errors introduced into the carbon values by the volatilisation of organic substances from the rubber were found to be very slight. Errors introduced by the ability of rubber to absorb foreign organic matter are more serious; even very volatile compounds are most tenaciously retained. Penetration of carbon dioxide from the atmosphere through the rubber causes perceptible error only with very long tubes. Cork absorbs moisture and carbon dioxide and is not more suitable than rubber for joining the combustion tube with the absorption apparatus. The common tap lubricants absorb carbon dioxide and may cause appreciable error if injudiciously applied. Heavy mineral oils emit appreciable amounts of carbon dioxide to the atmosphere. H. Wren.

Organic micro-combustion. G. Kemmerer and L. T. Hallett (Ind. Eng. Chem., 1927, **19**, 173—176).—Pregl's micro-combustion method is modified with regard to control and raising of the temperature of the furnace by substitution of an electric furnace built in sections. Further, the gas train is simplified by elimination of the air train to wash oxygen from the apparatus; the pyrex combustion tube is replaced by a silica tube. Micro-absorption tubes are used which are capable of being sealed by drops of mercury and on rotating through 90° allow the mercury to fall back into little pockets to leave free passage for air. Phosphoric oxide was the most satisfactory drying agent, whilst ascarite followed by 1 cm. layer of phosphoric oxide was used in the carbon dioxide

tubes. Water residues may be successfully analysed in this apparatus. D. G. HEWER.

Pyridine test as quantitative method for determination of small amounts of chloroform. W. H. COLE (J. Biol. Chem., 1926, **71**, 173—180).—The pink colour obtained by heating solutions containing chloroform with pyridine in presence of sodium hydroxide (cf. Ross, A., 1924, ii, 352) has been made the basis of a colorimetric method for the determination of chloroform in aqueous solution in concentrations of 0·1 to 0·0001% with an error of ±1%. Chloroform in animal tissues (in the absence of blood) may be determined by extraction of the material with acidulated distilled water, and direct application of the colorimetric method to the extract. If blood be present, the chloroform must first be separated by distillation, in which case the determination is not so accurate. C. R. HARINGTON.

Determination of ethyl iodide. I. STARR, jun., and C. J. GAMBLE.—See below.

Precipitation of bases as silver compounds. A. KRESEL (Z. physiol. Chem., 1926, **161**, 147—148).—The inconveniences of the introduction of nitric acid when silver nitrate is used for the precipitation of bases, and of the large volume necessary when silver sulphate is substituted, are avoided by using freshly-precipitated silver oxide in presence of sulphuric acid. Aspartic acid is readily separated from phenylalanine, and nuclein bases from "hexone" bases. C. HOLLINS.

Biochemistry.

Aerobic and anaerobic metabolism of the common cockroach (*Periplaneta orientalis*). II. W. K. SLATER (Biochem. J., 1927, **21**, 198—203; cf. this vol., 66).—After a period of anaerobiosis the cockroach not only uses an excess of oxygen, but also retains a considerable volume of carbon dioxide. The oxygen debt and the carbon dioxide retention are related through the removal of lactic acid. S. S. ZILVA.

Oxygen consumption of the kidney. K. TAMURA, S. WATANABE, and H. KABURAKI (Proc. Imp. Acad. Tokyo, 1926, **2**, 431—433).—In contrast to the conclusions of Barcroft and his associates and of Tashiro and Abe, the authors find that the oxygen consumption of the resting kidney of rabbits shows neither appreciable variations in different animals nor time variations in the same individual. J. M. GULLAND.

Colorimetric determination of the oxidation of hæmocyanin. L. HOGBEN (Nature, 1927, **119**, 122—123).—Polemical (cf. Stedman and Stedman, A., 1926, 1164). A. A. ELDRIDGE.

Determination of minute amounts of ethyl iodide. Determination of blood flow by ethyl iodide. I. STARR, jun., and C. J. GAMBLE (J. Biol. Chem., 1927, **71**, 509—535).—Small amounts of ethyl iodide vapour in air may be determined by keeping the sample for 16 hrs. in contact with excess of standard silver nitrate in concentrated nitric acid, followed by titration by means of Volhard's method. A similar procedure may also be applied to dilute solutions of ethyl iodide in water and in blood (in the latter case after preliminary distillation of the ethyl iodide). The average error of the method is 2·3%. The coefficient of distribution of ethyl iodide between air and water is 2·7; that between air and normal whole blood is 7·6; the latter figure is reduced in the case of plasma and of anæmic whole blood. The method of Henderson and Haggard (Amer. J. Physiol., 1925, **73**, 193) for the determination of blood flow is criticised both on the ground of the inaccuracy of their method of determining ethyl iodide and also because the rate of destruction of ethyl iodide in the blood has been found to be much slower than was previously supposed. C. R. HARINGTON.

Heat denaturation of proteins. IV. Free basic and acidic groups of fresh and denaturated hæmoglobin. P. S. LEWIS (Biochem. J., 1927, **21**, 46—53).—In the equivalent of hæmoglobin (mass = 16,660) there are 24 or 25 free basic and 16 acidic groups. Heat denaturation is without effect on the free basic or acidic groups of the hæmoglobin molecule, and consequently no rupture of the polypeptide linking can take place in the process. S. S. ZILVA.

Reaction between globin and hæmatin. R. HILL and H. F. HOLDEN (J. Physiol., 1926, **61**, Proc. xxii).—At p_H 5—9, globin reacts with hæmatin, forming methæmoglobin. The oxyhæmoglobin thence obtained is spectroscopically indistinguishable from the original oxyhæmoglobin. A. A. ELDRIDGE.

Mechanism of blood clotting. I. N. KUGELMASS (Third Colloid Symposium Monograph, 1925, 158—207).—Fibrin formed as an amphoteric protein has a hydrogen-ion concentration (C_H) lower than the initial C_H of the mixture of all components necessary and sufficient for clotting. The diminution in the C_H on coagulation is the greater the higher is the original C_H. In 24 hrs. at 38°, clotting takes place at p_H 5—8, being optimal at p_H 7. Diminution of electrical conductivity, partly due to loss of ionic calcium, occurs during clotting. The effects of calcium buffers are considered. The speed of coagulation is determined by serozyme, a highly dispersed, thermolabile catalyst. A "nephelelectrometer" is used to determine the degree of dispersion in colloidal systems. Coagulation is an autocatalytic process of two stages. A torsion viscosimeter and an inverse ultrafilter are described. CHEMICAL ABSTRACTS.

Cholesterol content of normal human plasma. I. J. A. GARDNER and H. GAINSBOROUGH (Biochem. J., 1927, **21**, 130—140).—The free and ester cholesterol contents of the plasma of 48 normal individuals have been determined. The individuals differed widely both in the total cholesterol and in the ratio of the

so-called free cholesterol to cholesterol in the form of esters. These variations could not be ascribed to the direct absorption of varying quantities of cholesterol from the food. S. S. ZILVA.

Cholesterol content of normal human plasma. II. Attraction of the proteins of plasma for sterols. J. A. GARDNER and H. GAINSBOROUGH (Biochem. J., 1927, **21**, 141—147).—About 80% of the cholesterol and cholesteryl esters of the plasma were accounted for in the precipitation of its various protein fractions with ammonium sulphate. By repeated reprecipitation and redissolution of these fractions, however, the total plasma cholesterol retained in the proteins was reduced to 16·36%. The greater portion of this cholesterol was associated with the euglobulin. S. S. ZILVA.

Source of error in the determination of carbamide in blood. E. KAHANE (Bull. Soc. chim., 1927, [iv], **41**, 110—113).—The high percentage of protein present in blood plasma renders a correction necessary for the volume change occasioned by the size of the protein precipitate, when methods of determining carbamide, valid for urine, are applied to its determination in blood. The correction factor 1·936 in place of 2·0, as generally used, is proposed for calculating the carbamide concentration in the plasma from the concentration determined in the clear filtered liquid. Alternatively, the plasma may be diluted sufficiently to render this correction insignificant (cf. Nicloux and Welter, A., 1921, ii, 523; 1922, ii, 170). R. BRIGHTMAN.

Micro-determination of chlorine in whole blood-serum or corpuscles. F. H. SMIRK (Biochem. J., 1927, **21**, 31—35).—The organic matter of the blood is destroyed by ammonium persulphate and concentrated nitric acid, and the chlorine precipitated as silver chloride with excess of silver nitrate. The excess is titrated against alcoholic ammonium thiocyanate solution with concentrated ferric iron alum as indicator. The maximum error is usually 4 mg. of sodium chloride per 100 c.c. of blood. Larger errors in the third place of decimals occur in about one tenth of the samples. S. S. ZILVA.

Micro-determination of iron in blood. F. H. SMIRK (Biochem. J., 1927, **21**, 36—39).—The organic matter of the blood is destroyed with ammonium persulphate and nitric acid and the iron is determined colorimetrically as ferric thiocyanate against an artificial standard consisting of a mixture of cochineal, methyl-red, and hydrochloric acid. 0·2 C.c. of blood can be employed in this method. S. S. ZILVA.

Kinetics of hæmolytic systems. II. Series of Ryvosh. III. Time-dilution curves and zones of action. E. PONDER (Biochem. J., 1927, **21**, 56—65, 119—126).—II. The series of Ryvosh (Pflüger's Arch., 1907, **116**, 229) has been reinvestigated quantitatively and the results are mainly confirmed.

III. A series of tables comparing experimental and calculated results for different hæmolytic systems is given. A method for determining the dimensions of the zone of action round the cells of a hæmolytic system is described. The radii of the zones are determined for the cells of different animals, and it is shown that the cells arranged in order of increasing size of zone of action fall into Ryvosh's series. The volume of the zone of action is proportional to the resistance of the cell to the lysin. S. S. ZILVA.

Changes in the amino-acids in the proteins of the hen's egg during development. R. H. A. PLIMMER and J. LOWNDES (Biochem. J., 1927, **21**, 254—258).—Determination of the amino-acids in the hen's egg during development by the modified Van Slyke method (A., 1926, 313) has shown an increase of about 2% in the diamino-nitrogen of which the arginine increases about 1% of the total nitrogen of the egg proteins. The monoamino-acid nitrogen decreases by about 4% during development with a corresponding decrease in the amino-nitrogen. S. S. ZILVA.

Stomach oil of the Fulmar petrel (*Fulmarus glacialis*). O. ROSENHEIM and T. A. WEBSTER (Biochem. J., 1927, **21**, 111—118).—The stomach oil is not a glyceride, but a liquid wax of similar composition to sperm oil. It gives the arsenious chloride reaction approximately to the same degree as cod-liver oil, and its content of vitamin-*A* is of the same order as its colour value. The oil also contains vitamin-*D*. S. S. ZILVA.

Echinochrome. R. K. CANNAN (Biochem. J., 1927, **21**, 184—189).—Echinochrome from the eggs, perivisceral fluid, and test of *Arbacia punctulata* is not a dissociable compound in combination with molecular oxygen, but is the oxidant of a reversible oxidation–reduction system. It therefore probably functions as an "activator" rather than as a "carrier" of oxygen if it takes part in any respiratory mechanism. The electrode potentials of the system have been measured over a p_H range 2·2—9·76. The normal electrode potential is +0·1995. The rate of oxidation of reduced echinochrome by atmospheric oxygen is too great to be measured by the ordinary technique. S. S. ZILVA.

Inorganic phosphate and a labile form of organic phosphate in the gastrocnemius of the frog. P. EGGLETON and G. P. EGGLETON (Biochem. J., 1927, **21**, 190—195).—The supposed inorganic phosphate of muscle is in certain conditions mainly organic phosphate, "phosphagen," in a very labile condition which becomes hydrolysed during the determination by the acidity of the reagents (Neumann's, Embden's, or Briggs' method). Determinations performed in slightly alkaline solution yield more correct results in such cases. In a resting frog's gastrocnemius 70 mg. of phosphorus per 100 g. of muscle out of the 100 mg. of "inorganic" phosphorus obtained by the Briggs or Embden method are of "phosphagen" origin. In rapidly induced fatigue, the true inorganic phosphate is doubled at the expense of the "phosphagen," but considerably more "phosphagen" disappears than could account for the rise in inorganic phosphate. When muscle goes into rigor, the "phosphagen" disappears entirely and the inorganic phosphate rises to about four times the resting value. S. S. ZILVA.

Sensitising and stabilising action of the skin on colloidal solutions. A. JANEK and B. JIRGENSONS

(Biochem. Z., 1927, **180**, 193—200).—The non-colloid portion of a solution obtained by rubbing two clean fingers together in distilled water and filtering sensitises colloidal solutions of ferric hydroxide, silver, and arsenic trisulphide, whereas the colloidal portion sensitises ferric hydroxide solution, but stabilises the silver sol and the arsenic trisulphide sol.

P. W. CLUTTERBUCK.

Biochemistry of tooth growth. Y. MATSUDA (J. Biol. Chem., 1927, **71**, 437—444).—During growth the ash content of the incisor teeth of rats increases, whilst the water content decreases, the content of organic matter showing no marked change. The alterations are continuous in character, except for a break which occurs at puberty. The calcium and phosphorus content of the ash does not alter with age, but the magnesium tends to increase. Minor differences are observed between the upper and lower incisors.

C. R. HARINGTON.

Biochemistry of the aqueous humour. S. DUKE-ELDER (Biochem. J., 1927, **21**, 66—77).—All the colloidal substances found in the normal aqueous humour are in much smaller concentration than in the serum; the proteins, however, are found in the same proportion as in the blood. The diffusible non-dissociated substances are partitioned between serum and the aqueous humour in approximately equal amounts, whilst in the case of dissociated diffusible substances, the latter fluid contains an excess of acidic radicals. The sugar content of the aqueous humour lies between that of arterial and venous plasma. Diffusible substances find their way freely into the aqueous humour when injected intravenously. Only traces of colloidal substances diffuse in this way. Aqueous humour seems, therefore, to be a dialysate of the capillary blood. Evidence is produced to show that this is also the case in abnormal aqueous humour.

S. S. ZILVA.

Constituents of hen bile. A. WINDAUS and A. VAN SCHOOR (Z. physiol. Chem., 1926, **161**, 142—146; cf. Windaus, Bohne, and Schwarzkopf, A., 1925, i, 405).—From the products of hydrolysis of 150 g. of hen bile with 10% potassium hydroxide at 135—140° there are isolated succinic acid (0·4 g.), aliphatic acids (60 g.), a *hydroxystearic acid* (6 g.), m. p. 81—82° (*sodium* salt; *methyl* ester, m. p. 52—53°), which is oxidised by chromic-acetic acid to a *ketostearic acid*, m. p. 83—84° (*sodium* and *potassium* salts; *methyl* ester, m. p. 48°), reducible by Clemmensen's method to stearic acid, m. p. 79—80°, and a bile acid identical with the chenodeoxycholic acid obtained from goose bile (*loc. cit.*) and human bile (Wieland and Reverey, *ibid.*, 181). Hydroxystearic acid is absent from goose bile.

C. HOLLINS.

Electrometric titration of gastric juice as a method for the determination of its degree of buffering. K. A. SOUKAREV (Biochem. Z., 1927, **180**, 117—126).—The mean p_H of pure gastric juice at the isoelectric point, of dog and of man, either fasting or after a test meal, is a little less than 6·2. The total hydrochloric acid may therefore be determined by titration of juice to p_H 6·2. The following quantities characterise the degree of buffering of the juice: (*a*) the ratio free hydrochloric acid : p_H calculated for the total hydrochloric acid, which if greater than 0·5 indicates poor buffering power and inversely; (*b*) the number of c.c. of 0·1*N*-sodium hydroxide used to increase the p_H from 6·2 to 8·5 (*i.e.*, from the isoelectric point to the point of colour change of phenolphthalein), which in well-buffered juice lies between 5 and 14, but in poorly-buffered solutions lies between 0·5 and 5; (*c*) the maximal increase in p_H on adding 1 c.c. of 0·1*N*-sodium hydroxide, which for well-buffered solutions is about 1, but for poorly-buffered juice may lie between 2 and 3. The buffering power of pure juice from the isolated stomach is remarkably constant.

P. W. CLUTTERBUCK.

Electrometric determination of small amounts of hydrochloric acid in gastric juice. K. A. SOUKAREV (Biochem. Z., 1927, **180**, 127—131).—Electrometric titration (see preceding abstract) is used to determine small amounts of the hydrochloric acid in cases of subacidity and small changes in its concentration.

P. W. CLUTTERBUCK.

Milk of the Monotreme. H. R. MARSTON (Austral. J. Exp. Biol., 1926, **3**, 217—220).—The absence of glycerides of the volatile fatty acids from the milk fat is the only peculiarity noted.

W. ROBSON.

Variations in chemical composition of normal human colostrum and early milk. M. F. LOWENFELD, S. T. WIDDOWS, M. BOND, and E. I. TAYLOR (Biochem. J., 1927, **21**, 1—15).—The protein and ash content of the milk vary regularly according to the day of lactation, being very high in *primiparæ*, less so in *multiparæ* on the second and third days, and falling rapidly during the first week, to reach an approximately normal level. The sugar content varies also according to the day of lactation, but inversely as the protein and the ash. The sugar content of the milk appears to be higher at the beginning than at the end of a feed. The fat content of the milk varies only according to the physical conditions of the breast and the extraction of the milk. In *primiparæ* the general behaviour is reversed in the first days of lactation. The calcium content of the milk varies up to the fifteenth day with the individual. There is a suggestion of the possibility that the protein content rises slightly at the end of a single feed.

S. S. ZILVA.

Iron in nutrition. III. Effects of diet on iron content of milk. C. A. ELVEHJEM, R. C. HERRIN, and E. B. HART (J. Biol. Chem., 1927, **71**, 255—262).—Whilst the iron content of the milk of cows and goats showed considerable variations from one animal to another, it could not be increased by addition of ferric oxide, ferrous sulphate, or combinations of these with fresh cabbage (cf. A., 1925, i, 1354) to the diet. Young rabbits, when fed on the milk of animals treated in these ways, developed the same nutritional anæmia as has been observed to result from a diet of ordinary cow's milk.

C. R. HARINGTON.

Phosphorus compounds of milk. III. Dephosphorised caseinogen. Action of alkali on caseinogen. C. RIMINGTON (Biochem. J., 1927, **21**, 204—207).—The amide nitrogen of "dephosphorised"

caseinogen, *i.e.*, the protein produced by treating caseinogen with 0·25*N*-sodium hydroxide for 24 hrs. at 37° (Rimington and Kay, A., 1926, 970), is distinctly lower than that of caseinogen. There is also some decrease in the arginine-nitrogen accompanied by an increase in the lysine + cystine fraction of the "dephosphorised" protein. The "dephosphorised" compound is only slowly attacked by proteolytic enzymes and is not coagulated by rennin.

S. S. Zilva.

Phosphorus nucleus of caseinogen. S. Posternak (Compt. rend., 1927, **184**, 306—307).—Hydrolysis of caseinogen with a very active trypsin yields α-, β-, and *γ-lactotyrins* of compositions $C_{64}H_{111}O_{43}N_{15}P_4$, $C_{87}H_{116}O_{44}N_{16}P_4$, and $C_{72}H_{124}O_{47}N_{18}P_4$, respectively. The α-compound, $[\alpha]^{\text{w}5}$ −67·84°, after long-continued hydrolysis with 25% hydrochloric acid, yields glutamic acid (3 mols.), aspartic acid (0·6 mol.), *iso*leucine (3 mols.), serine (3 mols.), and phosphoric acid (4 mols.), small quantities of dipeptides, larger quantities of tripeptides, and some tetrapeptides all containing serine, the decomposition being represented by the equation $C_{64}H_{111}O_{43}N_{15}P_4 + 18H_2O = 3C_5H_9O_4N + C_4H_7O_4N + 4C_6H_{13}O_2N + 7C_3H_7O_3N + 4H_3PO_4$. Hence the phosphorus-containing nucleus of caseinogen is probably formed of four serine-phosphoric acid residues. J. W. Baker.

Determination of chlorine in milk. A. D. Husband and W. Godden (Biochem. J., 1927, **21**, 259—261).—It is essential for accuracy that the protein be removed before the addition of the silver nitrate in the determination of chlorine in milk volumetrically by precipitation of the chlorine as silver chloride. S. S. Zilva.

Total carbohydrate content of normal urine. B. Glassmann (Z. physiol. Chem., 1927, **162**, 149—154).—The total carbohydrate in the fasting urines of twelve normal individuals of varying ages, determined by the colorimetric micro-method of the author (A., 1926, 192), varies from 0·48% to 0·94%, with an average of 0·66% (calculated as dextrose). This value is determined by the polysaccharides and urinary dextrin, and no part is contributed by nucleoproteins. The intake of food causes fluctuations, slight rises following breakfast and the mid-day meal. Age has no influence on the total carbohydrate content. Normal urine and whole blood contain about the same amount of total carbohydrate after hydrolysis (cf. *ibid.*, 1169). A. Wormall.

Nature of urinary sugars. S. H. Eagle (J. Biol. Chem., 1927, **71**, 481—495).—By the use of sufficiently large amounts of yeast, dextrose in urine, up to 0·4%, can be completely fermented in 40 min. at 37—38°. After treatment of normal urine with Lloyd's reagent, no fermentable sugar was ever detected in the filtrate, although dextrose added to the filtrate was rapidly fermented; normal urine does not, therefore, contain any dextrose. It is thought that the positive results obtained by previous workers have been due to the bacterial decomposition, during the prolonged periods of fermentation employed, of some substances which are removed by the treatment with Lloyd's reagent. Ingestion of dextrose in amounts below that which causes an actual glycosuria, and ingestion of an ordinary meal, both cause an increase in the excretion of non-fermentable reducing substances. Alimentary glycosuria in a normal individual may continue after the blood-sugar has fallen below the original threshold value.

C. R. Harington.

Picrate obtained from normal urine by the method of Findlay and Sharpe. F. D. White (J. Biol. Chem., 1927, **71**, 419—427).—Application of the method of Findlay and Sharpe (Quart. J. Med., 1920, **13**, 433) to normal human urine led to the isolation of no dimethylguanidine picrate, as claimed by these workers. A picrate was indeed obtained which, on purification, proved to be potassium creatinine picrate. The method of Findlay and Sharpe is therefore not applicable to the determination of guanidines in urine. C. R. Harington.

Lipin excretion. IV. Relation of bile to fæcal lipins. Cholesterol metabolism. W. M. Sperry (J. Biol. Chem., 1927, **71**, 351—378).—Following artificial exclusion of bile from the intestine, dogs, on a lipin-free diet, excrete 1·5—4·5 times as much lipin in the fæces as they do under normal conditions; the composition of the fæcal lipins is, however, very similar to that of the fæcal lipins of normal dogs under the same dietary conditions. This indicates that the source of the fæcal lipins (including cholesterol) is the same in each group of animals and is therefore not the bile; further support is thus afforded to the view that such cholesterol as passes into the intestine with the bile is normally completely reabsorbed, but not to the author's recently expressed opinion (A., 1926, 859) that a function of the normal fæcal lipin excretion is the removal from the body of waste sterols. C. R. Harington.

Changes in inorganic constituents of the blood following adrenalectomy in cats and rabbits. E. J. Baumann and S. Kurland (J. Biol. Chem., 1927, **71**, 281—302).—Following adrenalectomy, there was observed in cats and rabbits a fall in the sodium and chloride content of the blood plasma; in the cat, the potassium, magnesium, and sometimes the calcium were increased in amount. No alkalosis was observed. C. R. Harington.

Proteins having the Bence-Jones reaction. Reversibility of heat coagulation. R. Willheim (Biochem. Z., 1927, **180**, 231—246).—Bence-Jones proteins must be regarded as different individuals having in common a heat coagulability at 60° with subsequent dissolution at 100°. The redissolution occurs only in presence of other substances, chiefly electrolytes. If the heat-coagulated protein is repeatedly dissolved by boiling and precipitated by cooling, a portion—modification *B*—remains in solution, but can be reconverted into a heat-coagulable substance by passing in carbon dioxide or adding a weak acid. There appears, therefore, to be a reversibility of heat coagulation in presence of electrolytes. Modification *B* becomes increasingly ionised during heating and shows cathodic migration, whereas the original protein shows anodic migration. Similarly, the coagula of serum proteins, when heated with potassium thiocyanate, or with alkali salicylates, benzoates, or phthalates, can be dissolved, and after

removal of the salts by dialysis the protein remains in solution in coagulable form.

P. W. CLUTTERBUCK.

Effect of extirpation of the liver on the cholesterol metabolism of dogs. Appearance of a yellow pigment in the blood. E. ENDERLEN, S. J. THANNHAUSER, and M. JENKE (Arch. exp. Path. Pharm., 1927, **120**, 16—24).—In those animals that survived the operation for the longest periods there was a notable increase in the cholesterol esters of the whole blood. The increase was much less marked in the serum. The reddish-yellow colour of the serum of such animals is not due to bilirubin, but to a new pigment, *xanthorubin*. This may be extracted by chloroform or, from acid solution, by ether. In the spectrum of the ethereal solution, two weak bands are found at 552—535 and 512—483 The instability of the pigment renders its solubilities inconstant.

R. K. CANNAN.

Preferential utilisation of carbohydrates in diabetes. W. R. CAMPBELL and J. MARKOWITZ (J. Clin. Investn. [Proc.], 1926, **2**, 608).—No preferential utilisation of lævulose, insulin, glycerol, or dihydroxyacetone occurred in depancreatised dogs.

CHEMICAL ABSTRACTS.

Theory of Lang's gold-sol reaction on the cerebrospinal fluid in syphilis and metalues of the central nervous system. E. EPSTEIN and H. RUBINSTEIN (Kolloid-Z., 1926, **40**, 307—318).—A discussion of the theory of Lang's reaction.

E. S. HEDGES.

Glycolytic power of cell-free extracts from tumour and other tissues. N. ALDERS, H. CHIARI, and D. LASZLO (Biochem. Z., 1927, **180**, 46—60).—A method is described for preparation of cell-free tissue filtrates which enables the testing after any time interval of the carbohydrate content without endangering sterility. In the great majority of cases, the sterile filtrates from mouse and tissue carcinoma showed glycolytic power, the amount being a very considerable part of the total glycolytic power of the tissue. The glycolytic agent of kidney and muscle-tissue of normal animals was detected in the filtrates, but the filtrate from liver pulp never showed activity.

P. W. CLUTTERBUCK.

Glutathione contents of malignant tumours, especially the Rous chicken sarcoma. H. YAOI and W. NAKAHARA (Proc. Imp. Acad. Tokyo, 1926, **2**, 449—456; cf. Hopkins, A., 1921, i, 635).—The nitroprusside test and determination by titration with 0·01*N*-iodine solution show that glutathione occurs in the Rous chicken sarcoma in negligible quantity, whilst it is present in abundance in other malignant tumours and normal tissues. These results are remarkable in view of the rapid growth of the Rous sarcoma, and its unique ability to withstand desiccation may be connected with the absence of glutathione.

J. M. GULLAND.

Carbohydrate metabolism. II. Influence of alkali phosphates and some other electrolytes on carbohydrate metabolism. B. KOBORI (Biochem. Z., 1927, **180**, 218—230).—The increased production of carbon dioxide which accompanies the normal metabolism of dextrose in rats is considerably reduced by administration with the carbohydrate, of alkali phosphates, calcium chloride, or sodium hydrogen carbonate. Similarly, phosphate inhibits the oxidation of calcium hexosediphosphate, dihydroxyacetone, sucrose, and rice starch. Lævulose, however, behaves differently, phosphate having little or no effect (cf. A., 1926, 539). P. W. CLUTTERBUCK.

Differences in chemical and biological behaviour of surviving muscle of different kinds of fish. I. Sea-fish. G. EMBDEN, H. J. DEUTICKE, E. LEHNARTZ, and H. PERGER. **II. Fresh-water fish.** G. MARTINO (Z. physiol. Chem., 1927, **162**, 155—171, 172—187).—I. The isolation of lactacidogen as the osazone compound is more difficult, and the yield less, with muscle of the cod, which dies quickly after removal from the water, than with that of the sole, which survives longer in the air. Thus there appears to be a causative relationship between the rapid disappearance of lactacidogen from cod muscle and the death of the fish in the air. There is a noticeable decrease in the inorganic phosphoric acid content of fresh sole muscle kept at 17° in a sodium hydrogen carbonate solution containing sodium fluoride, and this disappearance, due to synthesis of lactacidogen, is increased by the addition of glycogen. These changes are almost insignificant with apparently fresh cod muscle, and the difference in the two fishes is attributed to quicker changes in the muscle colloids of the cod. A small but significant disappearance of lactic acid takes place under anaerobic conditions after addition of sodium fluoride.

II. The rates of disappearance of inorganic phosphoric acid from trout and carp muscle are compared, using fresh muscle and muscle which has been kept for 2 hrs. in 2% hydrogen carbonate solution at 40—45°. The trout, which dies quickly after removal from the water, loses the power to cause disappearance of inorganic phosphoric acid much more quickly than does the carp, which survives longer in the air, thus supporting the contention of the preceding paper. The differences in biological behaviour of the two fishes are not due to differences in glycogen content, for these are approximately equal. A marked anaerobic disappearance of lactic acid in the fresh muscle pulp was observed after the addition of sodium fluoride in varying concentrations. A. WORMALL.

Significance of phosphorus in muscular contraction. P. EGGLETON and M. G. EGGLETON (Nature, 1927, **119**, 194—195).—Muscle tissue appears to contain an organic phosphorus compound, "phosphagen," readily yielding inorganic phosphate in determinations of the latter. Phosphagen, which is intimately connected with the chemical mechanism of contraction and may be "active" hexosemonophosphate, is stable in neutral or slightly alkaline solution. Whilst unstriated muscle contains about the same amount of genuine inorganic phosphate as does skeletal muscle, it appears not to contain phosphagen. Embden's observation of the disappearance of inorganic phosphate in a suspension of minced muscle in sodium fluoride solution is criticised.

A. A. ELDRIDGE.

Influence of diet on fat reserves. P. BELIN (Bull. Soc. Chim. biol., 1926, **8**, 1120—1150).—The

fat deposited in living organisms when the only available source of such fat is carbohydrate has an iodine value which is characteristic for each species. This result holds for organisms ranging from bacteria to mammals, and so it appears that the fat-forming process differs from species to species. If the diet is rich in fats with a low iodine value, the iodine value of the fats deposited is only slightly lower than the characteristic iodine value found when the same species is fed almost exclusively on carbohydrates. If, however, the fats administered have a high iodine value, the fats deposited have much above the characteristic iodine value, but not exceeding and usually somewhat below that of the fats administered. With such feeding, the fats of the egg in the case of fowls and of the embryo in the case of mammals have an iodine value lower than that of the fats deposited in the parent. W. O. KERMACK.

Fat metabolism. VIII. Behaviour of cetyl acetate in the animal body. R. MANCKE (Z. physiol. Chem., 1927, **162**, 238—263).—In a case of human chyluria, the administration *per os* of a solution of 50 g. of cetyl alcohol in olive oil produced no increase in the unsaponifiable matter of the fat in the urine, and no cetyl alcohol could be detected. The Reichert–Meissl value of the milk fat of goats and sheep, to which considerable amounts of cetyl acetate were given daily for 12 days, showed no variation which could be attributed to the presence of the ester, and the unsaponifiable matter of the milk fat contained no cetyl alcohol. A goose fed on a fat-deficient diet and given 20—25 g. of cetyl alcohol per day stored no cetyl acetate in the fat depots. After intravenous injection over 6 days of 16·5 c.c. of a 10% well-dispersed emulsion of cetyl acetate into a rabbit, or 51 c.c. of a 20% emulsion over 12 days into a dog, no unchanged cetyl acetate or either of its components could be detected in the organs or fat depots. The conclusion is reached that the ester is saponified in the blood-stream or on passing into the tissues and that the cetyl alcohol is probably oxidised to palmitic acid. The same oxidation process takes place in the intestinal epithelium or the lymphatics during absorption. A. WORMALL.

Comparative metabolism of aromatic acids. XI. Fate of diphenylacetic acid in the animal body. S. R. MIRIAM, J. T. WOLF, and C. P. SHERWIN (J. Biol. Chem., 1927, **71**, 249—253).—After administration of diphenylacetic acid to man, the dog, and the rabbit, the greater part of the substance can be recovered unchanged from the urine; in all cases there was, however, obtained a small amount of *diphenylacetylglycuronic acid*, m. p. 180—185° (decomp.), $[\alpha]^{20}$ −34·75°. *Diphenylacetylglycine* has m. p. 157°. C. R. HARINGTON.

Diet determinations. D. W. RICHARDS, jun., and A. F. COBURN (Arch. Int. Med., 1927, **39**, 93—97).—A nomographic diagram is given for the determination of the individual constituents of a diet when the total calorie requirement is known and the amount of one food constituent is fixed. C. R. HARINGTON.

Diet and assimilation of calcium. VIII. Calcium level and sunlight as affecting calcium equilibrium in milking cows. E. B. HART, H. STEENBOCK, H. SCOTT, and G. C. HUMPHREY. **IX. Influence of cod-liver oil on calcium assimilation in lactating animals.** E. B. HART, H. STEENBOCK, S. W. KLETZIEN, and H. SCOTT (J. Biol. Chem., 1927, **71**, 263—269, 271—280).—VIII. Milking cows, on a typical "summer diet," consisting largely of green grasses, remained in a negative calcium balance whether they were exposed to sunlight or not; the calcium balance could be made positive by addition of calcium carbonate to the diet. The results indicate that, whilst the supply of vitamin-*D* in such a diet is sufficient, the food should be supplemented with calcium salts.

IX. Administration of the unsaponifiable matter of cod-liver oil to lactating goats had no effect when the material was given in gelatin capsules; this result was apparently due to failure in absorption of vitamin-*D*, since the same material, administered in solution in maize oil (which was itself physiologically inert), improved the calcium assimilation considerably. The same effect could be obtained by feeding whole cod-liver oil provided that the animals were first accustomed to this material, so that loss of appetite did not result from its administration. C. R. HARINGTON.

Physiological effects of diets unusually rich in protein or inorganic salts. T. B. OSBORNE, L. B. MENDEL, E. A. PARK, and M. C. WINTERNITZ (J. Biol. Chem., 1927, **71**, 317—350).—Good growth in rats can be obtained on diets containing a large proportion of protein provided that sufficient fresh green food be given to maintain an adequate supply of vitamins. Neglect of the latter factor probably accounts for the failure of other workers to secure good growth under these conditions. The rats on the high protein diet had a higher concentration of non-protein nitrogen in the blood than the normal animals, but their urine showed no indications of nephritis; there was observed a marked hypertrophy of the kidneys, which manifested itself after a very short time, but was not associated with significant morbid anatomical changes (cf. Addis and others, this vol., 170). Addition of abnormally large amounts of various inorganic salts or of carbamide to an ordinary mixed diet failed to bring about a similar renal hypertrophy. Retrogression in the size of the kidneys was not observed on changing from a diet rich in protein to one poor in protein. C. R. HARINGTON.

Nutritional protein value of beef liver, heart, and kidney. H. H. MITCHELL and J. R. BEADLES (J. Biol. Chem., 1927, **71**, 429—435).—As determined on rats, the biological values of the proteins of beef liver, heart, and kidney are closely similar to one another, being somewhat higher than the values for beef and pork muscle, but lower than that of milk protein. C. R. HARINGTON.

Nutritive value of plastein. H. H. BEARD (J. Biol. Chem., 1927, **71**, 477—480).—Good growth was obtained in white mice which received the whole of their nitrogen in the form of plastein, prepared by the method of Wasteneys and Borsook (A., 1925, i, 102). C. R. HARINGTON.

Specific dynamic action of food. V. Influence of sodium phosphate on gaseous exchange after ingestion of meat. J. ABELIN and B. KOBORI (Biochem. Z., 1927, **180**, 211—217).—The increase in gaseous exchange in rats on ingestion of meat is considerably decreased by adding sodium phosphate to the food, an action analogous to the effect on carbohydrate metabolism (cf. A., 1926, 539).

P. W. CLUTTERBUCK.

Tryptophan feeding. I. C. S. HICKS (Austral. J. Exp. Biol., 1926, **3**, 193—202).—A diet lacking in tryptophan causes a falling off in heat production commensurate only with starvation wasting. Respiratory exchange measurements furnish no evidence that this amino-acid is required for the elaboration of the thyroid hormone. Tryptophan added to a synthetic diet differs in its action from that present in a normal protein diet. An addition of 2% or more of tryptophan per 100 g. of protein produces toxic symptoms.

W. ROBSON.

Feeding she-goats with glycine as a substitute for protein. J. WILLIGER (Biochem. Z., 1927, **180**, 156—192).—Glycine cannot replace protein in the diet. By feeding glycine, the percentage of dry matter of the fæces is increased and a considerable amount of nitrogen is retained probably as ammonia in the blood. Only in one case was a stimulation of the mammary gland found, the fat of the milk being increased for from 2 to 3 days.

P. W. CLUTTERBUCK.

Quantitative law of minimal nitrogen usage. E. F. TERROINE and H. MATTER (Compt. rend., 1927, **184**, 166—168).—Finding that the minimal nitrogen usage bears a constant relation to calories produced, the authors have enunciated the following law: the minimal nitrogen usage in the adult, per unit body-weight, is directly proportional to the minimal intensity of heat production.

W. ROBSON.

Behaviour of 2 : 5-diketopiperazines in the animal body. E. ABDERHALDEN and S. BUADZE (Z. physiol. Chem., 1927, **162**, 304—314).—Glycyl-*d*-alanyl anhydride and *dl*-leucylglycyl anhydride were administered *per os* to a dog. The former could not be detected unchanged in the urine, but glycyl-*d*-alanine was present, indicating the decomposition of this anhydride in the body. After feeding with *dl*-leucylglycyl anhydride, in keto- and enol-forms, four fifths of the amount given were recovered from the urine, and small amounts were detected in the fæces. The anhydride could be detected in the blood 1 hr. 20 min. after feeding, was at a maximum after 5 hrs., and disappeared in 8 hrs. The significance of these results in relation to the structure of proteins is discussed.

A. WORMALL.

Changes of metabolism under various conditions. I. Influence of adrenaline and pilocarpine on the excretion of nitrogenous substances. II. Influence of potassium and calcium on the excretion of nitrogenous substances. L. PINCUSSEN. (Biochem. Z., 1927, **180**, 132—135, 136—140).—I. [With A. WALTER.]—Injection of adrenaline in rabbits causes an increase in the urea-nitrogen (expressed as a percentage of the total nitrogen), whilst injection of pilocarpine appears slightly to decrease it.

II. [With E. COELHO.]—In rabbits on a diet poor in calcium, injection of calcium causes an increase in urea-nitrogen excreted, but injection of potassium has little effect.

P. W. CLUTTERBUCK.

Blood changes in strychnine convulsions. J. VON MIKÓ and T. PALA (Arch. exp. Path. Pharm., 1927, **119**, 273—284).—In strychnine convulsions, the blood calcium rises 25—30% above the normal. The red corpuscles increase, but the oxygen saturation and carbon dioxide content of the blood fall.

R. K. CANNAN.

ψ-Morphine. Separation and determination of morphine, ψ-morphine, and related substances. A. K. BALLS.—See this vol., 264.

Local anæsthetics and antipyretics of the thiophen series. H. STEIDLE (Arch. exp. Path. Pharm., 1927, **120**, 100—119).—Substitution of the benzoyl group in cocaine, eucaine, and stovaine by the radical of thiophen-2-carboxylic acid and the addition of the latter group to quinine and *p*-phenetidine reduced the toxicity of these substances without notably changing their pharmacological activity.

R. K. CANNAN.

Alcohol poisoning. II. E. KEESER and I. KEESER (Arch. exp. Path. Pharm., 1927, **119**, 285—290).—In contrast to chronic poisoning, there is no disturbance of protein metabolism in acute poisoning with alcohol. One hr. after administering 110 c.c. of alcohol there was a fall in the cholesterol, phosphatides, and fatty acids and bile pigment in the serum, followed in 10 hrs. by an excessive rise above normal. In acute poisoning there was an increased activity of the lipase, phosphatase, catalase, and oxydase of the serum. In chronic poisoning, the activity of these enzymes (with the exception of phosphatase) was decreased.

R. K. CANNAN.

Depression of oxidative metabolism and recovery from dilute potassium cyanide poisoning. Antagonistic and additive effects of anæsthetics and potassium cyanide. J. W. BUCHANAN (J. Exp. Zool., 1926, **44**, 285—306; 307—325).—Four hrs.' exposure of *Planaria dorotocephala* to dilute potassium cyanide solution depressed the oxygen consumption to a constant minimum level; removal of the cyanide caused the oxygen consumption to rise above, and then to reach the normal value. The depressive action is probably largely physical. There is no evidence for the reconstitution of a residual substance containing oxygen or for the accumulation of oxidisable substances during depression. With dilute cyanide solutions, ethyl ether and ethyl alcohol are protective; the action of more concentrated cyanide solutions is accelerated by ethyl ether.

CHEMICAL ABSTRACTS.

Toxicological detection of hydrocyanic acid. G. SENSI and M. REVELLO (Annali Chim. Appl., 1926, **16**, 603—611).—Hydrocyanic acid is not detectable in the animal organism if administered in quantities just sufficient to cause death. When poisoning is effected by means of gaseous hydrogen cyanide, detection of the latter is impossible, since the quantity

absorbed never exceeds the minimum fatal dose. If the body is examined shortly after death, the tests give positive results if at least three times the fatal dose is administered, but otherwise four times this dose is necessary to ensure response. In any case, the poison does not remain in the organism later than the twentieth day after death. T. H. POPE.

Spectroscopic detection of hydrocyanic acid in blood. G. SENSI (Annali Chim. Appl., 1926, **16**, 612—622; cf. preceding abstract).—Kobert's reaction (A., 1892, 361) and Schonbein's reaction for the spectroscopic detection of hydrocyanic acid in blood are positive only when the poison is detectable also by chemical tests. They serve, however, as control tests, Schonbein's reaction being more sensitive than that of Kobert. T. H. POPE.

Toxicology of lead and its compounds. P. W. DANCKWORTT and W. UDE (Arch. Pharm., 1926, **264**, 712—740).—The increasing risk of lead poisoning in cattle due to weed-killers and insecticides (cf. Danckwortt, Deuts. Tierarztl. Woch., 1926, **34**, 639), fumes from smelting-works, and lead-containing effluents has led to a survey of methods for the determination of small quantities of lead in biological material, and an improved method is described. The minced organs (400—500 g.) are treated with sufficient pure nitric acid to cover about half the mass. The mixture is kept for some time and is then heated on the water-bath until all organic matter except fat is destroyed. Troublesome frothing takes place if the mixture is heated immediately. The solution is evaporated to a syrup in a silica capsule (porcelain cannot be used, as it always gives up traces of lead), and this syrup is gently evaporated to dryness, dilute nitric acid being added from time to time to facilitate the process. After repeated evaporation to dryness, the ash, which must not have been overheated or lead may have been lost, is dissolved in dilute nitric acid. The lead is precipitated as sulphide and determined by the chromate method, or, if traces only are present, by the "triple-nitrite test" (cf. Fairhall, A., 1922, ii, 659; 1924, ii, 61). From nitric acid weaker than $N/3$, lead sulphide is quantitatively precipitated, and the precipitation of small quantities is facilitated by adding 10 mg. of copper to the solution. Quantities as small as 1 mg. of lead per 100 g. of oxygen can be determined (cf. Geilmann and Holtje, *ibid.*, 1926, 591).

Using the above methods, lead poisoning has been studied experimentally in dogs. Lead is disseminated in all the organs in varying amounts. The curative action of various substances, administered by intravenous injection, has also been investigated. Colloidal silica is useless. Sodium sulphate and potassium iodide are possibly useful, but relapses may occur. The best medicament, which is useful also as a prophylactic, is colloidal sulphur.

The properties and composition of the soil of certain areas in the Innerste valley and the composition of certain well-waters were investigated. Adsorption of lead by the soil is independent of the phosphoric acid content. W. A. SILVESTER.

Anticoagulant power of certain dyes and arsenic compounds. G. LEFROU (Compt. rend., 1927, **184**, 241—243).—Malachite-green in very small quantities has a powerful anticoagulating influence on blood. Fuchsine and crystal-violet are somewhat less effective, and only a slight effect is observed with methylene- and toluidine-blues. Under similar conditions, phenylarsenates have no action, but the compound "Bayer 205" is a strong anticoagulant. It is suggested that the presence of several amino-groups, either free or substituted, in the compound is necessary to render it anticoagulant.

J. W. BAKER.

Effects of salts on the penetration of brilliant-cresyl-blue into *Nitella*. M. IRWIN (J. Gen. Physiol., 1927, **10**, 425—436).—Cells of *Nitella* previously exposed to solutions of salts containing univalent cations are penetrated less readily by brilliant-cresyl-blue when subsequently immersed in a solution of this dye in a borate buffer mixture. Salts with bivalent and tervalent cations do not produce this effect, but rather neutralise the effect of the univalent cations. W. O. KERMACK.

The two components of malt diastase. E. OHLSSON (Compt. rend. Trav. Lab. Carlsberg, 1926, **16**, [7], 1—68).—In accordance with modern usage, the two enzymes present in malt (cf. A., 1923, i, 620) have been renamed dextrinogenamylase and saccharogenamylase. In a filtrate from green malt, p_H 4·20, dialysed against distilled water, the activity of saccharogenamylase is reduced to about half and that of dextrinogenamylase to 1—2% of its former value. The preparation of a solution of one enzyme free from admixture of the other is described. Results obtained with such solutions indicate that there is present in the malt some substance—protein in character—which has an inhibitory effect on dextrinogenamylase. The activity of this substance is destroyed by heat, is dependent on the p_H of the medium, and shows minimum activity at p_H 5—5·5. The optimum activity of saccharogenamylase occurs in the zone p_H 4—5·75, whilst that of dextrinogenamylase is at p_H 5·5—6·0. The relationship of the activities of these enzymes to the modern theories of starch hydrolysis is discussed. W. ROBSON.

Enzyme action. XXXIX. Lipase actions of extracts of the whole mouse at different ages. K. G. FALK and H. M. NOYES (J. Gen. Physiol., 1927, **10**, 359—368).—The relative ester-hydrolysing actions of an extract of a whole mouse tested on a series of simple esters varies according to the age of the mouse. The action of extracts of embryo mice is similar to that of embryo rats or rat tumour, and not to that of a mouse carcinoma, whilst the extracts of adult mice and rats are similar in lipase activity.

W. O. KERMACK.

Oxidation–reduction potential of the luciferin–oxyluciferin system. E. N. HARVEY (J. Gen. Physiol., 1927, **10**, 385—393).—The oxidation–reduction potential of the system luciferin–luciferase appears to lie between that of sodium anthraquinone-2 : 6-disulphonate ($E_0' = -0{\cdot}22$ at p_H 7·7) and that of quinhydrone ($E_0 = +0{\cdot}24$ at p_H 7·7). The system luciferin–luciferase does not appear to be truly reversible, since it is always unaffected at an oxidation–reduction potential lying between the above two values, although any reducing agent stronger than

the anthraquinonedisulphonate will reduce the oxidised form and any oxidising agent stronger than quinhydrone will oxidise the reduced form. Although luciferin is readily oxidised in absence of oxygen by many reagents and is also oxidised at a high temperature by oxygen in absence of luciferase, luminescence is always absent except when oxidation takes place by oxygen in presence of luciferase.

W. O. KERMACK.

Acceleration of enzymic synthesis of proteins by lipoidal emulsions. H. R. MARSTON (Austral. J. Exp. Biol., 1926, 3, 233—236).—Colloidal emulsions of egg-fat greatly increase the reaction velocity of the re-synthesis of protein from its digestion products by trypsin. W. ROBSON.

Stages of the peptic hydrolysis of egg-albumin. J. MCFARLANE, V. E. DUNBAR, H. BORSOOK, and H. WASTENEYS (J. Gen. Physiol., 1927, 10, 437—450).—The method of protein fractionation of Borsook and Wasteneys (cf. A., 1925, i, 97) has been applied to the products of peptic digestion of egg-albumin by pepsin at p_H 1·6. The amounts of the fractions present at various times up to 168 hrs. have been followed in detail. It is concluded that the process of peptic hydrolysis consists of a primary stage during which the original protein is split directly into fragments belonging to the various protein fractions, and a secondary stage, during which proteose and subproteose fractions are slowly split up into simpler fragments. Although acid metaprotein is formed from egg-albumin by the action of acid, it appears that this is not an essential step during peptic hydrolysis since such acid metaprotein is less readily hydrolysed than the denatured protein itself. W. O. KERMACK.

Autodestruction of pepsin in relation to its ionisation. A. M. GOULDING, H. BORSOOK, and H. WASTENEYS (J. Gen. Physiol., 1927, 10, 451—467).—The destruction of pepsin at a definite hydrogen-ion concentration is found to follow the law of unimolecular reaction. There is evidence that pepsin is a univalent acid (pk—6·85) or a base (pk—7·39). In the first case, the dissociated ions alone are regarded as undergoing destruction, whilst in the second case only the undissociated molecule would be destroyed. The rate of destruction of pepsin increases rapidly with the hydroxyl-ion concentration. In these experiments, the active pepsin was determined by allowing it to act for a given time on albumin at p_H 1·6, precipitating with trichloroacetic acid, and determining the nitrogen content of the filtrate.

W. O. KERMACK.

Influence of bile on the digestion of protein by pancreatic juice. S. MATSUKURA (Proc. Imp. Acad. Tokyo, 1926, 2, 447—448).—Digestion of protein by pancreatic juice in presence of duodenal extract begins most quickly in absence of bile, which inhibits digestion during the first few hours, but appears to be necessary for prolonged digestion.

J. M. GULLAND.

Tyrosinase–tyrosine reaction. VI. Production from tyrosine of 5 : 6-dihydroxyindole and 5 : 6-dihydroxyindole-2-carboxylic acid—the precursors of melanin. H. S. RAPER (Biochem. J., 1927, 21, 89—96).—Tyrosine was incubated with tyrosinase at p_H 6—6·5 for several hrs. After completely precipitating the enzyme with acetic acid from the resulting red solution, the latter was allowed to remain in an atmosphere of hydrogen until it turned pale brown. The concentrated solution was then methylated with methyl sulphate under hydrogen and the crystalline 5 : 6-*dimethoxyindole*, m. p. 154—155°, was extracted with ether from the reaction mixture. It was identical with the synthetic compound. In the methylated alkaline solution, traces of 5 : 6-*dimethoxyindole-2-carboxylic acid*, m. p. 202°, were found. This latter acid, which was identical with the synthetic compound, predominates if the red solution is decolorised with sulphurous acid. 5 : 6-Dimethoxyindole was also prepared as above from the red substance obtained by treating 3 : 4-dihydroxyphenylalanine with tyrosinase (cf. A., 1926, 977). The red pigment produced from tyrosine is probably the 5 : 6-quinone of dihydroindole-2-carboxylic acid. S. S. ZILVA.

The uricolytic enzyme. I. Liver perfusions. II. Destruction of uric acid by ammonia. A. SCHITTENHELM and F. CHROMETZKA (Z. physiol. Chem., 1927, 162, 188—202, 203—218).—I. The surviving livers of the rabbit, dog, and pig oxidise uric acid to allantoin. Perfused human liver can also decompose uric acid, but no definite decomposition products could be isolated.

II. The preparation of enzyme extracts from dried ox liver by Willstatter's methods is described, the processes involving extraction by glycerol, washing, adsorption on various precipitates and colloids, and dialysis. Ammonia itself has a uricolytic action, but the uricolytic power of such extracts is not due solely to ammonia. A. WORMALL.

Products of oxidation of uric acid by hydrogen peroxide. F. CHROMETZKA (Z. physiol. Chem., 1927, 162, 219—222).—The acceleration by ammonia of the oxidation of uric acid to allantoin by oxygen (cf. preceding abstract) is not observed with other amines. Methyl-, ethyl-, and trimethyl-amine have no similar catalytic action, when tested at p_H 8 for 24 hrs. at 38° with a stream of air passing through the solution. These amines in 33% solution oxidise uric acid to allantoin if they are previously heated gently with hydrogen peroxide. This uricolysis may be due to some hydrogen peroxide remaining after the reaction, since hydrogen peroxide will effect the same oxidation. A. WORMALL.

Preparation of yeast-juice by Buchner's method. A. HARDEN and F. R. HENLEY (Biochem. J., 1927, 21, 196—197).—In preparing yeast juice by the grinding method from English top-yeast, it is usually advantageous to preserve the ground mass for 2 hrs. at air temperature before pressing out the juice. Preservation of the expressed yeast-juice does not produce the same effect. S. S. ZILVA.

Growth of yeast. III. Influence of volume of medium employed. G. L. PESKETT (Biochem. J., 1927, 21, 104—110).—The conclusions previously arrived at by the author (A., 1925, i, 1011) were not justified by the results reported at that time. A

reinvestigation of the problem, however, leads to the same conclusions. S. S. ZILVA.

Influence of hydrogen-ion concentration on alcoholic fermentation. VI. E. HAGGLUND and T. ROSENQVIST (Biochem. Z., 1927, **180**, 61—64).—Further experiments on the fermentation of pyruvic acid (cf. A., 1926, 543) confirm that the activity of carboxylase completely disappears in faintly alkaline solution. The p_H-activity curves rise very rapidly near the neutral point and then flatten out over the optimal range of p_H 3·5—6. P. W. CLUTTERBUCK.

Reductase (hydrogenase) of yeast. V. H. VON EULER and R. NILSSON (Z. physiol. Chem., 1926, **162**, 72—84).—The ability of washed dried yeast to reduce methylene-blue is restored by the addition of a hydrogen donator and a co-reductase preparation, but is not restored by the addition of a hydrogen donator alone (sodium succinate). Both reductase and co-reductase (wash-water or "Kochsaft") must be present. Fermentation sodium hexosephosphate appears to be a better hydrogen donator for yeast reductase than sodium succinate. The activating power of hexosephosphate is not due to the products of its hydrolysis by phosphatase. H. D. KAY.

Pyruvic acid as an intermediate product of alcoholic fermentation. G. RIMINI (Annali Chim. Appl., 1926, **16**, 488—490).—Traetta-Mosca's results (A., 1926, 978) may indicate the formation of pyruvic acid in small proportion during the alcoholic fermentation of dextrose, but by no means prove that this acid is a product intermediate between dextrose and alcohol. The fermentation of 10% dextrose solution by fresh distillery yeast in presence of rather more brucine than is necessary to keep the liquid saturated with this base gives practically the theoretical yield of alcohol. It was not found possible to crystallise any salt of brucine from the fermented liquid after evaporation. T. H. POPE.

Specific activators of fermentation enzymes. I. H. VON EULER and R. NILSSON (Z. physiol. Chem., 1927, **162**, 264—271; cf. this vol., 77).—The stability of co-zymase and co-reductase at high temperatures is studied, and these activators show a marked similarity in this respect. After heating at 100° for 1½ hrs., a highly purified co-zymase preparation retained 4·8% of the original co-zymase power and 5·7% of the co-reductase value. After heating for 1 hr. at 90°, the figures were 31% in each case. No alteration in p_H occurred in these heating processes. Dried bottom yeast loses on washing both co-zymase and co-reductase, whilst washed dried top yeast retains its co-zymase, but loses most of its power to reduce methylene-blue. This, however, is not due to the loss of the co-enzyme, but to removal of the hydrogen donators, since methylene-blue can be reduced if a hydrogen donator (hexosephosphate) is added. A. WORMALL.

Enzymes, co-enzymes and biocatalysts in coproporphyrin-rich yeasts. II. H. VON EULER and H. FINK (Z. physiol. Chem., 1927, **162**, 272—303; cf. A., 1926, 1176).—There is no close relationship between increases in invertase and porphyrin, since the former may increase five-fold with no marked rise in the content of the latter. Top and bottom yeasts behave differently after preliminary treatment with porphyrin; in the former case, the quantity of invertase is greatly diminished, whilst in the latter there is a rise up to two- or three-fold. Glycogen storage takes place, but the increase is about the same with top and bottom yeasts. The observation, reported in the first paper, that after drying, the co-enzymes of copro-yeasts were not extracted by washing, is investigated further. After "regeneration" of the copro-yeast in beer wort, the co-enzyme was again removed by water. The relation between coproporphyrin and the co-enzyme (co-reductase) is discussed. The copro-yeasts used contain 0·06—0·25 mg. of coproporphyrin per 30 g. of fresh yeast. The absorption bands of cytochrome could be observed to a varying extent with extracts of copro-yeasts, and these yeasts contain more total pyrrole colouring matter (coproporphyrin+hæmochromogen) than do ordinary yeasts. The relationship between porphyrin- or cytochrome-formation and the type of nitrogenous nutrients supplied is studied and briefly discussed. A. WORMALL.

Action of yeast on sugars rendered optically inactive by dilute alkalis. A. FERNBACH, M. SCHOEN, and M. MORI (Compt. rend., 1927, **184**, 168—170).—The action of the yeast of Sauterne differs from that of beer yeast on sugars rendered optically inactive by dilute alkalis; thus with dextrose the products are dextrorotatory in the former case and lævorotatory in the latter. W. ROBSON.

Fission of starch by *Saccharomyces sake*. K. SJOBERG (Z. physiol. Chem., 1927, **162**, 223—237).—Dihexosan, amylobiose, and an unidentified *substance* ($[\alpha]_D^{18}$+172°) were isolated. A. WORMALL.

Soluble enzymes secreted by *Hymenomycetes*: antioxygenous actions superimposed on reducing actions. L. LUTZ (Compt. rend., 1927, **184**, 173—174).—Experiments were carried out to verify the hypothesis that the addition of an antioxygenous substance to a reducing medium must favour reducing actions in catalysing, inversely, oxidations brought about by the living mycelium of *Hymenomycetes*. W. ROBSON.

Respiratory intensity of *Aspergillus niger* during development. A. HÉE (Compt. rend., 1926, **183**, 1351—1353).—*A. niger* is cultivated on media containing no nitrogeneous substances or on media containing no nitrogen or carbohydrates. The dry weight of the culture falls after the second or third day, and the respiratory intensity falls to one tenth its original value by the ninth day. When there are no carbohydrates in the culture medium the respiration intensity is about one half.

L. F. HEWITT.

Imitations of moving amœbæ, infusoria, and other organic and cellular structures and forms. A. L. HERRERA (Mem. R. Accad. Lincei, 1926, [vi], 2, 195—202).—A fuller account of work already published (A., 1926, 435), with photographic reproductions of the phenomena. T. H. POPE.

Reversible gelation and fixation of tissues. M. A. VAN HERWERDEN (Proc. K. Akad. Wetensch.

Amsterdam, 1926, 29, 975—978; cf. *ibid.*, 1924, 27, 867).—It is suggested that histological fixation involves an irreversible coagulation, but that there is a gradual transition reversible through a gelation of protoplasm to complete fixation. If *Paramœcium aurelia* is kept in 1% formaldehyde, death results, but in 0·01—0·1% solutions a solidification occurs which is not a fixation, but a reversible gelation, since conditions return to normal after washing the animals in ditch water. Similarly, the Brownian movement of another protozoon, *Actinophrys sol*, is stopped by adding a 0·01% formaldehyde solution and completely restored after rinsing out.

J. S. Carter.

Acids as intermediate stages in the oxidation of sugars by fungi. W. Butkewitsch (Jahrb. wiss. Bot., 1925, 64, 637—650).—Gluconic and citric acids are formed apparently directly from sugar by *Aspergillus niger*, *Citromyces glaber*, *Penicillium glaucum*, and related fungi. Low acidity favours the formation of gluconic, and high of citric acid. The general occurrence of gluconic acid indicates that it is a normal intermediate product in the aerobic oxidation of sugars. Chemical Abstracts.

Dependence of the amount of growth of fungi on the quantity of food factors. R. Meyer (Z. Pflanz. Düng., 1926, A, 8, 121—163).—Alterations in the concentration of total foodstuffs (except water) give results that indicate that Mitscherlich's law (cf. A., 1911, ii, 760) can be applied only with difficulty. The law is not strictly valid, for with varying concentrations of ammonium sulphate as the source of nitrogen the amount of growth is influenced by the hydrogen-ion concentration, whilst with sodium nitrate, differences in growth curves are obtained with different concentrations of sugar. With alterations in carbamide concentration, no agreement with the law is found. Variation in the concentration of phosphoric acid gives better agreement, but if the concentrations of two foodstuffs are varied, the results do not agree with the law. A. Wormall.

Conditions for symbiosis of nitrogen-fixing bacteria and maize. G. Truffaut and N. Bezssonoff (Compt. rend., 1926, 183, 1065—1067).—Maize may be grown on a solid medium containing no nitrogen if inoculation with *Clostridium Pastorianum*, *Azotobacter chroococcum*, *A. Vinelandii*, and *Bacillus Truffauti* be made after germination, if the plants are exposed to bright illumination and grown in sand containing up to 0·6 g. of iron per kg.

L. F. Hewitt.

Significance of gelatin for bacterial growth. B. S. Platt (Biochem. J., 1927, 21, 16—18).—Pneumococcus does not grow in peptone-water, but will do so on addition of gelatin. Optimum growth is obtained with 3% gelatin. Growth can also be obtained in absence of peptone on media containing 15% of gelatin solution autoclaved for 20 hrs. and 0·5% of sodium chloride. The concentrated washings of commercial gelatin or the washed gelatin also induce growth in peptone. The ash of "Gold Label" gelatin and of the washings or the concentrated dialysate of the washings promote growth of pneumococcus in 2% washed gelatin–peptone media. 4% of Ringer–Locke solution has a similar effect. Growth was also obtained in a 3% gelatin–peptone medium of several strains of *Bacillus diphtheriæ*, of meningococcus, and of streptococcus. The first did not grow in bouillon or peptone-water. The strains of gonococcus examined would not grow in any of these media.

S. S. Zilva.

Effects of chemical and physical changes in environment on resting bacteria. J. H. Quastel and W. R. Wooldridge (Biochem. J., 1927, 21, 148—168).—Resting *Bacillus coli* was exposed to the following conditions and substances and its activation of a number of compounds determined by the methylene-blue technique; changes of temperature from that of liquid air to 77°, changes of hydrogen-ion concentration from p_H 2·2 to p_H 11, varying concentrations of sodium chloride at varying p_H and for different times, varying concentrations of sodium nitrite at varying p_H and for different times, methylene-blue, benzene, toluene, phenol, ether, chloroform, propyl alcohol, *cyclo*hexanol, colloidal ferric hydroxide, and dilute solutions of cuprous sulphate and mercuric chloride. Selectivity of destructive action on the activating mechanisms was exhibited by such treatment. A step-by-step degradation occurred. The order of sensitivity or of disappearance of the mechanisms was approximately the same in all cases. The activations of the sugars appear to take place at the more fatty or lipoidal fraction of the surface, those of substances such as succinic acid, formic acid, etc. at the less lipoidal. The activation of dextrose as a hydrogen donator seems also to bring about glycolysis. Inactivation by propyl alcohol, *cyclo*hexanol, copper, or mercury is reversible. Sodium hyposulphite has a restorative action. The results are in accordance with the hypothesis that the activations of substrates are intimately associated with surface structure (cf. A., 1926, 434).

S. S. Zilva.

Peroxide formation by pneumococcus and its relation to bacterial oxidation-reduction reactions. B. S. Platt (Biochem. J., 1927, 21, 19—25).—Aerated cultures of pneumococcus free from catalase, when grown on gelatin–peptone, produce considerably less hydrogen peroxide than when grown on gelatin–bouillon. There is no corresponding difference in the amount of growth in the two cases. Peroxide is not produced in gelatin–bouillon in appreciable amounts until near the end of multiplication of the bacteria. The addition of sodium lactate or dextrose, but not of sodium thiolactate to gelatin–peptone cultures of pneumococcus increases the production of hydrogen peroxide in this medium. The rates of growth of, and peroxide formation by, pneumococci are compared under various conditions. It is suggested that lactic acid and indirectly dextrose function as hydrogen donators in the presence of the pneumococcus, peroxide being formed when oxygen acts as hydrogen acceptor. S. S. Zilva.

Cellobiose fermentation by the coli–aerogenes group. S. A. Koser (J. Infect. Dis., 1926, 38, 506—510).—In the fermentation of cellobiose, the differentiation of intestinal *Bacillus coli* and the ærogenes–cloacæ group is distinct. With the so-called

intermediate forms obtained from soil a correlation between all the tests is not obtained.

CHEMICAL ABSTRACTS.

Mineral nutrition of *Bacillus tuberculosis*. A. FROUIN and M. GUILLAUMIE (Bull. Soc. Chim. biol., 1926, 8, 1151—1177).—The only mineral elements essential for the growth of *B. tuberculosis* are sulphur, phosphorus, potassium, and magnesium. Potassium cannot be replaced by sodium, cæsium, or rubidium, nor magnesium by calcium, strontium, or the rare earths. The growth is increased by sodium vanadate in a glycerol medium. Salts of copper, arsenic, manganese, and zinc are almost without action, whilst those of calcium reduce the yield. The effect of salts of other metals, *e.g.*, iron, depends very largely on the other conditions of the medium. The constitution of the ash obtained by incineration of the bacilli depends on the reaction of the medium and the other conditions of growth, as well as on the mineral constituents of the medium.

W. O. KERMACK.

Carbon nutrition of *Bacillus tuberculosis*. A. FROUIN and M. GUILLAUMIE (Bull. Soc. Chim. biol., 1926, 8, 1178—1197).—The influence of the addition of glycerol, certain mono-, di-, and tri-saccharides, and of salts of iron on the weight of the culture of *B. tuberculosis* obtained when grown on a medium otherwise standardised has been investigated. Glycerol, dextrose, and trehalose are found to increase the yield of culture. Iron salts always increase the yield in a glycerol medium, but in a dextrose medium only when the reaction is acid. The fat content of the bacilli is greater in media containing glycerol than in those containing dextrose. W. O. KERMACK.

Generality of the distinction between two categories of fatty matter; constant element and variable element. P. BELIN (Bull. Soc. Chim. biol., 1926, 8, 1081—1102).—A distinction between the two categories of fatty acids can be drawn in the case of micro-organisms as in higher animals. *Aspergillus niger* and Timothy grass bacillus, relatively poor and rich in fatty matter, respectively, both show varying powers of synthesising fats from the sugar, but not from the protein of the medium. Alteration of the medium in sugar content only produces considerable variation in the fat content (cf. Terroine and Lobstein, A., 1923, i, 633), showing the existence of a variable element. Inanition causes the fatty acid content of *A. niger* to fall to approximately 1·37% dry weight, a value independent of the initial fat content. This low limit (constant element) is irreducible and agrees roughly with the amount left after extraction of the same organisms with carbon tetrachloride or light petroleum.

A. WORMALL.

Action of neon light on bacteria. A. PHILIBERT and J. RISLER (Compt. rend, 1926, 183, 1137—1139).—Cultures of staphylococcus, *Bacillus diphtheriæ*, pneumococcus, and streptococcus are sterilised by exposure to the light of a neon lamp when rendered sensitive by a solution of methyl-violet, in periods ranging from 1 to 30 min., whilst neither treatment alone has any bactericidal effect. *B. coli* was unaffected. When eosin or methylene-blue was used in place of methyl-violet, sterilisation did not occur even after exposure for 1 hr. J. W. BAKER.

Secondary action of *X*-rays on micro-organisms. J. J. TRILLAT (Compt. rend., 1926, 183, 1304—1307).—Surface cultures of *Bacillus prodigiosus* were exposed to the radiations caused by *X*-rays impinging on metals. The effect of the irradiation increases with the atomic number of the metal. Thus bactericidal action is observed in 10 min. with bismuth, lead, gold, and platinum, in 20 min. with silver and tin, and in 35 min. with zinc, copper, nickel, and iron. Even after 1 hr., aluminium gives practically no effect. The phenomenon is ascribed to the fact that absorption of *X*-rays by elements, and hence emission of secondary radiations, increases with the fourth power of the atomic number. For effective bactericidal action, the metal must be close to the culture. L. F. HEWITT.

Chemical structure as affecting the staining and therapeutic properties of dyes. R. W. FRENCH (Stain Tech., 1926, 1, 74—77).—Toxicity resulting from the oxidation of methyl groups in certain therapeutic dyes seems to arise from the formaldehyde produced; this might be overcome by ethylation instead of methylation. In the triphenylmethane series, apparent differences in staining and bactericidal value appear to depend on differences in chemical structure. A rosaniline base is, in general, superior to pararosaniline compounds.

H. W. DUDLEY.

Fluorescein dyes as bacterial stains, particularly for soil preparations. H. J. CONN and W. C. HOLMES (Stain Tech., 1926, 1, 87—95).—A discussion of the relative merits of 13 members of this group of dyes as stains. H. W. DUDLEY.

Mechanism of stain action with basic dyes. W. C. HOLMES (Stain Tech., 1926, 1, 98—102).—The chemical theory of staining is discussed. Additive compounds as well as salts of the dyes may play a part in the reactions. H. W. DUDLEY.

Relation of age of bacteria to bacteriostatic properties of aniline dyes. J. W. CHURCHMAN (Stain Tech., 1926, 1, 103—104).—Cultures of organisms (*Bacillus coli*, *B. prodigiosus*, *B. subtilis*, and *Staphylococcus aureus*) become less resistant to gentian-violet as their age increases. This holds even for organisms which are undergoing sporulation.

H. W. DUDLEY.

Chemical nature of metachromasy. W. C. HOLMES (Stain Tech., 1926, 1, 116—124).—The phenomena of metachromasy are analogous to the colour changes of aqueous solutions of the dyes, and probably arise from tautomeric changes of these substances. H. W. DUDLEY.

Thiazine dyes as biological stains. I. Staining properties of thionine and its derivatives as compared with their chemical structures. R. HAYNES (Stain Tech., 1927, 2, 8—16).—Eight ethyl and methyl derivatives of thionine have been studied. A general correlation exists between the degree of ethylation or methylation of the compounds and their staining properties. Passing down the series from tetraethylthionine to thionine, there is a progressive

decrease in the amount of green, and an increase in the amount of red, in the preparations; at the same time, the metachromatic effects and the intensity of nuclear staining increase. H. W. DUDLEY.

Rôle of insulin in protein metabolism. N. W. JANNEY and I. SHAPIRO (Arch. Int. Med., 1926, **38**, 96—108).—In fasting persons receiving dextrose and dextrose-insulin, the additional fall in nitrogen output represented 9·93—13·97% of the nitrogen output with dextrose alone. There was also a fall in blood-, urea-, and non-protein-nitrogen. The protein tissues are regarded as the seat of activity of insulin. Protein sparing by carbohydrate is increased by insulin. Diabetes may be a result of deficient protein metabolism. CHEMICAL ABSTRACTS.

Carbohydrate metabolism. II. Influence of methylglyoxal and other possible intermediaries on insulin hypoglycæmia. W. O. KERMACK, C. G. LAMBIE, and R. H. SLATER (Biochem. J., 1927, **21**, 40—45).—No significant difference could be observed in the time taken to recover from insulin hypoglycæmia following intravenous dihydroxyacetone administration as compared with dextrose (cf. Campbell and Hepburn, A., 1926, 979; Hewitt and Reeves, Lancet, 1926, i, 703). Methylglyoxal, sodium pyruvate, sodium lactate, glycerol, sodium citrate, and rhamnose do not cause animals to recover from insulin hypoglycæmia. The first two compounds appear to have a toxic action. S. S. ZILVA.

Fate of deoxyglucose in the rabbit. L. B. WINTER (Biochem. J., 1927, **21**, 54—55).—The injection of deoxyglucose into rabbits suffering from convulsions induced by the administration of insulin does not effect complete recovery, although the subsequent administration of dextrose restores the animals. Deoxyglucose does not seem to be metabolised by the animal. S. S. ZILVA.

Action of insulin. I. On normal animals. E. GRAFE, H. REINWEIN, and H. SINGER (Arch. exp. Path. Pharm., 1926, **119**, 91—101).—Fragments of liver taken from an animal after injection of insulin and suspended in Ringer solution show less glycogenolysis than do fragments from the same animal before the injection of insulin. W. O. KERMACK.

Action of insulin on the permeability of the human kidney. H. ELIAS and J. GÜDEMANN (Arch. exp. Path. Pharm., 1926, **119**, 119—126).—In the normal and in the diabetic subject, the minimum blood-sugar concentration at which dextrose begins to appear in the urine is not altered by the injection of insulin. This conclusion is true whether the raising of the blood-sugar concentration is effected by either peroral or intravenous administration of dextrose. W. O. KERMACK.

Action of insulin on the sugar, phosphate, lactic acid, and glycogen contents of blood. A. I. VIRTANEN and H. KARSTRÖM (Z. physiol. Chem., 1926, **161**, 218—244).—A large number of determinations of the sugar, phosphate, lactic acid, and glycogen of the blood of sheep with and without insulin are tabulated and discussed in relation to the author's theory of the mechanism of insulin action (cf., A., 1926, 760). P. W. CLUTTERBUCK.

Phosphorus distribution in muscle and liver under different conditions, especially under the influence of hormones. Y. ODA (J. Biochem. [Japan], 1926, **6**, 179—210).—Insulin and pituitrin separately, but not together, cause an increase in the water content of the muscles. The combined phosphate and total phosphorus increase after the administration of insulin or dextrose, both in muscle and liver, but the effect of simultaneous administration is not a summation. Adrenaline and pituitrin reduce the amount of combined phosphate in muscle and liver; on simultaneous administration, there is antagonism in the muscle, but neither antagonism nor synergism in the liver. Both for muscle and liver, insulin and adrenaline or insulin and pituitrin are antagonistic in their effect on the combined phosphoric acid. The curves of the rate of autolytic splitting of phosphorus are different for muscle and for liver. CHEMICAL ABSTRACTS.

Effect of quinine and of some hormone preparations on the phosphoric acid hydrolysis during autolysis of muscle and liver. Y. ODA (J. Biochem. [Japan], 1926, **6**, 367—382).—Insulin, pituitrin, adrenaline, and quinine, in the concentrations used, have no effect on the rate of phosphoric acid hydrolysis in the autolysing muscle or liver-tissue. CHEMICAL ABSTRACTS.

Determination of the hormone content of corpus luteum preparations. Female sex-hormones. XI. S. LOEWE and F. LANGE (Arch. exp. Path. Pharm., 1927, **120**, 48—64).—Physiological methods are described. R. K. CANNAN.

Female sex-hormones (thelytropins). XII. Oestrus-producing substances (thelykinins) obtained from the vegetable kingdom. S. LOEWE, F. LANGE, and E. SPOHR (Biochem. Z., 1927, **180**, 1—26).—A substance having the action of thelykinin, the hormone which induces the œstrus cycle in mice, is found in vegetable sources and its distribution is investigated. Blossom is the most abundant source of plant thelykinin, female willow catkins containing up to 200 mouse units per kg. of fresh material. Vegetable thelykinin is detected also in *Nuphar luteum*. The separated stigma contains much less thelykinin (less than 14 mouse units per kg. of fresh material) than the whole blossom. *Impatiens parviflora* and *Althæa rosea*, after removal of the blossom, contain only minute quantities of the hormone. P. W. CLUTTERBUCK.

Growth-promoting effect of irradiated fat in the diet, of direct irradiation, and of cod-liver oil. H. GOLDBLATT and A. R. MORITZ (J. Biol. Chem., 1926, **71**, 127—137).—Whilst growth in young rats on a diet lacking vitamins-*A* and -*B* is promoted to an equal extent by addition of irradiated fat to the diet or by direct irradiation of the animals, neither of these methods is so efficacious as administration of cod-liver oil; irradiation does not prolong the life of the animals, nor does it prevent the occurrence of xerophthalmia. C. R. HARINGTON.

Fractionation of irradiated cholesterol. I. Chemical observations. M. J. SHEAR and B.

KRAMER. **II. Antirachitic potency of fractions.** B. KRAMER, M. J. SHEAR, and D. H. SHELLING (J. Biol. Chem., 1926, **71**, 213—220, 221—233).—I. Cholesterol was irradiated for 1—2 hrs. with ultra-violet light; on recrystallisation of the product, the mother-liquor yielded, on evaporation, 5—10% of a yellow oil, of which about 40% was not precipitated by digitonin. The oil gave a strong reaction with aniline and hydrochloric acid, as well as the Liebermann–Burchard and Salkowski reactions for cholesterol; the latter reaction was not obtained with perfectly pure cholesterol.

II. The above-described oil protected young rats against rickets when fed in a concentration of 0·1% of the diet; when dissolved in cotton-seed oil, it retained its antirachitic properties during storage for 2 months. C. R. HARINGTON.

Glass screens for transmission of antirachitic light radiations. E. M. LUCE (J. Biol. Chem., 1926, **71**, 187—190).—Growing rats were exposed to direct sunlight and to sunlight filtered through various screens, with results indicating that light of wave-length >300 μμ fails to protect from rickets, whilst ultra-violet light of wave-length 240—300 μμ is as strongly antirachitic as full sunlight.

C. R. HARINGTON.

Is antiscorbutic effect due to two substances ? N. BEZSSONOFF (Compt. rend., 1926, **183**, 1309—1310).—One half the usual dose of fresh lemon juice is sufficient to protect guinea-pigs from scurvy if 60 c.c. of milk heated at 120° for 1 hr. are administered, but if used alone, fresh milk is necessary for antiscorbutic effect. One half the antiscorbutic effect of orange juice is lost on heating at 130° for 1 hr. By fractionation with lead acetate, a crystalline product is obtained from cabbage, which in a dose of 40 mg. will protect guinea-pigs from scurvy when boiled milk is administered at the same time, whilst without the milk 160 mg. are without effect. The boiled milk may be replaced by 1·5 c.c. of boiled lemon juice. It is therefore suggested that vitamin-*C* is in reality two substances, one probably derived from the other, one being heat-stable and the other decomposed by heating. L. F. HEWITT.

Water, fatty acid, and cholesterol content of suprarenal glands of normal and scorbutic guinea-pigs. L. RANDOIN and A. MICHAUX (Compt. rend., 1926, **183**, 1055—1057).—The suprarenal glands of normal guinea-pigs contain about 68·6% of water, 5·5% of cholesterol, and 8·85% of fatty acids. When fed on diets deficient in vitamin-*C*, the water content remains constant, the cholesterol content falls as low as 2·7%, whilst the fatty acid content first falls and then increases to the normal or above normal value. The ratio of cholesterol content to fatty acid content (lipocytic coefficient) thus falls with the progress of scorbutic symptoms. L. F. HEWITT.

Influence of surface-active substances on the forms of growth of *Soor neonatorum* in respect to water-soluble vitamins. F. V. VON HAHN (Kolloid-Z., 1926, **40**, 321—327).—A study of the physico-chemical conditions for the mycelial formation of *Soor neonatorum* revealed no difference between the natural, vitamin-rich products and artificial solutions of high surface activity. This supports the view that the vitaminoid state is essentially characterised by a certain surface tension.

E. S. HEDGES.

Diet and reproduction. II. G. GRIJNS and K. DE HAAN (Proc. K. Akad. Wetensch. Amsterdam, 1926, **29**, 873—877).—A continuation of previous work (A., 1926, 546), in which the reproductive power of rats supplied with a diet from which various possible fertilising factors were absent, has been examined. No definite fertility-controlling factor has as yet been recognised, and the only progress made in this direction is that, by controlling the diet, females in the first or second generation are unable to rear their young, fertility in both sexes in so far as the production of living young is concerned being very little altered. J. S. CARTER.

Apple physiology, growth, composition, and fruiting responses in apple trees. R. H. ROBERTS (Wisconsin Agric. Exp. Sta. Res. Bull., 1926, **68**, 1—72).—Blossom bud formation accompanies a condition of balance between the nitrogen and carbohydrate content. Apple trees may accumulate and use nitrogen reserve. The colour of the fruit varies inversely with the nitrogen content.

CHEMICAL ABSTRACTS.

Physiology of the nutrition of fruit trees. I. Effects of calcium and potassium starvation. C. E. T. MANN (Univ. Bristol Ann. Rep. Agric. Hort. Res. Sta., 1924, 30—45).—Deficiency of potassium leads to small apple leaves; deficiency of calcium to large ones. In dull light, transpiration is lower, and in bright sunlight higher, with leaves from trees deficient in potassium. Deficiency in potassium leads to a lower water content of gooseberry leaves.

CHEMICAL ABSTRACTS.

Oxygen requirements of plant roots. A. KUDRYASHEVA (Sci. Agron. J., 1924, **1**, 48—67).—The roots of a plant require much oxygen, and consume it immediately; deficiency of oxygen leads to the formation of nitrite in the nutrient solution (Hellriegel's). Oxygen requirements per g. of dry substance are: maize, 0·38 mg., peas, 1·37 mg. The consumption is maximal at the flowering period.

CHEMICAL ABSTRACTS.

Carbon assimilation by plants. J. C. BOSE (Scientia, 1926, **40**, 143—152).—Small traces of certain substances, particularly formaldehyde, largely increase the power of assimilation. Photosynthetic curves indicate that malic acid in the plant serves as a substitute for an external supply of carbon dioxide. The characteristic effects of different spectral regions are considered. The efficiency of the photosynthetic organ in *Hydrilla* is 7·4%. CHEMICAL ABSTRACTS.

Theory of the formation of lignin. W. FUCHS (Biochem. Z., 1927, **180**, 30—34).—Theoretical.

P. W. CLUTTERBUCK.

Comparative plant chemistry. XIV. *Oenothera biennis*. R. KLAPHOLZ and J. ZELLNER (Monatsh., 1926, **47**, 179—183).—The chemical composition of the evening primrose is in general similar to that of the related *Chamænerium angustifolium* (A., 1924, i, 815). The air-dried leaves and flowers,

respectively, contain: soluble in light petroleum, 2·45%, 4·07%; in ether, 1·77%, 3·05%; in alcohol, 17·23%, 26·50%; total water-soluble, 42·52% 41·18%; water-soluble mineral matter, 8·18%, 3·55%; soluble polysaccharides, 3·70%, 3·05%; free acid (as KOH), 4·52%, 5·31%; reducing sugars, 3·22%, 5·91%; crude fibre, 15·08%, 18·03%; nitrogen, 1·96%, 2·02%; crude protein (from nitrogen), 12·25%, 12·63%; ash, 10·54%, 6·89%. The petroleum extract of the leaves contains a phytosterol, m. p. 133° (acetate, m. p. 117°), identical with that obtained by Heiduschka and Luft (*ibid.*, 1919, i, 372) from the seeds; also (?)ceryl alcohol, m. p. 68—72°, and solid fatty acids. Phlobaphens, tannins, and invert-sugar are present in the alcohol extract, whilst the cold aqueous extract contains invertase. The polysaccharides appear to be entirely pentosans. The petals yield, in addition to the substances just mentioned, a saturated *hydrocarbon*, $C_{31}H_{64}$ or $C_{32}H_{66}$, m. p. 63°. H. E. F. Notton.

Presence of allantoic acid in *Phaseolus vulgaris*. R. Fosse (Compt. rend., 1926, **183**, 1114—1116; cf. A., 1926, 438).—The crude derivative obtained by the action of an acetic acid solution of xanthhydrol on the juice of *Phaseolus vulgaris* gives no crystalline lead salt on treatment with lead acetate, but after hydrolysis the liquor gives all the reactions of allantoic acid, thus proving the presence of this acid in the sugar, since xanthyluroxanic acid (which by simple crystallisation from pyridine is converted into dixanthylallantoic acid) gives a characteristic lead salt under these conditions. When treated with xanthhydrol, the juice of *Acer pseudoplatanus* gives a precipitate which on crystallisation from pyridine yields dimethylallantoic acid. J. W. Baker.

Respiration of tobacco leaves during drying. So-called tobacco fermentation. A. Fodor and A. Reifenberg (Z. physiol. Chem., 1926, **162**, 1–40).—Peroxydase, oxydase, and catalase have been detected in the green, macerated leaves. In the dried leaves are found peptidase, peroxydase, catalase, and an enzyme which decomposes nicotine to organic bases and ammonia, but no oxydase. The uptake of oxygen by the leaves when placed in water in a Barcroft micro-respirometer at various stages during the drying process, is dependent on their moisture content, being least when the leaves have been thoroughly dried. Potassium cyanide greatly reduces both oxygen uptake and carbon dioxide output. Iron salts do not affect oxygen uptake, but increase the carbon dioxide output of the leaves. Mercury salts diminish oxygen uptake without affecting carbon dioxide output. The respiratory phenomena are not due to bacterial action. If air, but not if hydrogen, is drawn slowly through slightly moist tobacco in a desiccator, the temperature may rise several degrees. Maximal heat production occurs when tobacco of optimal moisture content, and compressed into the smallest possible space, is slowly aerated. Pyruvic acid and certain other organic acids are decarboxylated by tobacco leaves. H. D. Kay.

Chemical changes accompanying tuberisation in potato. J. T. Rosa (Proc. Ann. Mtg. Potato Assoc. Amer., 1924, **11**, 107—108).—In the underground stems, the dextrose and sucrose content is high prior to stolon formation, low during this period, and increases when the tubers begin to form. Starch, at first practically absent, rapidly increases in the underground stems and leaves. The total nitrogen is maximal in the early development and thereafter decreases rapidly. Chemical Abstracts.

Biocatalysts in meadow and pasture plants. F. Boas and H. O. Diener (Z. Pflanz. Düng., 1926, **A, 8**, 164—176).—Considerable differences are exhibited by different plants with regard to fermentation catalysts. The most active extract is obtained by immersing the hay in hot water and extracting for 6 hrs. Some of the catalysts are destroyed by heat, but part of the activity resides in the salts of the extract. Potassium chloride, even in a dilution of 1 : 1,140,000, has a noticeable effect on the fermentation. Ultrafiltration results in a partial separation, and the recombined fractions have the same activity as the original extract. A. Wormall.

Colorimetric micro-method for determination of p_H. O. A. Walther and J. Ulrich (Bull. Soc. Chim. biol., 1926, **8**, 1106—1111).—Special precautions are taken to prevent evaporation of water and gaseous exchanges, and the method is applicable to quantities of fluid of the order of 0·1—1·0 mm.^{3} Standard amounts of the indicator and the solution are mixed in a special micro-pipette fitted with a micrometer screw and filled with mercury. A capillary tube, open at both ends, is filled with the mixture and plunged into paraffin oil. The colour is compared with that of appropriate standards in similar tubes by observation under the microscope or a lens. A. Wormall.

Colorimetric correction curves. S. L. Wright, jun. (J. Biol. Chem., 1926, **71**, 209—212).—Correction curves for colorimetric work such as those previously published by the author (Bull. Ayer Clin. Lab., 1925, **9**, 65) are largely a matter of individual observation, and should therefore be determined by each person for himself. This is particularly the case in connexion with the determination of creatinine in blood by the method of Folin and Wu (A., 1919, ii, 308). C. R. Harington.

Practical model of micro-pipette. R. Wolff (Bull. Soc. Chim. biol., 1926, **8**, 1112—1113).—A graduated capillary tube fitted with micrometer screw and measuring a total volume of 0·1 c.c. is described. A. Wormall.

Potentiometric determination of various cations and anions in biological research. P. D. von Neergaard (Kolloid-Z., 1926, **40**, 339—340).—The influence of ions other than that of hydrogen should not be overlooked in biology. E. S. Hedges.

BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

APRIL, 1927.

BI... PUBLICATIONS

General, Physical, and Inorganic Chemistry.

Spectral notation. W. M. HICKS (Phil. Mag., 1927, [vii], 3, 614—618).—A plea for the adoption of a uniform scheme of spectral notation to avoid ambiguity and confusion. A. E. MITCHELL.

Specific oscillations characteristic of continuous spectra. IV. A. WINTNER (Ann. Physik, 1927, [iv], 82, 346—354; cf. *ibid.*, 67; this vol., 81).—Mathematical.

Intensity distribution in the fine structure of the Balmer lines. G. E. HARRISON (Nature, 1927, 119, 393).—The relative intensities of the two components λ' and λ'' ($\lambda' < \lambda''$) of H_α are dependent on the conditions of the discharge, and in particular on the diameter of the tube in which the discharge takes place. A. A. ELDRIDGE.

Series spectra of boron, carbon, nitrogen, oxygen, and fluorine. I. S. BOWEN (Physical Rev., 1927, [ii], 29, 231—247).—Practically all of the unidentified strong lines of boron, carbon, nitrogen, oxygen, and fluorine occurring in the extreme ultra-violet spectra of the vacuum spark have been classified as due to jumps between levels in B I, C I, C II, N II, N III, O III, O IV, F I, F II, F III, and F IV. The levels thus found are correlated with those demanded by the Russell–Heisenberg–Pauli–Hund theory. A. A. ELDRIDGE.

Second green line of the auroral spectrum. L. VEGARD (Nature, 1927, 119, 349—350).—Further observations (cf. this vol., 91) indicate that the second green line of the auroral spectrum consists of a group of lines. Within the limits of experimental error, the wave-lengths of one of the components of the N_2 line from solid nitrogen corresponds with the maximum of the second green auroral line. A. A. ELDRIDGE.

Meteorological researches on some rays of neon and helium. A. PERARD (Compt. rend., 1927, 184, 447—449).—The Michelson interferometer has been used to determine for neon and helium the error between the observed fractional excess of the order of interference and that calculated using the red ray of cadmium as reference and the usually accepted approximate value of the wave-length of the ray studied. Intervals between 0 and 202 mm. have been used, and correction curves constructed for use in meteorology. With neon, when the lamp was observed on end the results confirmed those previously obtained; when it was observed across the axis there was a minimum of intensity in the central region. J. GRANT.

Flash arc spectrum of sodium. F. H. NEWMAN (Phil. Mag., 1927, [vii], 3, 364—368).—The method of excitation of the flash arc spectrum of sodium is similar to that described previously for the potassium spectrum (this vol., 2). In addition to the ordinary arc lines, most of the ordinary spark lines appear. These latter do not approach the *D*-lines in intensity. The flash arc spectrum observed comprises 99 lines between 5228 and 2493·8 Å. The spectrum is analogous to the neon red spectrum. The spectral centre is approximately 3300 Å., which is lower than the corresponding spectral centre of the lines in the potassium flash arc. It is suggested that the spectrum observed is the first spark spectrum of sodium. A. E. MITCHELL.

Persistent lines of hafnium. M. PETERSEN (Nature, 1927, 119, 352—353).—The three most persistent lines of hafnium, in decreasing order, are: 2773·40, 2866·35, and 2919·55 Å., which were observed in all the spectra examined. Less persistent lines are: 2516·85, 2887·15, 2898·25, 2904·40, 2904·80 (?), 2940·80, 2964·85, 3194·20 Å. (Hansen and Werner's wave-lengths, A., 1923, ii, 807). Regularities in the hafnium spectrum are at present conjectural. A. A. ELDRIDGE.

Polarisation of mercury lines emitted from a discharge tube in a magnetic field. H. W. B. SKINNER (Proc. Camb. Phil. Soc., 1927, 23, 508—515).—Both the quantum theory and the classical theory require that the light emitted by atoms in a magnetic field shall be unpolarised, but experiments yielding results to the contrary have been described. The polarisation of the lines emitted by a mercury-vapour arc under the influence of a magnetic field has therefore been examined. Two distinct types of polarisation have been observed, but both are probably due to the excitation being anisotropic. R. CUTHILL.

Duration of after-glow in mercury vapour. (FRL.) M. ASTERBLUM (Z. Physik, 1927, 41, 294—300).—The duration of the after-glow in a rapidly moving stream (75 metres/sec.) of mercury vapour, excited by a direct-current discharge between two electrodes inserted in the stream, has been measured for the lines 3132, 3650, 4047 (4344, 4347, 4358), 5461 Å. Linear relations are obtained between the logarithm of the intensity and the distance separating the point at which the intensity is measured from the exciting cathode. From these data, the mean time of duration (sec. $\times 10^{-4}$) of the after-glow has been determined for the above-mentioned lines as 0·77, 0·77, 1·1, 1·2, and 1·1, respectively. R. W. LUNT.

Reversal of lines in the explosion spectrum of lead. B. ARAKATSU (Mem. Coll. Sci. Kyoto, 1927, **10**, 171—174; cf. this vol., 2).—The self-reversal of lines in the spectrum of exploded lead wires has been investigated at higher pressures. The lines 4057 ($2p_2$—$2s$), 3740, 3684 ($2p_5$—$2s$), 3640 ($2p_3$—$2s$), and 3573, which were previously difficult of reversal, have now been obtained as clear absorption lines. The 4168 ($2p_1$—$3d_3$) and 4020 ($2p_1$—$3d_1$) lines show weak reversal. The 2802 ($2p_2$—$3d_1$) and 2614 ($2p_3$—$3d_2$) lines are broadened symmetrically on both sides, whilst the other reversed lines in the diffuse series are fairly sharp. It seems probable that the continuous spectrum has many centres of development. R. A. MORTON.

Ultra-violet arc spectrum of freshly-prepared uranium oxide. H. NAGAOKA and T. FUTAGAMI (Proc. Imp. Acad. Tokyo, 1926, **2**, 533—535).—The method of purifying uranium is described. In the region 2300—3100 Å., some 1400 lines have been measured. It appears that metals of the rare-earth and platinum groups are responsible for about a third of the lines. Lines from bismuth, lead, thallium, and helium, impurities or possible disintegration products of uranium, were also found. No definite conclusions can yet be reached concerning the uranium spectrum. R. A. MORTON.

Vacuum grating spectrograph for the extreme ultra-violet and for *X*-rays: a grating with tangential incidence. J. THIBAUD (J. Phys. Radium, 1927, [vi], **8**, 13—24).—The theory of a diffraction grating with tangential incidence and a description of a vacuum spectrograph employing the principle are given. A glass grating, with 200 lines per mm., was found superior to one of speculum metal for wave-lengths of less than 500 Å. The spectrum from 6000 to 140 Å. is obtained on one plate. The spark spectrum of copper in particular has been studied, the results confirming those of Millikan. Evidence of new lines in the extreme ultra-violet spectrum of copper is given. W. E. DOWNEY.

Spectrography of *X*-rays of long wave-length, *N*- and *O*-series, and the junction with the extreme ultra-violet. A. DAUVILLIER (J. Phys. Radium, 1927, [vi], **8**, 1—12).—A method of spectrographing the region 20—136 Å. is given. Slow electrons bombard an anticathode covered with a film of the element under examination. The film is constantly re-formed by evaporation from the cathode. The Schumann plate is protected from the general light of the *X*-ray tube by a screen, transparent to *X*-rays. This screen consists of a film of celluloid covered with a thin deposit of magnesium.

Using this spectrograph, the *K*-series has been completed by the measurement of the $K\alpha$ lines of oxygen, carbon, and boron. The spontaneous appearance of the $K\alpha$ line of carbon has been confirmed and its appearance controlled. By means of a Wehnelt cathode, covered on its underside, a given spectrum of an element can be obtained, and the method was used to follow the appearance of the $L\alpha$ and $M\alpha$ lines. The unknown *N*- and *O*-series have been obtained for thorium. The observed lines have approximately the calculated wave-lengths. The *O*-lines (the $O\beta$ line of thorium has wave-length 121 Å.) establish, for the first time, the link between the *X*-ray region and the extreme ultra-violet region of Millikan. W. E. DOWNEY.

Intensities of *L* *X*-ray spectra. A. JONSSON (Z. Physik, 1927, **41**, 221—229).—Using stationary potentials (max. 20 kilovolts) and a filament tube with an oil-cooled anticathode, the relative intensities of the lines $L\beta_1$, $L\beta_2$, and $L\gamma_1$ have been determined for molybdenum, ruthenium, palladium, silver, cadmium, indium, tin, and antimony. The intensities of the β_2- and γ_1-lines increase linearly with the atomic number from 42 to 46, increase suddenly at element 47 (silver), and then at a diminishing rate in the range 48—51, and approach the values obtained previously by the author (*ibid.*, 1926, **36**, 426) for 74 and 78 (tungsten and platinum). The results are in agreement with the theory of Main-Smith and Stoner concerning the electronic orbits in an atom. R. W. LUNT.

Intensity of *X*-ray spectra as a function of the exciting current. D. NASLEDOV and P. SCHARAVSKI (Z. Physik, 1927, **41**, 155—163).—The intensity of the lines Cu $K\alpha$, Cu $K\beta$, measured by an ionisation method, has been found to increase linearly with the exciting current up to 4 milliamps. in a tube of the Coolidge type. For larger currents, the increase remains linear, but at a diminished rate. The critical value, 4 milliamps., is independent of the exciting potential, which was stationary, in the range examined, 30—45 kilovolts. R. W. LUNT.

***L* *X*-Ray spectra of the lighter elements.** J. H. VAN DER TUUK (Z. Physik, 1927, **41**, 326—331).—The anomalies presented by the *L* spectra of copper and cobalt are discussed with reference to Bohr's theory of the periodic system. R. W. LUNT.

Exact *X*-ray absorption measurements, in the *K* region, of cobalt and its compounds. F. DE BOER (Arch. Neerland., 1927, III A, **5**, 101—130).—Using an improved form of Siegbahn's spectrograph, which is described in detail, the limits of *X*-ray absorption in the *K* region have been determined for the following substances: cobalt, cobaltous oxide, chloride, nitrate, carbonate, phosphate, acetate, sulphate, and chromate, and several cobaltammine derivatives. The limiting wave-lengths for cobalt and the above cobaltous compounds are, respectively: 1604·2, 1602·7, 1603·0, 1602·9, 1602·7, 1602·8, 1602·9, 1602·7, and 1603·2 X. The mean for the seven cobaltammine derivatives examined was 1602·2. The results are held to show that this limiting frequency is associated with valency and chemical constitution. R. W. LUNT.

Exact determinations of the *K*-series of palladium and silver. G. KELLSTROM (Z. Physik, 1927, **41**, 516—523).—Using the technique of Larsson (cf. following abstract), the following wave-lengths have been assigned to the lines Pd $K\alpha_1$, $K\alpha_2$, $K\beta_1$, $K\beta_2$, $K\beta_3$, Ag $K\alpha_1$, $K\alpha_2$, $K\beta_1$, $K\beta_5$, and $K\beta_3$, respectively: 584·266, 588·632, 519·474, 509·181, 520 093, 558·277, 562·669, 496·009, 486·030, and 496·647 X. R. W. LUNT.

Exact determinations of the *L*-series of tantalum. I. WENNERLOF (Z. Physik, 1927, **41**, 524—

529).—Using the technique of Larsson, the following wave-lengths have been assigned to the tantalum lines α_2, β_1, β_2, β_3, β_4, γ_1, γ_2, and γ_3: 1518·85, 1529·8, 1324·23, 1281·90, 1304·1, 1343·1, 1135·58, 1102·9, and 1097·1 X. R. W. LUNT.

Selective displacement of 0·0153 Å. in *X*-ray spectral lines. F. H. LORING (Chem. News, 1927, 134, 65—67).—It is shown that by the addition of 0·0153 Å. to the wave-lengths of hitherto apparently unidentified *X*-ray lines, they may often be brought into position with normal known lines. The coincidence or phenomenon seems to be selective, in that the lines of a given element may be normal except for one or two displaced by the above amount towards the shorter wave-length side. R. W. LUNT.

Selective displacement of *X*-ray spectral lines. F. H. LORING (Chem. News, 1927, 134, 97—99; cf. preceding abstract).—A unit of 0·01527 Å. or integral multiples of this unit when added to certain unidentified *X*-ray wave-lengths gives numbers in agreement with known lines. The relation of this quantity to Planck's constant h is discussed. R. A. MORTON.

Electron affinity of hydrogen and the second ionisation potential of lithium. L. PAULING (Physical Rev., 1927, [ii], 29, 285—291).—With certain assumptions, the electron affinity of hydrogen atoms is computed as $E_H = -1·85$ kg.-cal./mol., and the second ionisation potential of lithium as 76·2 volts. A. A. ELDRIDGE.

Influence of oxygen on the optical absorptive power and the photo-electric electron emission of potassium. R. FLEISCHER (Ann. Physik, 1927, [iv], 82, 243—253; cf. this vol., 180).—By removing gas from potassium, it was shown earlier that the wave-length of maximum absorption and of maximum electronic emission could be shifted to 313 μμ. This shift has now been extended as far as 302 μμ, and the exact location of the maximum is shown to depend on the nature of the gas contaminating the potassium. The photo-electric maximum at 313 μμ with potassium–oxygen mirrors cannot wholly be related to the optical absorption, although the latter is not essentially different from the absorption of the outgassed mirror. R. A. MORTON.

Influence of the gas content on the velocity distribution of photo-electrons from platinum, aluminium, and palladium. J. KLUGE (Ann. Physik, 1927, [iv], 82, 432—448).—It is shown, for platinum and aluminium, that the connexion between emergence velocity and wave-length limit is independent of the gas content, in accordance with Einstein's equation. The velocity distribution alters with outgassing in such a manner that V alters in the same sense as V_{max}. W. E. DOWNEY.

Photo-electric emission as a function of composition in sodium–potassium alloys. H. E. IVES and G. R. STILWELL (Physical Rev., 1927, [ii], 27, 252—261).—The curve showing the relation between the atomic composition and the ratio of emission with the electric vector in the plane of incidence to that with the electric vector perpendicular thereto exhibits maxima at 20, 50, and 90 at.-% of sodium. A. A. ELDRIDGE.

Variable mass of the electron. L. T. JONES (Phil. Mag., 1927, [vii], 3, 622—624).—It is pointed out that the mass of the electron is not a function of the velocity alone, but that it must depend on the potential at which the electron is emitted. Since measurements of the mass of the electron are made always at the potential of the observer, and not at the higher relative potential of the emission, it then follows that variations in the mass of the electron can never be shown by ordinary methods of measurement. A. E. MITCHELL.

Velocity distribution of electrons issuing from small holes. R. H. DALTON and W. P. BAXTER (Physical Rev., 1927, [ii], 29, 248—251).—When the sides of a perforation in a copper plate were coated with lampblack, the percentage of 50-volt electrons transmitted without appreciable energy loss rose from 70 to 95. A. A. ELDRIDGE.

Application of method of magnetic spectrum to the study of secondary electronic emission. C. F. SHARMAN (Proc. Camb. Phil. Soc., 1927, 23, 523—530).—The velocity distribution in a secondary electron emission has been investigated by the magnetic spectrum method. From the results obtained it appears that two distinct types of electrons are emitted. One group, which is only a small fraction of the whole, consists of electrons with nearly the same energy as the primary beam, and are electrons which have collided closely only with atoms, probably in the surface layer. The other group includes electrons with energies from zero up to that of the primary beam, and into this group would fall any "characteristic" corpuscular radiation from the atoms of the target excited by the primary beam, and also the electrons resulting from collisions between primary electrons and "free" electrons in the target. The form of the energy distribution curve does not, however, agree with the results obtained by the retarding potential method (cf. Becker, A., 1925, ii, 8). R. CUTHILL.

Electron "reflexion" in a vacuum. D. BROWN and R. WHIDDINGTON (Nature, 1927, 119, 427).—A fraction of the electrons emitted from a filament and accelerated towards a reflecting plate under potential V are "reflected" with energy corresponding with the full potential V, and energies immediately less than about 12 volts below V were not observed. This gap is probably real, and not instrumental (cf. Sharman, preceding abstract). A. A. ELDRIDGE.

Conductivity of clouds dispersed from an arc. II. H. P. WALMSLEY (Phil. Mag., 1927, [vii], 3, 587—600).—It has been shown previously (A., 1926, 654) that the ionisation currents obtained from the cloud of particles produced from an arc between cadmium electrodes show an initial fall in current strength, followed by a subsequent rise. It is shown that the subsequent rise is due either to the production of new charges within the cloud as it ages or to an increase in the mobility of the existing ions. A. E. MITCHELL.

Ionisation equilibrium in stellar atmospheres and in the earth's atmosphere. A. PANNEKOEK (Proc. K. Akad. Wetensch. Amsterdam, 1926, **29**, 1165—1171).—Although the Saha ionisation formula is not strictly applicable to stellar atmospheres, since these are not gases in thermodynamical equilibrium, true values for the ionisation are obtained by substitution of the effective temperature for the atmospheric temperature and the introduction of a constant correction factor. Using the modified formula, the ionisations of hydrogen, nitrogen, and oxygen in the upper layers of the earth's atmosphere, due to photo-electric ionisation by solar radiation, have been calculated. If the temperature be assumed to be −55°, it appears that on descending from great heights, the number of electrons increases regularly to a maximum value of 10^5—10^6 electrons/c.c., and then rapidly falls to zero because of increasing absorption of the radiation. For nitrogen and oxygen, the maximum values are at 145 and 128 kilometres, respectively, the minimum at 130 and 113 kilometres, respectively. The number of electrons agrees very well with that deduced from wireless experiments, although the lower limit lies at a greater height than that usually accepted. The presence of a considerable number of electrons at a height of 90 kilometres would indicate a much lower temperature of these upper layers than is generally assumed. For hydrogen, the region of ionisation begins at about 700 kilometres. Ionisation at such an altitude would extinguish all solar wavelengths below 766 Å., which are the frequencies necessary for the ionisation of nitrogen and oxygen. The existence of a hydrogen atmosphere above the nitrogen and oxygen atmosphere makes the existence of a Heaviside layer due to photo-electric ionisation impossible. Unless this layer may be explained by other causes (*e.g.*, impacts by particles), hydrogen cannot occur in the atmosphere in the usually accepted quantities. J. S. CARTER.

Magnetic moment of the hydrogen atom. T. E. PHIPPS and J. B. TAYLOR (Physical Rev., 1927, [ii], **29**, 309—320).—Stern and Gerlach's atomic-ray method, applied to atomic hydrogen produced in a discharge tube by Wood's method, indicates that the magnetic moment of the hydrogen atom is one Bohr magneton. A quantitative result was not obtained from atomic hydrogen produced by Langmuir's hot filament method. Experiments with the product of the exposure of a mixture of mercury vapour and hydrogen to ultra-violet light were unsuccessful; possibly only small amounts of atomic hydrogen are formed, or the active substance may consist of excited hydrogen or mercury hydride molecules. A. A. ELDRIDGE.

Paramagnetism of the elements comprised between calcium and zinc. A. CARRELLI (Atti R. Accad. Lincei, 1926, [vi], **4**, 569—574).—Just as Cabrera (A., 1925, ii, 358) found with the rare-earth metals, so also with the elements lying between calcium and zinc, spectroscopic data indicate a double period of variation in the number of magnetons as a function of the atomic number. T. H. POPE.

Constant paramagnetism of quinquevalent vanadium. N. PERRAKIS (Compt. rend., 1927, **184**, 445—447).—Quinquevalent vanadium has a paramagnetism independent of temperature between 17° and 77° in vanadium pentoxide and in sodium vanadate, and between 17° and 45° in ammonium vanadate. The mean value (to within 10%) of the coefficient of atomic magnetisation of quinquevalent vanadium derived from these determinations is $44{\cdot}0\times10^{-6}$. Vanadium pentoxide has the same paramagnetism in the solid state as in solution. Like the atomic moment, the paramagnetism may have many different values in the same atom (cf. A., 1924, ii, 586). J. GRANT.

Magnetic properties of manganese pyrophosphate at various temperatures; measurement of the moment of the manganous ion. G. FOEX and (MLLE.) A. BRUNET (Compt. rend., 1927, **184**, 443—445).—The coefficients of magnetisation of manganese pyrophosphate have been determined between the temperatures −80° and +485°, and the existence of the manganous ion with 30 magnetons has been established from the molecular Curie constant. The manganese pyrophosphate follows Weiss' law and remains unchanged in its magnetic properties between these temperatures. Since this is maintained for at least 6 months, the compound is suggested as a standard of magnetic susceptibility. The coefficient of magnetisation ($103{\cdot}1\times10^{-6}$ at 16·1°) varies inversely as the quantity, temperature Abs.+23°, instead of following Curie's law. J. GRANT.

Atomic moment in the complexes of the iron family. P. WEISS (Compt. rend., 1927, **184**, 417—419).—The "effective atomic number" (N') of an ion is obtained by subtracting its valency (v) from the atomic number (N) of the corresponding atom. Thence a simple rule is obtained which enables the moments of complex ions of the iron family to be correlated with those of the normal ions. Thus $N-v+2i$ gives the number of electrons surrounding the central atom, where i is the co-ordination index; and $N'=N-v+2(i-p)$, where p is the number of pairs of electrons with zero moment formed as a result of chemical combination. A curve is given from which the ionic moment is obtainable from the value of N', and is used to show that the diamagnetic carbonyls of nickel and iron possess zero moments. J. GRANT.

Degenerated gases and paramagnetism. W. PAULI, jun. (Z. Physik, 1927, **41**, 81—102).—By identifying the electrons in metals from which electrical conductivity arises with the valency electrons, and by considering these electrons as a degenerated ideal gas to which the statistical restriction of Fermi is applied, it is shown that, in the solid state, paramagnetism should be weak and approximately independent of temperature. The values calculated for the susceptibility of sodium, potassium, rubidium, and cæsium are in qualitative agreement with those observed. R. W. LUNT.

Intrinsic fields in ferromagnetic substances. J. DORFMAN (Nature, 1927, **119**, 353).—Experiments on the deflexion of β-particles passing through nickel foil indicate that no magnetic field exceeding 10^5

gauss exists in a ferromagnetic substance. Hence Weiss' " molecular field " cannot be purely magnetic. A. A. ELDRIDGE.

Hall effect in bismuth with small magnetic fields. C. W. HEAPS (Physical Rev., 1927, [ii], **29**, 332—336).

Atomic weight of silver. B. BRAUNER (Nature, 1927, **119**, 348).—Riley and Baker's value of 107·864 ± 0·0013 for the at. wt. of silver (A., 1926, 1190) is regarded as being too low, since it leads to the improbable values of 35·452—35·450 and 13·999 for chlorine and nitrogen, respectively. If, as appears to be the case, silver is appreciably volatile at 1000°, the low value would be explained, losses of 0·08—0·14 mg. occurring. A. A. ELDRIDGE.

[Atomic weight of silver.] H. B. BAKER and H. L. RILEY (Nature, 1927, **119**, 348—349).—A reply to Brauner (preceding abstract). The experimental conditions preclude the loss of silver as vapour, neither is there any evidence of the deposition of silver on the cooled parts of the weighed tube. Further, in each determination the silver obtained, after being melted several times, attained constancy of weight to within 0·01—0·02 mg. A. A. ELDRIDGE.

Radioactivity and the heat of the earth. J. W. EVANS (Nature, 1927, **119**, 424—425).—Polemical (cf. Lawson, this vol., 225). A. A. ELDRIDGE.

Missing element 87. G. VON HEVESY (Kgl. Danske Videnskab. Selsk. math.-fys. Medd., 1926, **7**, No. 11, 1—11).—As only radioactive isotopes of the elements following number 86 (radon) are known, it is improbable that inactive isotopes of the missing element 87 can be discovered. Since this element has an odd atomic number, it is expected that it can be found only as a comparatively short-lived body. Attempts were made to discover by the scintillation method an α-particle from mesothorium-2; the emission of an α-particle by this element (89) would lead to the formation of element 87. It was found that, if such a disintegration occurs at all, fewer than 1 in 200,000 atoms of mesothorium-2 can disintegrate in this way. Trials to find 87 as a β-product of radon, by removing chemically all the known members of the active deposit of 100 millicuries, failed. It is suggested that it may be possible to find an inactive isotope of polonium, and the possible formation of the element 85 is discussed. W. CLARK.

Computation of the distribution of range of α-particles. M. VON LAUE and (FRL.) L. MEITNER (Z. Physik, 1927, **41**, 397—406).—An expression has been derived for the distribution of the range of α-particles about the normal when measured by the Wilson cloud method by considering the change in range due to the alteration of pressure necessary to produce the cloud. The data of Schoch on the tracks of α-particles in argon, nitrogen, and oxygen saturated with water vapour have been analysed on this basis. The scattering coefficient of argon is thus found to be 0·013, in good agreement with Bohr's theoretical value 0·0119 and that of Meitner and Freitag, 0·0121 (A., 1926, 772). The values for nitrogen, and oxygen particularly, are higher than those of Bohr or of Meitner and Freitag; the discrepancy is attributed to the effect of the water vapour present. R. W. LUNT.

Effect of α-particles on paraffin. W. T. RICHARDS (Proc. Camb. Phil. Soc., 1927, **23**, 516—522).—The chemical effect of α-particles on paraffin, measured by the volume of hydrogen produced, is the same whether the paraffin be in the solid or in the liquid state. Where divergences from this behaviour occur with other substances, they are probably due to secondary action. R. CUTHILL.

Behaviour of materials of different atomic numbers towards Hess' ultra-γ-rays; natural radioactivity of the elements. G. HOFFMANN (Ann. Physik, 1927, [iv], **82**, 413—431).—On the assumption that Hess' rays are ultra-γ in character, the scattered radiation is discussed in terms of the Compton theory. Determination of the absorption coefficients of radiations in lead distinguishes clearly between Hess' rays and other radiation, and it is concluded that there are various reasons for supposing the existence of a very penetrating radiation. Measurements of absorption in lead, zinc, copper, iron, aluminium, and water show that there is a distinct scattering of this radiation of the kind to be expected if it is an ultra-γ radiation. The equality of the ionisation from the metals examined after allowance is made for the direct and scattered very penetrating radiation indicates that the natural radioactivity of these metals is less than 10^{-14} g. of radium per g. metal.

This conclusion is in agreement with the earlier experiments on the natural radioactivity of the elements (A., 1922, ii, 184). W. E. DOWNEY.

Emission of short-wave radiation by poor conductors. E. BODIN (Ann. Physique, 1927, [x], **7**, 35—102; cf. Reboul, Compt. rend., 1920, **171**, 1502; 1921, **172**, 210, **173**, 1162; 1922, **174**, 1452; J. Phys. Radium, 1922, [vi], **3**, 341).—When a *P.D.* of a few hundred volts is applied between two points on a piece of paper, short-wave radiations capable of affecting a photographic plate are emitted from various centres; the same type of emission can be obtained from materials other than paper so long as they are heterogeneous in structure and are poor conductors of electricity. On account of their superior power to withstand moderate voltages, pastilles of agglomerated powders can be used for obtaining more intense emission. No relationship has been found between chemical constitution and the emission of these rays, although sulphates and some oxides give the best results. The radiation is complex in nature both for paper and powders, and its penetration varies directly as the time and the applied voltage. The intensity across the centres of emission falls off with time and does not conform with Ohm's law. The distribution of *P.D.* indicates a connexion between emission and a discontinuity produced at the point of contact of the metallic electrode with the surface under consideration. Those substances which are ineffective as sources of emission do not exhibit voltage discontinuities. In some cases (*e.g.*, copper carbonate), the emission occurs from one electrode only and the voltage discontinuities behave similarly.

Usually the emission appears mainly at the positive pole. The radiations appear to extend as far as 50 Å. R. A. MORTON.

Luminescence due to radioactivity. D. H. KABAKJIAN (Proc. Nat. Acad. Sci., 1927, **13**, 4—7).—The luminescence produced by α-, β-, and γ-rays is the result of changes in molecular energy. Three distinct types of luminescence due to radioactivity are recognised: (*a*) a reversible type in which the exciting rays supply the required energy and are capable of forming and destroying the molecular modification in the substance; (*b*) luminescence due to the action of rays on certain previously-heated substances, the configurations of higher quantum state formed as a result of molecular agitation at a higher temperature being destroyed by the rays with production of luminescence; (*c*) the so-called thermo-luminescence of crystals, the energy being furnished by the rays and liberated as a result of molecular agitation in the crystal. In this last case, the amount of energy which can be absorbed by the crystal increases with decreasing temperature, the molecular configurations of higher quantum state being more stable at low temperatures. When the temperature is raised, the large amount of energy absorbed at the lower temperature is released as luminescence. Luminescence is not always due to the presence of minute quantities of impurities in the various substances examined, since a number of pure compounds have been shown to luminesce under the action of α-, and γ-rays. In most substances, all three types of luminescence co-exist with varying degrees of intensity. It is, however, possible to select compounds where one of the three possible types predominates. J. S. CARTER.

Chemical effects of penetrating radium radiation. Organic compounds containing nitrogen. A. KAILAN (Monatsh., 1927, **47**, 643—658).—The action of penetrating radiation from radium on aqueous solutions of uric acid in presence and absence of lithium carbonate has been investigated. In both cases, the number of molecules of uric acid which underwent chemical change (*m*) was of the same order as the number of ion pairs (*n*) formed: m/n—0·2. Pyridine in the undried and dried states and also an aqueous solution have been subjected to the action of the radiation for considerable periods. For the ratio m/n, the values obtained were 0·7 for the solution and 0·3 for the dried and undried pyridine. In each instance, irradiation brings about an increase in the density and electrical conductivity. For aniline, m/n is 0·4; the density is increased whilst the conductivity remains constant. After three or four months' irradiation, aniline and pyridine develop a reddish-brown coloration. The same result is observed with either wet or dry nitrobenzene. On the basis of the production of *o*- and *p*-nitrophenol in the latter reaction, the ratio m/n is 0·1. Although these are not the only products formed, it seems clear that *m* and *n* are always of the same order of magnitude. With *o*-nitrotoluene, the colour changed from yellowish-green to green after irradiation for 2000 hrs. A collateral change occurred in the conductivity and alkali titre. R. A. MORTON.

Transmutation of the elements. E. PATERNO (Atti R. Accad. Lincei, 1926, [vi], **4**, 541—544).—An extract from a paper read by the author at the VIth International Congress of Applied Chemistry, Rome, 1906. The transmutation of metals in the laboratory is considered unlikely. T. H. POPE.

Fulminating matter. Spontaneous and almost noiseless decomposition of certain ball-lightnings of great diameter. E. MATHIAS (Compt. rend., 1927, **184**, 312—314; cf. *ibid.*, 1925, **181**, 1038).—Uncharged spherical ball-lightnings decompose spontaneously and almost without noise if they are thermally homogeneous. Otherwise explosions occur which are not dangerous. Charged ball-lightning may give rise to dangerous explosions by the ejection of charged matter. If the fulminating matter (an unknown compound of oxygen and nitrogen) is pure, spontaneous decomposition occurs without the production of vapour or sparks. If animal or vegetable corpuscles are absorbed, a state of thermal heterogeneity is produced which results in partial explosion and the expulsion of incandescent matter. The latter produces electrocution if it comes from a charged source. J. GRANT.

Effect of intense light on the energy levels of atoms. A. E. RUARK (Nature, 1927, **119**, 389).—The broadening or shift of the sodium *D* lines in absorption on illumination of the vapour, sought but not observed by Kuhn (A., 1926, 985), should admit of detection, if it exists, in the solar spectrum or in the spectra of very hot stars. Kuhn's assumption that the atoms are subjected to an electric force *E* obtained from the equation energy density $=E^2/4\pi$ is criticised. A. A. ELDRIDGE.

Energy of the crossed-orbit model of the hydrogen molecule. E. HUTCHISSON (Physical Rev., 1927, [ii], **29**, 270—284).—With the classical quantum theory, the energy of a model of the hydrogen molecule, similar to the crossed-orbit model of the helium atom, with the nucleus separated into two parts is computed as 45·2 volts, whereas the experimental value is 31·42 volts. Also the moment of inertia is computed as $4{\cdot}91\times10^{41}$ g. cm.^{2} A. A. ELDRIDGE.

Calculation of atomic fields. L. H. THOMAS (Proc. Camb. Phil. Soc., 1927, **23**, 542—548).—A method of calculating from theoretical considerations the approximate fields of heavy atoms is described. R. CUTHILL.

Atomic model for the chemist. (MRS.) F. LANGWORTHY (Chem. News, 1927, **134**, 113—117).—A contention that atomic systems resemble the solar system. S. I. LEVY.

Quantum mechanics of multi-charged atoms and resonance. W. HEISENBERG (Z. Physik, 1927, **41**, 239—267).—The author's theory of the spectra of atomic systems associated with two electrons (this vol., 5) has been extended to the cases in which the number of electrons is greater than two. In particular, from a consideration of resonance phenomena explanations are advanced for the anomalous variations of intensity in rotation band spectra. R. W. LUNT.

Quantum theory of continuous spectra. J. R. OPPENHEIMER (Z. Physik, 1927, **41**, 268—293).—Schrödinger's mechanics have been employed to derive the characteristic function of systems exhibiting extended absorption. From this point of view, the hydrogen atom, the coefficients of continuous *X*-ray absorption, the polarisation and energy distribution in the continuous *X*-ray emission spectra, and the velocity and distribution in direction of photo-electrons have been discussed at length. This analysis also leads to derivations of the formula of Compton and of Kramers. R. W. LUNT.

Quantum mechanics of atoms. A. UNSOLD (Ann. Physik, 1927, [iv], **82**, 355—393).—The meaning of "penetrating" and "outer" orbits in terms of Schrödinger's quantum mechanics is investigated. The older shell-model gives only qualitative results for penetrating orbits. The *S* terms for helium, Li^+, and stripped atoms are calculated. The behaviour of atoms in a heterogeneous electric field is the basis of the calculation of the outer orbits. The calculation to a first approximation proves and extends Pauli's quadripole summation proposition, whilst the second approximation leads to the problem of the dispersion theory. The "middle" terms for the outer orbits of the alkaline-earths are then calculated and the separations of the singlet–triplet systems for some alkaline-earth terms. Finally, the Stark effect of series spectra is determined. W. E. DOWNEY.

Wave mechanics and the rotation of homopolar molecules. D. M. DENNISON (Nature, 1927, **119**, 316—317).

Radiation and absorption on Schrödinger's theory. J. C. SLATER (Proc. Nat. Acad. Sci., 1927, **13**, 7—12).—Mathematical. The author has previously shown (A., 1925, ii, 478) that the radiation and absorption of light by atoms can be treated by replacing the atoms by a set of oscillators, the frequencies of which are the frequencies of quantum transitions. Use of the Schrödinger wave-mechanics enables the theory to be placed on a more satisfactory foundation. The essential features of the author's treatment of absorption have already been put forward by Dirac (A., 1926, 1078). J. S. CARTER.

Band spectrum of mercury from the excited vapour. (LORD) RAYLEIGH (Nature, 1927, **119**, 387; cf. this vol., 82).—The green, visual band, extinguished by heat, partly recovers as the excited vapour moves to a cold part of the tube. The "forbidden" line 2270 was observed, and a separate stretch of band spectrum reaches from this point to the band 2345 Å. Below 2270 Å., and from 2345 to 2537 Å., the background of the spectrum is dark. A. A. ELDRIDGE.

Band spectrum of mercury from the excited vapour. (LORD) RAYLEIGH (Nature, 1927, **119**, 423).—The "forbidden" line at 2655·73 Å. has been observed (cf. preceding abstract). A. A. ELDRIDGE.

Infra-red oscillation spectrum of water molecules and its variation with state. J. W. ELLIS (Phil. Mag., 1927, [vii], **3**, 618—621).—A collection of data for the infra-red spectrum of water showing that the spectra for the various states can be explained as being combinations of two primary bands, each pair being characteristic of the special state. A. E. MITCHELL.

Infra-red absorption by the N·H linking. I. Aniline and alkylaniline. J. W. ELLIS (J. Amer. Chem. Soc., 1927, **49**, 347—356).—Infra-red absorption spectra below 2·8 μ are recorded for aniline and some mono- and di-alkyl derivatives. The absorption bands at 1·47 μ and 1·04 μ are associated with the N·H linking; together with the band at 2·8 μ (Bell, A., 1925, ii, 928) these bands form members of a parabolic series: $\nu=376n-18{\cdot}3n^2$, where ν is the frequency in waves per mm. The bands near 2·0 μ and 1·2 μ may be produced by the combination of N·H frequencies and a fundamental C·H frequency. S. K. TWEEDY.

Absorption of ultra-violet light by copper sulphate solutions. L. KWIECINSKI and L. MARCHLEWSKI (Bull. Inter. Acad. Polonaise, 1926, *A*, 247—253).—Beer's law is obeyed for the ultra-violet absorption of *N*/10- and *N*/20-copper sulphate. R. A. MORTON.

Absorption spectra of "saturated" and "unsaturated" organic substances. J. E. PURVIS (Proc. Camb. Phil. Soc., 1927, **23**, 588—592).—The vapour of *cyclo*hexanone between 100° and 200° gives a large absorption band at about 2777 Å. Comparison of the absorption of geraniol with that of the pelargonic ester shows that weighting the geraniol molecule with the heavy pelargonic radical shifts the position beyond which absorption occurs towards the red. Pentabromophenol and tetrabromo-*o*-cresol show bands comparable with those of phenol. R. CUTHILL.

Spectrochemical studies of hydroxyazo-compounds. II. T. UEMURA, N. YOKOJIMA, and T. ENDO (Bull. Chem. Soc. Japan, 1927, **2**, 10—15; cf. this vol., 238).—The absorption spectra of neutral and alkaline solutions of benzeneazopyrocatechol, benzeneazoquinol, *p*-nitrobenzeneazopyrocatechol, *p*-nitrobenzeneazoquinol, *m*-nitrobenzeneazophenol, *o*-nitrobenzeneazophenol, *o*-nitrobenzeneazoresorcinol, *p*-nitrobenzeneazoguaiacol, and *p*-nitrobenzeneazoquinol monomethyl ether have been studied, and the results correlated with the colour and the structure of the compounds. L. L. BIRCUMSHAW.

Absorption of ultra-violet light by *d*-galactose. L. KWIECINSKI and L. MARCHLEWSKI (Bull. Int. Acad. Polonaise, 1926, *A*, 255—262).—Purification of galactose brings about the disappearance of selective absorption at 265 μμ. Aqueous solutions of pure galactose (m. p. 165—165·5°) exhibit feeble general absorption in the ultra-violet down to 228 μμ. The rotation $[\alpha]_D^{20}$ falls from +107° to 81·23° in 9 hrs., but a concomitant change in absorption cannot be detected with certainty. If the carbonyl group causes selective absorption, then it seems that aqueous solutions of galactose must contain only two stereoisomerides in equilibrium, neither of which possesses an aldehyde group. R. A. MORTON.

Fluorescence spectra of the sulphur group. J. C. MCLENNAN, I. WALERSTEIN, and H. GRAYSON SMITH (Phil. Mag., 1927, [vii], **3**, 390—395).—New fluorescence spectra have been found in the saturated

vapours, at comparatively low temperatures, of sulphur, selenium, and tellurium, excited by intense illumination from a quartz mercury arc. The fluorescence spectrum of sulphur consistsof a large number of bands extending from 5670 to 4050 Å. The bands are mostly sharp, and there are certain sequences of approximately equally spaced bands. There is marked absorption of the diffused mercury spectrum below 4050 Å., indicating that this is probably the active region for the excitation of this sulphur spectrum. At 325°, selenium exhibits a fluorescence spectrum extending from 5079 to 2229 Å., which is apparently analogous to the ultra-violet fluorescence spectrum of iodine. Above 325°, this spectrum disappears and is replaced at 430° by a spectrum comprising nine faint broad bands between 4178 and 4829 Å. At 550°, tellurium vapour shows two groups of regularly-spaced bands covering the region 6580—4130 Å. These spectra are all different from the fluorescence spectra found for these elements by Diestelmeier and others, using superheated vapours. At 500°, bismuth vapour exhibits a fluorescence spectrum showing eighteen fairly sharp lines in the region 4890—4410 Å. A. E. Mitchell.

Polarisation of the resonance fluorescence of sodium vapour. W. Hanle (Z. Physik, 1927, **41**, 164—183).—The polarisation of the fluorescence of sodium vapour when excited by circular polarised light, using a silica discharge tube containing sodium vapour and a little argon as the light source, has been determined as a function of the pressure of the sodium vapour in the range 10^{-7} to 8×10^{-6} mm., and in fields from 60 to 600 gauss. At 600 gauss and 10^{-7} mm., a maximum value corresponding with 87% of the theoretical was observed, the difference being attributed to errors introduced by the apparatus. The depolarisation produced by the introduction of argon, nitrogen, hydrogen, and helium–neon mixtures has also been recorded as a function of the temperature. R. W. Lunt.

Line fluorescence of cadmium vapour. W. Kapuscinski (Z. Physik, 1927, **41**, 214—220).—The fluorescence of cadmium vapour, carefully purified from mercury and occluded gases, has been examined in the temperature range 200—900°. In addition to the resonance lines 2289, 3261 Å., the following lines of the arc spectrum have also been observed, using the light from a condensed cadmium spark discharge to excite the fluorescence: 3614·6 (2^3P_2—3^3D_1), 3467·8 (2^3P_1—3^3D_1), 3403·7 (2^3P_0—3^3D_1), 3613·0 (2^3P_2—3^3D_2), 3466·3 (2^3P_1—3^3D_2), 3610·7 (2^3P_2—3^3D_3) (maximum intensity at 600°); above 450°, 5086·1 (2^3P_2—2^3S), 4800·1 (2^3P_1—2^3S), 4678·4 (2^3P_0—2^3S), and 3133·3 Å. (2^3P_1—3^3S). Using iron electrodes, the triplet 5086, 4800, 4678 Å. was observed, and also a weak emission of the triplets 3613, 3467, 3404 Å., in addition to the resonance line 3261 Å. The resonance lines 3261 and 5086, 4800, 4678 Å. were excited by the spark spectra of zinc, magnesium, and aluminium; and 3261 by the light from copper and carbon electrodes, and from the mercury arc. The lines 2573 and 2749 Å. were also observed, using cadmium electrodes, and are thought to correspond with absorption by atoms in the 2^3P_1 state, whereby they become in the 2^3S or 3^3D_j state, from which they return to the 2^3P_i state, emitting the corresponding radiation (2^3P_i—3^3D_j and 2^3P_i—2^3S). When excited with the light from zinc electrodes, cadmium vapour emits the zinc lines 2502 and 2558 Å. R. W. Lunt.

Line fluorescence of tellurium vapour. (Mme.) H. Rakowicz-Pogorzelska (Bull. Inter. Acad. Polonaise, 1926, *A*, 243—245).—Tellurium exhibits an intense bluish-green fluorescence when illuminated by an incandescent lamp. The emission shows a banded spectrum. Under the light of a mercury-vapour lamp, the fluorescence is much less intense. The spectrograms indicate a number of fine lines between 413 and 542 μμ which are regularly spaced. The wave-lengths of the more intense lines have been tabulated. The exciting rays are shown to belong to the visible region, with maximal activity in the bluish-violet region extending from 400 to 435 μμ. R. A. Morton.

Fluorescence bands of mercury vapour. F. G. Houtermans (Z. Physik, 1927, **41**, 140—153).—Mercury vapour when excited by the mercury line 2537 Å. exhibits a short and a long afterglow. The former commences at 2537 and shows a maximum at 4850 Å.; it is attributed to the 2^3P_1 state. The latter commences at 2560 and exhibits a maximum at 3300 Å.; it is attributed to the 2^3P_0 state. R. W. Lunt.

Anticathodic luminescence of organic compounds. J. K. Marsh (J.C.S., 1927, 125—130).—Observations have been made of the light emitted by various organic substances when placed on an anticathode in a discharge tube. The conditions under which the discharge tube was operated are not described, except that the substance on the anticathode was kept at the temperature of liquid air. The light emitted was examined by a glass spectroscope, but for the following substances only was it sufficiently intense to photograph: toluene, *p*-cymene, *m*-xylene, mesitylene, naphthalene, tetrahydronaphthalene, octahydroanthracene, acenaphthene, triphenylmethane, diphenylmethane, α-methylnaphthalene, β-methylnaphthalene, α-naphthol, and β-naphthol. It is shown that between the short wave-length boundary of the absorption and fluorescence spectra and that of the anticathodic luminescence of these substances there is an approximately constant wave-number difference of 1500 ± 100. R. W. Lunt.

Polarisation of the glow from canal rays. E. Rupp (Physikal. Z., 1926, **27**, 796—799; cf. A., 1926, 450, 875).—The glow from canal rays sometimes exhibits marked polarisation. The phenomenon has been studied by means of photographic photometry. Viewing the stream at an angle of 90°, the fraction of the light polarised in a direction parallel to the direction of the canal rays is greater than the fraction polarised in a direction perpendicular to the stream. The difference is great for hydrogen (velocity, $6\cdot4\times10^7$ cm./sec.: lines, H_β, H_γ, ratio 0·65). The $2p$—$3d$ line of lithium shows a considerable effect, as also do the $2p$—md and $2P$—mD series of orthohelium and parhelium. For the $1\cdot5s$—mp and $2p$—ms series of lithium, the $2p$—$4s$ series of orthohelium, and the

$2S-3P$, $2P-4S$ series of parhelium the polarisation is very small. The results are discussed theoretically by the author and others. R. A. MORTON.

Influence of lighting the cathode with ultra-violet light on the self-dependent glow discharge. E. SALZWEDEL (Ann. Physik, 1927, [iv], **82**, 305—345).

Investigation of gas discharges by means of an exploring electrode. K. G. EMELÉUS (Proc. Camb. Phil. Soc., 1927, **23**, 531—541).—The distribution of potential in the glow discharge in air, oxygen, nitrogen, and hydrogen has been determined by Langmuir's method, using an exploring electrode. At pressures of about 0·1 mm., nearly the whole of the *P.D.* is across the cathode dark space, but at higher pressures there may be a considerable *P.D.* across the remainder of the discharge. With hydrogen at low pressure, the cathode edge of the negative glow is at a higher potential than the anode. In the negative glow, there are two groups of electrons, with one fast group at the anode boundary of the cathode dark space, and a slow group in the Faraday dark space. R. CUTHILL.

Activation of molecular hydrogen by electron impact. G. GLOCKLER (Science, 1926, **64**, 505—506).—Activated hydrogen, produced in a 4-electrode tube, reacted with copper oxide, the water produced being removed by freezing and the decrease of pressure being determined as a function of the accelerating voltage. A sharp decrease occurs with electrons of 11·4 volts energy. Hence hydrogen molecules react at the ordinary temperature with copper oxide after having been brought into their first higher quantum state by electron impact. A. A. ELDRIDGE.

Photo-electric activity of the silver halides and silver sulphide. F. C. TOY, H. A. EDGERTON, and J. O. C. VICK (Phil. Mag., 1927, [vii], **3**, 482—495).—An investigation of the photo-electric activity of the silver halides and of silver sulphide has been made with light of wave-length less than 2800 Å. With silver halides prepared either by exposure of metallic silver to the halogens or by fusion of the resulting halide, the order of photo-electric activity has been found to be iodide>bromide>chloride. This order is probably the same for the halides prepared by precipitation from aqueous solution. Silver sulphide prepared by exposing metallic silver to hydrogen sulphide was found to be from two to three times as active as the iodide, and about twenty-five times as active as the bromide prepared in an analogous manner. Traces of silver sulphide in either silver bromide or iodide have been shown to cause no abnormal increases of photoelectric sensitivity. Small amounts of silver iodide in silver bromide did not result in any appreciable shift of the critical photo-electric wave-length towards the visible spectrum comparable with the chromatic sensitisation observed photographically. The results indicate that there is no parallelism between the photo-electric properties of the pure silver halides and the photographic properties of silver halide emulsions.
A. E. MITCHELL.

Thermionic theory of the electrical conductivity of dielectrics. H. SAEGUSA (Sci. Rep. Tôhoku Imp. Univ., 1926, **15**, 795—803; cf. *ibid.*, 1925, **14**, 319).—It is assumed that the conductivity of dielectrics is due to some of the loosely-bound electrons becoming freed from their atoms and that the number of these electrons is given by Richardson's formula for thermionic emission. Using the electron gas theory of conductivity, an expression is obtained for the conductivity of dielectrics which is in reasonable agreement with the author's previous results (*loc. cit.*) for quartz. W. HUME-ROTHERY.

Dielectric constants of liquid and solid nitrogen. L. EBERT and W. H. KEESOM (Proc. K. Akad. Wetensch. Amsterdam, 1926, **29**, 1188—1192).—Preliminary measurements. Using the same apparatus as for oxygen (A., 1926, 661), the dielectric constant of liquid nitrogen has been examined over the temperature range 63·9—76·5° Abs. The values of ε at the lower and higher temperatures are 1·472 and 1·440, respectively. The mean value of the molecular polarisation is 4·39, that for gaseous nitrogen being 4·34. The Maxwell relation and the equation of Clausius and Mosotti are approximately valid for gaseous and liquid nitrogen. The dielectric constant of solid nitrogen at 60° Abs. is of the order 1·45—1·46. J. S. CARTER.

Dielectric constant of bromine. A. BRAMLEY (J. Franklin Inst., 1927, **203**, 251—260).—The variation of the dielectric constant ε of bromine vapour with pressure, temperature, and electric intensity has been studied. Curves have been obtained by plotting $\varepsilon-1$ against pressure for different temperatures and electric fields. In the curves obtained at 23·9°, the quantity $\varepsilon-1$ increases with pressure more rapidly than the first power. The curve at 28·5° is linear and is independent of the electric gradient. It corresponds with the classical theory, except that $\varepsilon-1$ is about twice as large as the value expected from the refractive index. The curves at 77—80° show a decreasing tangent with increasing pressure, the reverse of the effect found at 23·9°. When the field was changed from 58 to 285 volts, a considerable variation was observed at 80°, the effect depending on the pressure of the vapour.

If the band spectrum of a diatomic gas is due to the rotational and vibrational energies of the two ions comprising the molecule, the molecular moment should depend on the distance separating the ions. It is shown theoretically that the temperature variation of the dielectric constant is related to a constant ε_0 corresponding with a wave-length For water $\lambda_0=3{\cdot}0$ μ, which agrees with the maximum in the absorption band of water vapour; for bromine vapour $\lambda_0=0{\cdot}9$ μ. As no data were available to test this result, the absorption spectrum of bromine vapour was studied in this region. A broad absorption band makes its appearance at 0·95 μ, and extends as far as 1·5 The theory is thus vindicated in this respect. R. A. MORTON.

Determination of the dielectric constant of air by a discharge method. A. P. CARMAN and K. H. HUBBARD (Physical Rev., 1927, [ii], **29**, 299—308).—A mean value of 1·000594 is obtained for the dielectric constant of air at 0° and 760 mm.
A. A. ELDRIDGE.

Temperature variation of the dielectric constants of gases. H. J. VON BRAUNMUHL (Physikal. Z., 1927, **28**, 141—149).—The dielectric constants of hydrogen, carbon monoxide, argon, carbon dioxide, nitrous oxide, hydrogen sulphide, and hydrogen chloride have been measured by a heterodyne method at the frequency 10^6 cycles per sec. in the temperature range 280—400° Abs., and are found to vary in accordance with the equation of Debye, $m(\varepsilon-1)T/4\pi\rho=aT+b$, where ε is the dielectric constant, m the molecular mass, ρ the density, T the temperature Abs., and a and b are characteristic constants. The following expressions are given for a and b: $a=\Sigma n_i e_i^2/f_i$ and $b=\mu^2/3k$, where is the number of particles of charge e_i per molecule, f_i the restoring force, μ the electric moment of the dipole, and k the Boltzmann constant. Values of a and μ are obtained in this way from the experimental data. R. W. LUNT.

Dielectric properties of ionised gases. H. GUTTON and J. CLÉMENT (Compt. rend., 1927, **184**, 441—443).—The dielectric properties of hydrogen have been observed at various pressures and degrees of ionisation by the resonance method, and curves obtained which show the relation between the resonance wave-length and the square of the resonance current for constant pressures and an increasing degree of ionisation. Two current maxima are obtained, corresponding with zero and complete ionisation, the former being the greater. At low pressures an apparent decrease in ε is indicated by a diminution in the wave-length; this increases with the ionisation. At high pressures, the curves indicate the existence of forces analogous to friction, and the curves are similar to those obtained for a solution of an electrolyte as the concentration increases. J. GRANT.

Electric moments of disubstituted benzene derivatives. R. N. KERR (Phil. Mag., 1927, [vii], **3**, 330—336).—The dielectric constants of a number of disubstituted benzene derivatives in the liquid state at 58° have been determined for a wave-length of 95 metres. All the isomeric compounds show a gradation of the dielectric constant from *ortho*- through *meta*- to *para*-. In some cases, there is an increase in the value in this order, whilst in others there is a decrease. The theory of Thomson (A., 1923, ii, 683) regarding the method in which the magnetic moments of such isomerides should vary is shown to hold when both substituents are the same, but to fail in several cases when the latter are different. A. E. MITCHELL.

Molecular volumes of the halopentammine-cobaltic and chromic halides. R. KLEMENT (Z. anorg. Chem., 1927, **160**, 165—170).—Ephraim and Schütz's values (A., 1926, 785) for the molecular volumes of chloro- and bromo-pentamminecobaltic halides are criticised, since they do not accord with the atomic volumes of the halogens; bromopentammine-cobaltic bromide is reported as having a smaller molecular volume than chloropentamminecobaltic bromide, although the atomic volume of bromine is greater than that of chlorine. The possible sources of error are discussed, and new determinations given which are in agreement with the order of atomic volume of the halogens. H. F. GILLBE.

Changes in volume in the formation of halides, oxides, and sulphides. C. DEL FRESNO (Anal. Fís. Quím., 1926, **24**, 707—716).—The contraction in volume, expressed by the negative fraction $V_m/\Sigma V_a$ (where V_m is the molecular volume and ΣV_a the sum of the atomic volumes), increases with the atomic volumes of the metals for the halides of elements of the first two groups. For different halides of the same metal, excepting hydrogen, the opposite relationship obtains. The contraction is smaller in the oxides than in the sulphides. Whilst the formation of homopolar compounds appears to be accompanied by dilatation, contraction is observed with the hydrogen halides. This may be explained on the assumption that the hydrogen nucleus penetrates the electronic layer of the other atom, whilst the electron remains with the other electrons, the hydrogen atom thereby losing its identity. With the oxides of elements of groups III—VI, the curve connecting contraction with atomic volume passes through a minimum. G. W. ROBINSON.

Dependence of free space on temperature. W. HERZ (Z. Elektrochem., 1927, **33**, 76—77).—The influence of temperature on the free space, V_f, of liquids (A., 1926, 670) can be represented by relations similar to those for the effect of temperature on molecular volume, viz.: $(V_{t_2}-V_{f_1})/$ and $(V_f-V_{f_0})/V_f=kt_1$, where V_{f_2}, V_{f_1}, and V_{f_0} denote the free space at t_2, t_1, and 0°, respectively, and α and k are constants. Data for pentane, hexane, heptane, and octane are quoted. H. J. T. ELLINGHAM.

Measurement of index of refraction of gases at higher temperatures. E. W. CHENEY (Physical Rev., 1927, [ii], **29**, 292—298).—For air, nitrogen, ammonia, carbon dioxide, and sulphur dioxide, values of $(n-1)10^7$ at 0° and 760 mm. for 5852, 6143, and 6678 Å., respectively, are: 2925, 2985, 3795, 4485, 6637; 2919, 2977, 3785, 4473, 6615; 2912, 2969, 3771, 4465, 6598. For visible light the thermal coefficients do not differ from those of density change between 0° and 300°. Between 25° and 300°, the coefficient of (linear) expansion of quartz has the constant value $0{\cdot}946\times10^{-6}$. A. A. ELDRIDGE.

Refractivity of some anisotropic molecules. T. H. HAVELOCK (Phil. Mag., 1927, [vii], **3**, 433—448).—By treating the molecule as a structure of isotropic polarisable constituents in fixed relative positions, expressions are obtained, in terms of the constants of the constituents and of the structure, for the refractivity and the depolarisation ratio of a gas the molecules of which are of three types: (*a*) three equal atoms at the corners of an equilateral triangle with a fourth atom equidistant from them, but not necessarily in the same plane, (*b*) four equal atom at the corners of a regular tetrahedron with a fifth at the centroid, (*c*) four equal atoms at the corners of a square with a fifth equidistant from them, but not necessarily in the same plane. Numerical results are deduced for some suggested models for ammonia and methane, and are discussed in relation to other members of the series of compounds of the form XH_n. A. E. MITCHELL.

Action of magnetic fields on the refractive index of gaseous carbon dioxide. E. T. S.

APPLEYARD (Nature, 1927, **119**, 353).—The observations of Ghosh and Mahanti (A., 1926, 1194) cannot be attributed to molecular orientation. Further, repetition of Ghosh and Mahanti's experiments gave a straight line when pressure was plotted against fringe-shift whether the field was on or off.

A. A. ELDRIDGE.

Diffraction of X-rays by liquids. F. ZERNIKE and J. A. PRINS (Z. Physik, 1927, **41**, 184—194).—From a consideration of the effect of the relative motion of the molecules in a liquid an expression is obtained for the variation of the intensity of the scattered radiation with the angle of scattering when a liquid is irradiated with monochromatic *X*-radiation. The general characteristics of the experimental curves are reproduced, particularly the rapid increase in intensity, rising to a sharp maximum, which is observed as the angle of scattered radiation is increased from zero to $\pi/4$. This analysis also leads to the conclusion that, for small angles of scattering, the ratio of the intensities for a liquid and its vapour is equal to the ratio of the compressibilities of the two states. R. W. LUNT.

Anomalous dispersion of a silicate solution for wave-lengths between 50 and 60 cm. E. FRANKENBERGER (Ann. Physik, 1927, [iv], **82**, 394—412).—Using a Lecher-wire system, the band of anomalous dispersion at about 56 cm. wave-length in the refraction of water, found by Weichmann (A., 1922, ii, 5, 331), is shown not to appear with pure water. $1{\cdot}5\times10^{-4}N$-Sodium hydrogen silicate in water shows anomalous dispersion between 50 and 60 cm. wave-length. If the solution is prepared in the same manner, it always gives the same dispersion, even after keeping for a week. The dispersion band can be split up into three parts, each of which corresponds with a mode of resonance. The results fit the ordinary optical dispersion formula. The measured values of absorption coefficient agree in order of magnitude with those calculated from the dispersion–wave-length curve. It is necessary to note that water itself shows a fairly considerable absorption for these short waves. W. E. DOWNEY.

Intensity of anomalous dispersion in non-luminous vapours of thallium and cadmium. W. KUHN (Kgl. Danske Videnskab. Selsk. math.-fys. Medd., 1926, **7**, No. 12, 1—87).—From an extension of the theory of dispersion, an expression is developed for longitudinal magnetic double refraction for certain anomalous Zeeman effects. Previous results of anomalous dispersion and absorption in the neighbourhood of spectral lines are recalculated to a common basis and extended by more recent data. Anomalous magnetic rotation dispersion in non-luminous vapours of thallium and cadmium were measured, and the *f*-values for a number of lines are given. The absolute and relative *f*-values are discussed from various theoretical points of view. W. CLARK.

Rotatory dispersion of asparagine in the ultra-violet. (MLLE.) J. LIQUIER and R. DESCAMPS (Bull. Soc. chim. Belg., 1926, **35**, 459—465).—The rotatory dispersion of aqueous solutions of asparagine containing hydrogen chloride, sodium hydroxide, sodium chloride, potassium chloride, potassium sulphate, calcium chloride, and various mixtures of these substances has been studied in the ultra-violet, with results in accordance with previously expressed opinions (A., 1926, 906). L. F. GILBERT.

Magnetic rotary dispersion of water, alcohol, and water–alcohol mixtures. D. J. STEPHENS and E. J. EVANS (Phil. Mag., 1927, [vii], **3**, 546—565).—The magneto-optical rotation of water at temperatures between 13·2° and 20° has been examined over the region of wave-lengths 0·5997—0·2383 μ; the results show that in this spectral region the only absorption band which contributes materially to the magnetic rotation is at 0·1192 μ. Similar measurements at 12·2—13° have been made with 99·4% ethyl alcohol over the spectral range 0·4390—0·2600 μ; the results indicate that the absorption band making the major contribution to the rotation is at 0·1114 μ. Examination of the magneto-optical rotation at 12·2—13° of various ethyl alcohol–water mixtures in the region 0·2753—0·3363 μ shows that the value of Verdet's constant diminishes initially with an increase in the percentage of alcohol up to 30%; between 30 and 70% alcohol its value is constant, and above 70% it decreases. A. E. MITCHELL.

Influence of solvents on the rotation of optically active compounds. XXIV. Menthyl benzenesulphonate, menthyl naphthalene-α-sulphonate, and menthyl naphthalene-β-sulphonate in various solvents. T. S. PATTERSON and (MISS) I. M. MCALPINE (J.C.S., 1927, 353—355; cf. *ibid.*, 1916, **109**, 1204).—The specific rotations of each of the above substances in six different solvents for three different colours of light have been determined. From the data so obtained, it is concluded that there is no region of anomalous rotation dispersion. The dispersion ratios for the series of substances are practically constant. W. E. DOWNEY.

Molecular scattering of light in a binary liquid mixture. K. C. KAR (Phil. Mag., 1927, [vii], **3**, 601—604).—It is shown that the attempted improvement by Raman and Ramanathan (*ibid.*, 1923, [vi], **45**, 213) of Einstein's equation for molecular scattering of light in a binary liquid mixture introduces a vanishingly small correction term, and is therefore unjustified. A. E. MITCHELL.

Absolute measurement of the intensity of light diffused by benzene in the liquid state. J. CABANNES and P. DAURE (Compt. rend., 1927, **184**, 520—522).—The intensity of light diffused through thiophen-free, non-fluorescent benzene has been compared with that found for gaseous ethyl chloride (A., 1925, ii, 753). In this, and in 66 liquids, the ratios of the intensity of the light diffused through the liquid to that of the gas indicates that the former diffuses less light than would be expected when the result is calculated from Einstein's formula corrected for anisotropy. Avogadro's constant (N) is $6{\cdot}5\times10^{23}$ for the gas and $7{\cdot}8$—$8{\cdot}0\times10^{23}$ for the liquids. The method therefore is not suitable for the determination of N in liquids. J. GRANT.

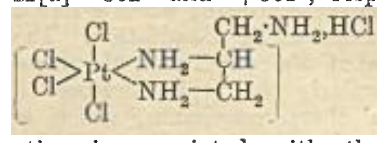
Magnetism and molecular structure. E. C. STONER (Phil. Mag., 1927, [vii], **3**, 336—356).—The magnetic properties of uninuclear and simple bi-

nuclear systems are discussed in relation to their spectroscopic and chemical properties. For inert gas atoms and ions of similar configuration, the magnetic susceptibilities are roughly of the same order as those to be expected from ionisation potential data. For helium, the magnetic data suggest a model with two parallel approximately circular orbits. The model with $k=\frac{1}{2}$ for each electron orbit leads to a value for the susceptibility one sixth of that observed by Will and Hector (A., 1924, ii, 293). The magnetic moments of the ions of the first transition series of elements are shown to be almost all in disagreement with values predicted from the work of Hund (A., 1925, ii, 912). Ions with fewer electrons behave magnetically, as though they were in S-states. The simpler binuclear diamagnetic systems behave analogously to ^1S atomic configurations. From numerical values of the susceptibilities it is shown that the anomalous increase in molecular susceptibility at low pressures observed by Glaser (*ibid.*, 82) cannot be due to an orientation phenomenon, and it is suggested that Glaser's results are due to some unrecognised experimental factor inherent in his method. The significance of the high value of the susceptibility of hydrogen is discussed, and it is suggested that in the hydrogen molecule the two electronic orbits are parallel to each other and to the plane of nuclear rotation, that the electrons move in opposite directions in quantum orbits for which the total quantum number is greater than one, that the molecule as a whole behaves as a ^1S-system, and when strongly quantised assumes a single definite orientation in a magnetic field. This view is in agreement with Mulliken's interpretation (A., 1926, 8) of the spectroscopic data. The magnetic moments of the binuclear paramagnetic systems NO and O_2 suggest that these two molecules form a sequence with N_2, the three molecules behaving as atom-like configurations in ^1S-, ^2S-, and ^3S-states. The various lines of evidence suggest that in the simpler molecules the outer electrons distribute themselves about the binuclear centre similarly to the electrons of atoms. A. E. Mitchell.

Co-ordination theory in organic and physiological chemistry. P. Pfeiffer (Ver. Ges. Deut. Naturforsch. Aerzte, 1926, **19**, 1100—1108).—An address in which the theory of co-ordination compounds and complex metallic salts is considered in relation to complex organic molecular compounds etc. of medical interest. The implications of adsorption are also discussed. R. A. Morton.

Isomerism of molybdenyl monochloride. W. Wardlaw and R. L. Wormell (J.C.S., 1927, 130—139).—The authors report the existence of two forms of the co-ordination compound $MoOCl,4H_2O$. Assuming that tervalent molybdenum has a co-ordination number of six (from certain experimental evidence on ionisation values), and that the associating units are situated at the vertices of a regular hexagon, the authors show that two stereoisomerides of this compound are possible. From a consideration of the action of these compounds with sodium monosalicylate, using the salicylate group as an unsymmetrical chelate group, the authors assign a *cis*-configuration to the brown compound and a *trans*-configuration to the green compound. R. W. Lunt.

Novel type of optically active complex metallic salt. F. G. Mann and (Sir) W. J. Pope (Nature, 1927, **119**, 351).—It is established that an auxiliary valency linking can render a carbon atom asymmetric. Tetrachloro-(triaminopropane monohydrochloride)-platinum (cf. A., 1926, 1234) has been resolved into optically active components by means of silver *d*- and *l*-camphorsulphonates, the hydrochlorides regenerated from the salts *l*-base-*d*-acid and *d*-base-*l*-acid having $M[\alpha]$ $-502°$ and $+501°$, respectively. Hence the hydrochlorides must be represented by the annexed formula, where the enantiomorphism of configuration is associated with the asymmetry of the β-carbon atom of the triaminopropane molecule.



A. A. Eldridge.

Magnetic birefringence constant of benzene. C. V. Raman and K. S. Krishnan (Compt. rend., 1927, **134**, 449—451).—The Cotton–Mouton constant for benzene is calculated from the authors' formula (this vol., 92) on the assumption that the molecule has the hexagonal structure suggested by Pauling (A., 1926, 662). The values obtained for each method of linking of the electrons are calculated and a result is obtained which agrees with the observed value ($5{\cdot}90\times10^{-13}$) when it is assumed that all the carbon–carbon electronic orbits are in the plane of the hexagon and those of carbon–hydrogen are perpendicular to it. J. Grant.

Diameter of molecules at the b. p. S. G. Mokroushin (J. Russ. Phys. Chem. Soc., 1926, **58**, 491—494).—By combining the author's earlier formula (A., 1924, ii, 820) $d=k\sqrt{T/\gamma}$, where T is the b. p., γ the surface tension, d the molecular diameter, and $k=1{\cdot}98\times10^{-8}$, with Kistiakowski's modification of the Ramsay and Shields expression (J. Russ. Phys. Chem. Soc., 1902, **34**, 74) $\gamma=(M/s)^{2/3}=1{\cdot}15T$, where s is the liquid density, a relation is obtained: $d=k_1/\sqrt[3]{M/s}$, the value of k_1 being $1{\cdot}79\times10^{-8}$.

Molecular diameters given by this formula are compared with values obtained by other methods, including the kinetic theory of gases. The latter do not agree, since they are so-called "collision diameters." The views of Langmuir, Adam, and Marcelin as to the unimolecular nature of surface layers are adopted. M. Zvegintzov.

Illinium. W. A. Noyes (Nature, 1927, **119**, 319).—Priority is claimed for Hopkins (cf. Rolla and others, this vol., 190) in the discovery of illinium. A. A. Eldridge.

Element of atomic number 61: florentium [illinium]. L. Rolla and L. Fernandes (Z. anorg. Chem., 1927, **160**, 190—192).—See this vol., 190.

Discovery and the *K*-absorption edge of the element of atomic number 61. R. Brunetti (Z. anorg. Chem., 1927, **160**, 237—241; cf. this vol., 190).—A claim for priority. H. F. Gillbe.

***X*-Ray analysis of single crystals.** R. L. Aston (Proc. Camb. Phil. Soc., 1927, **23**, 561—577).—Muller's method of determining the orientation

of a single crystal of metal by measuring the reflexion of characteristic *X*-rays from surface layers (Proc. Roy. Soc., 1924, **A**, **105**, 500) has been applied to iron crystals. Details of improvements in the technique are given. R. CUTHILL.

Crystal form of boron nitride. Eventual ambiguity in the analysis of powder-spectrograms. F. M. JAEGER and H. G. K. WESTENBRINK (Proc. K. Akad. Wetensch. Amsterdam, 1926, **29**, 1218—1222).—Boron nitride was purified by a process of fractional sedimentation with water. The resulting substance, having d_4^{18} 1·99, was examined by the Debye–Hull powder-spectrogram method. The results of such measurements indicate that the underlying grating is simple cubic (a_0=7·44 Å.) or simple tetragonal (a_0=4·295, c_0=5·176 Å., $a:c$=1 : 1·2052). In the first case, the elementary cell would contain 20 mols. (an improbable figure), and in the case of tetragonal symmetry 4 or 5 mols. As all further necessary data are lacking, it is impossible to decide which structure is correct.

Conclusions as to crystal structure must not be drawn where only the results of powder-spectrograms can be used. Such data are valuable only when used in connexion with the results of other spectrographic methods, and of crystallographic measurements. J. S. CARTER.

Crystal structure of solid oxygen. J. C. MCLENNAN and J. O. WILHELM (Phil. Mag., 1927, [vii], **3**, 383—389).—*X*-Ray examination of solid oxygen at the temperature of liquid hydrogen (—252°) has shown that oxygen at —252° crystallises in the body-centred orthorhombic system with axial ratios $a:b:c$=1·44 : 1 : 0·9. The sides of the unit cell are a=5·50, b=3·82, and c=3·44 Å., whence if two molecules be supposed to be associated in each cell, d is 1·46. The accepted value of the density of solid oxygen is 1·426. If it is assumed that this lower value is for the second modification existent at temperatures above that of the observations, then the present results afford confirmation of the observation of Wahl (A., 1913, ii, 208) that the low-temperature modification is the denser of the two forms of solid oxygen.

The existence of two modifications of oxygen is in agreement with the results that have been obtained for the other members of the same group of elements in the periodic table. A. E. MITCHELL.

Determination of the lattice spacing and of the rhombohedral angle of magnesium carbonate from a micro-crystalline powder. J. BRENTANO and W. E. DAWSON (Phil. Mag., 1927, [vii], **3**, 411—418).—*X*-Ray examination of a microcrystalline powder of magnesite has given a value for the rhombohedral angle of 103° 19′, which is in close agreement with the value previously determined by Schroder (Ann. Physik, 1859, **106**, 226) by a goniometric method. The corresponding spacing d_{100} is 5·477± 0·005 Å. and the density 3·000. The corresponding values found by Levi and Ferrari (A., 1924, ii, 761) from *X*-ray measurement are 5·420 Å. and 3·08. The edge of the elementary cleavage rhomb is calculated to be 5·899 Å., corresponding with a unit cell of 4 molecules of magnesium carbonate. A. E. MITCHELL.

Crystal structure of magnesium platinocyanide heptahydrate. R. M. BOZORTH and F. E. HAWORTH (Physical Rev., 1927, [ii], **29**, 233—230).—The platinum atoms are located at 0, 0, 0 and $\frac{1}{2}$, $\frac{1}{2}$, and the magnesium atoms at 0, 0, $\frac{1}{2}$ and $\frac{1}{2}$, 0, in a tetragonal unit 14·6×14·6×3·13 Å. The magnesium and platinum atoms alternate in rows with shortest distance of separation 10·3 Å., the distance between any two adjacent atom-centres being 1·57 Å. A. A. ELDRIDGE.

Space-groups of the rhombic and monoclinic heptahydrates of the sulphates of bivalent metals [and of rhombic magnesium chromate]. H. G. K. WESTENBRINK (Proc. K. Akad. Wetensch. Amsterdam, 1926, **29**, 1223—1232).—The rhombic modifications of the heptahydrated forms of magnesium, zinc, and nickel sulphates and magnesium chromate have been examined by the *X*-ray spectrograph. The crystals have rhombic–bisphenoidal symmetry; the unit cell contains 4 molecules; V_4 is the only possible space-group. Similar measurements on the monoclinic–prismatic modifications of ferrous and cobalt sulphate heptahydrates lead to the conclusion that the unit cell contains 16 molecules and that the only possible space-group is C^6_{2h}.

		a_0		
Rhombic	$MgSO_4,7H_2O$	11·89	12·01	6·86 Å.
	$MgCrO_4,7H_2O$	11·89	12·01	6·89 Å.
	$NiSO_4,7H_2O$	11·86	12·08	6·81 Å.
	$ZnSO_4,7H_2O$	11·85	12 09	6·83 Å.
Monoclinic	$FeSO_4,7H_2O$	15 34	12·98	20·02 Å.
	$CoSO_4,7H_2O$	15 45	13·08	20·04 Å.

J. S. CARTER.

Crystal structure of calcium silicide. J. BOHM and O. HASSEL (Z. anorg. Chem., 1927, **160**, 152—164).—A study of the structure of the hexagonal crystals of calcium silicide, $CaSi_2$, and a discussion of the results with reference to Kautsky and Herzberg's views (A., 1924, ii, 852) on the structure of siloxen, $Si_6H_6O_3$. H. F. GILLBE.

***X*-Ray analysis of the system chromium–carbon.** A. WESTGREN and G. PHRAGMÉN (Kungl. Svenska Vet. Handl., 1926, [iii], **2**, 3—11; cf. Ruff and Foehr, A., 1918, ii, 399).—*X*-Ray analysis shows the existence of three chromium carbides. The compound Cr_4C has a cubic, face-centred lattice; the elementary cube has an edge 10·638 Å. and contains 120 atoms. The carbide considered by Ruff and Foehr to be Cr_5C_2 is hexagonal, the height of the elementary prism being 4·523 and the edge of the basal surface 13·98 Å.; axial ratio 0·324. Since the elementary prism contains 80 atoms, the most probable formula is Cr_7C_3. The compound Cr_3C_2 is rhombic. The dimensions of the elementary parallelepiped are 2·821, 5·52, 11·46 Å.; axial ratios 0·246 : 0·480 : 1. The elementary cell contains 20 atoms. J. S. CARTER.

Crystal structure of gallium. F. M. JAEGER, P. TERPSTRA, and H. G. K. WESTENBRINK (Proc. K. Akad. Wetensch. Amsterdam, 1926, **29**, 1193—1217).—Spectroscopically pure gallium has m. p. 30·2°, and is very susceptible to undercooling phenomena. Inoculation of the undercooled, molten metal yields crystals possessing ditetragonal–bipyramidal symmetry, $a:c$=1 : 1·6753. If, however, crystals are

allowed to grow slowly from the only slightly supercooled liquid, flat crystals much poorer in limiting forms are obtained. The ditetragonal-bipyramidal crystals have been examined by the *X*-ray spectrograph by different methods. The identity-distances of the fundamental grating in the direction of the *a* and *c* axes are 4·51 and 7·51 Å., respectively. The unit cell contains 8 atoms and is the only possible space-group. The parameters of the equivalent points are: $(u, u+\frac{1}{2}, v)$; $(u, \frac{1}{2}-u, v+\frac{1}{2})$; $(-u, \frac{1}{2}-u, v)$; $(u, u+\frac{1}{2}, v+\frac{1}{2})$; $(u+\frac{1}{2}, u, -v)$; $(u+\frac{1}{2}, -u, \frac{1}{2}-v)$; $(\frac{1}{2}-u, -u, -v)$; $(\frac{1}{2}-u, u, \frac{1}{2}-v)$, where *u* is about 0·2—0·225 and *v* about 0·15—0·175. A more precise determination of the parameters is at present impossible. Sufficient data are, however, available to indicate that the smallest distance of two gallium atoms is 2·56 Å., a result in agreement with W. L. Bragg's figure for the atomic radius of gallium, 1·3 Å. The proposed structure satisfactorily explains a number of the properties of solid gallium.

J. S. Carter.

Structure of colloidal stannic oxide. R. Forster (Physikal. Z., 1927, **28**, 151—152).—Using the Debye-Scherrer interference method, the grating constants for the *a*- and the *c*-axis of colloidal stannic oxide, dried over phosphorus pentoxide, have been determined: $a=4·91$, $c=3·47$ Å. (for cassiterite $a=4·67$, $c=3·14$ Å.). It is concluded that the colloidal particles from both modifications of stannic acid have the same structure as cassiterite.

R. W. Lunt.

Allotropy of germanic oxide. J. H. Muller (Proc. Amer. Phil. Soc., 1926, **65**, 193—199).—Pure germanium dioxide can exist in an insoluble (α-) modification, *d* 6·003 (the glassy oxide has *d* 3·3037). The *X*-ray powder spectra are different for the two forms. Chemical Abstracts.

Crystal lattices. I. Molecular space and atomic number. U. Panichi (Atti R. Accad. Lincei, 1927, [vi], **5**, 123—128).—With the halides of the alkali metals the molecular space increases with the sum of the atomic numbers corresponding with the atoms of the molecule; this sum is termed the molecular number. With analogous compounds of the same molecular number, the molecular space increases as the ratio between the atomic numbers of the metal and non-metal of the salt decreases. For non-analogous compounds, *i.e.*, for those with non-isovalent metals, the molecular space diminishes as the valency increases, if the above ratio remains almost constant. T. H. Pope.

Refraction and dispersion of *X*-rays in calcite. A. Larsson (Z. Physik, 1927, **41**, 507—515).—The author's investigation on the deviation from the Bragg equation $2d \sin\theta_n=n\lambda$ shown by calcite (*ibid.*, 1926, **35**, 401) has been continued using the molybdenum and iron $K\alpha_1$ lines. The quantity δ in the equation $\mu=1-\delta$, where μ is the refractive index, has been evaluated from the equation $\delta=\sin\theta_1 \sin\theta_2(n_2 \sin\theta_1-n_1 \sin\theta_2)(n_2 \sin\theta_2-n_1 \sin\theta_1)^{-1}$ in which θ_1 and θ_2 are the glancing angles, corrected for the effect of thermal expansion, corresponding with the two different orientations of the crystal to which n_1 and n_2 refer. The values of $\delta\lambda^{-2}$ so obtained for the line Mo $K\alpha_1$, 3·83 and $3·62\times10^{-6}$, and that for the line Fe $K\alpha_1$, $3·92\times10^{-6}$, agree well with that calculated from the dispersion formula $\delta\lambda^{-2}=Ne^2(2\pi mc^2)^{-1}=3·69\times10^{-6}$. The values of $\delta\lambda^{-2}$ have been employed to calculate the grating constant, *d*, using the corrected form of the Bragg equation, $n\lambda=2d \sin\theta_n(1-4\delta d^2n^{-2}\lambda^{-2})$; the value found for *d*, 3·02945 Å., is in good agreement with the absolute value given by Compton, Beets, and DeFoe (Physical Rev., 1925, [ii], **25**, 625), $3·02904\pm0·001$. Finally, from the alternative form of this equation $n\lambda=2d_n \sin\theta_n$, where $d_n=d(1-4\delta d^2n^{-2}\lambda^{-2})$, λ has been calculated from experimental values of θ; λ for Mo $K\alpha$ is 707·830, and for Fe $K\alpha_1$, 1932·058 X. R. W. Lunt.

Scattering power of lithium and oxygen determined from the diffraction-intensities of powdered lithium oxide. J. M. Bijvoet, A. Claassen, and A. Karssen (Proc. K. Akad. Wetensch. Amsterdam, 1926, **29**, 1286—1292).—The scattering power of both lithium and oxygen has been determined by photographic intensity measurements on lithium oxide powder with Cu $K\alpha$-rays, using an apparatus previously described (Rec. trav. chim., 1924, **43**, 680). The blackening of the photographic plate was measured by a Moll photometer. The scattering power found for lithium is in agreement with that given by Debye and Scherrer from photometric data on lithium fluoride (A., 1919, ii, 20). The scattering power of oxygen in lithium oxide appears to be much less dependent on the diffraction angle than was found by Claassen for oxygen in Fe_3O_4 (*ibid.*, 1926, 1072), and Hartree's calculated values for a free oxygen ion lie between the two. M. S. Burr.

Magnetisation of single crystals of iron. K. Honda and S. Kaya (Sci. Rep. Tôhoku Imp. Univ., 1926, **15**, 721—754).—The magnetisation of single crystals of iron has been measured for both rectangular and ellipsoidal specimens, and the results are discussed theoretically. The hysteresis loss of a single crystal of pure iron is very small, but it increases, at first rapidly and then more slowly, with increase of grain number per unit volume; this indicates that the hysteresis is chiefly caused by the irregular distribution of molecular magnets on the grain boundaries. The magnetisation curves in the direction of tetragonal, digonal, and trigonal axes are almost straight up to the intensities of magnetisation of 1400, 1000, and 900, respectively. The curves then show two sharp breaks or bends, and sometimes a third, which is not so well marked. The saturation of magnetisation is much more easily attained than with polycrystalline iron; its value amounts to 1717, and is reached at 70, 650, and 450 gauss in the directions of the tetragonal, digonal, and trigonal axes, respectively. In plane (100), the direction of the tetragonal axis is more easily magnetisable than that of the digonal, whilst in plane (110) the directions of the tetragonal, digonal, and trigonal axes are in decreasing order of magnetisability. In planes (100), (110), and (111), the parallel and perpendicular components of magnetisation vary with periods of 90°, 180°, and 60°, respectively. The parallel component in the (100) plane shows a maximum in the direction of the tetragonal and a minimum in the

direction of the digonal axis, while the perpendicular component vanishes along these axes, and shows maxima or minima in between. Below 3 and above 500 gauss, the parallel component is almost independent of the direction of the field. In the (110) plane, the parallel component shows maxima in the directions of the tetragonal and digonal axes and minima in the directions of 55° and 125° from the tetragonal axis. The perpendicular component vanishes along the tetragonal, digonal, and trigonal axes. In the (111) plane, the parallel component with weak fields is a maximum in the directions of the equilateral triangles of the lattice, and a minimum in the directions of the bisectors of the vertical angles of these triangles; but above 300 gauss the reverse is the case. The perpendicular components vanish in these directions. The above facts are in general agreement with the theory of Honda and Okubo (Sci. Rep. Tôhoku Imp. Univ., 1916, **5**, 153), when the effects of thermal oscillations are considered.

W. HUME-ROTHERY.

Magnetostriction of single crystals of iron. K. HONDA and Y. MASHIYAMA (Sci. Rep. Tôhoku Imp. Univ., 1926, **15**, 755—776).—The magnetostriction of single crystals of iron has been measured in varying magnetic fields for both rectangular and ellipsoidal specimens. The magnetic expansion in the direction of the tetragonal axis is positive, and that in the direction of the trigonal axis is negative for all magnetic fields. The expansion curves in other directions are composed of the above two effects. The longitudinal effect in the direction of the magnetic field and the transverse effect at right angles to the field were both measured; the transverse effect is always the reverse of the longitudinal. In the (100) plane, the longitudinal effect is a maximum in the directions of the tetragonal axes and a minimum in between; the expansion orientation curves are sinusoidal, having a period of 90°, the amplitude increasing with the field strength. In the (110) planes, the longitudinal effect is a maximum in the directions of the tetragonal axes; a second slight maximum is shown in the direction of the digonal axes, and a minimum along the trigonal axes. The expansion-orientation curves have a period of 180°. In the (111) plane, the lattice consists of a series of equilateral triangles, and if the bisector of the vertical angle of these is taken as zero, the longitudinal effect is a maximum in the directions 30°, 90°, and 150°, and a minimum for 0°, 60°, and 120°, the expansion-orientation curves having a period of 60°. The magnetostriction effects are much larger for single crystals than for polycrystalline iron, the smallness of the effect for the latter being due to the opposing expansion and contraction of the differently oriented crystals. W. HUME-ROTHERY.

Magnetic properties of evaporated nickel and iron films. R. L. EDWARDS (Physical Rev., 1927, [ii], **29**, 321—331).—An abrupt change in coercive force takes place with iron films at a critical thickness of 50 mμ; nickel has no such critical thickness. Peculiar hysteresis loops were obtained. The effect is probably caused by the nature of the crystalline state but may also depend on the aluminium base on which the films were deposited. A. A. ELDRIDGE.

Non-magnetic films of iron, nickel, and cobalt. L. C. JACKSON (Nature, 1927, **119**, 426—427).—"Non-magnetic" may indicate simply loss of ferromagnetism, or loss also of the magnetic moment of the metallic atom itself. Non-magnetic films may differ from metals in bulk in that (1) the metallic atoms are farther apart, (2) chemical combination, probably of a loose type, may have taken place, (3) there may have been an electronic rearrangement in the metallic atoms. A. A. ELDRIDGE.

Magnetic anisotropy of cubic crystals. J. FORREST (Phil. Mag., 1927, [vii], **3**, 464—476).—An application of previous work of the author (A., 1925, ii, 1133) to crystals belonging to the cubic system. It is indicated that the conception of doublets is sufficient to explain the known facts. The magnetic element is identified with the atom, and the agreement of the theoretical results with those of actual experiment, where such are available, appears to support the fundamental assumptions that the law of force between magnetic poles induced in a crystal is that of the inverse square, and that the ratio of the half length of a doublet to the distance apart of the nearest neighbours in an array of doublets is small.

A. E. MITCHELL.

Crystallographic and optical comparison of the chlorides of lead isotopes. D. KERR-LAWSON (Univ. Toronto Studies, Geol. Series, 1926, 37—43).—Values of p_0 (1·9959, 1·9953, 1·9954), q_0 (1·1875, 1·1871, 1·1869), and n_D^{20} (2·2602—2·2605) were essentially identical for lead chloride derived from a Katanga uraninite, a chemically "pure" sample, and that derived from thorite from Brevig, Norway.

CHEMICAL ABSTRACTS.

Polishing of surfaces. J. MUIR (Nature, 1927, **119**, 279).

[Polishing of surfaces.] N. K. ADAM (Nature, 1927, **119**, 279—280).

"Seizure" with sliding surfaces. J. M. MACAULAY (Nature, 1927, **119**, 425).—Actual fusion of the surfaces at the point of seizure is believed to occur (cf. also A., 1926, 998; Adam, this vol., 192).

A. A. ELDRIDGE.

Formation of twin metallic crystals. L. W. MCKEEHAN (Nature, 1927, **119**, 392—393; cf. this vol., 191; Carpenter and Tamura, *ibid.*, 191).

Tensile deformation of large aluminium crystals at crystal boundaries. R. L. ASTON (Proc. Camb. Phil. Soc., 1927, **23**, 549—560).—The deformation of an aluminium bar containing three large crystals when subjected to a tensile strain has been investigated by *X*-ray analysis of the orientation of the crystals. After deformation, the surface of the crystal showed effects similar to those observed by Carpenter and Elam (A., 1922, ii, 69). The deformation is less at the crystal boundaries than in the body of the crystals. R. CUTHILL.

Behaviour of aluminium crystals under tension. I. (FREIHERR) VON GOLER and G. SACHS (Z. Physik, 1927, **41**, 103—115).—A mathematical analysis of the simple and double slipping of aluminium crystals when under tension. R. W. LUNT.

Behaviour of aluminium crystals under tension. II. R. KARNOP and G. SACHS (Z. Physik, 1927, **41**, 116—139).

Stresses involved in tests of hardness, and a table of the comparative hardness of certain metallic elements. A. MALLOCK (Nature, 1927, **119**, 276—277).

Surface tension of crystal surfaces. E. PERUCCA (Atti R. Accad. Sci. Torino, 1926, **61**, 318—334).—It is held that the energy of a crystal surface is determined by an amorphous unimolecular layer, as suggested by Beilby, and of which no account is taken in the theories of Gibbs, Curie, and Born. *X*-Ray data obtained by the Debye–Scherrer method indicate that the energy of a crystal surface does not vary with the plane of cleavage. Further experiments are projected in which the energy of a crystal surface is to be determined from the angle of contact of a globule of mercury on the crystal surface. R. W. LUNT.

Pictet's rule and Born's grating theory. W. TARASOV (Z. Physik, 1927, **41**, 318—325).—For a crystal grating, such as sodium chloride, it is shown, on the basis of Born's theory, that $(R_s-R_0)/R_0=\alpha T_s$, where is the distance between the ion centres in the grating at the m. p., R_0 the distance at absolute zero, α the mean coefficient of linear expansion, and T_s the m. p. $(R_s-R_0)/R_0$ has been evaluated from quantities characteristic of the grating, 0·038, in good agreement with the values of αT_s for the chlorides, bromides, and iodides of sodium and potassium. R. W. LUNT.

Glass as a fourth state of matter. G. S. PARKS and H. M. HUFFMAN (Science, 1926, **64**, 363—364).—The transition between the glassy and liquid states is not gradual and continuous; thus *n*-propyl alcohol glass softens sharply within the interval 90—102° Abs., with an abrupt 80% increase in heat capacity during the process. A glass, like a liquid, possesses a random arrangement of its units, and, like a crystalline substance, is held together by fixed, rigid linkings between these component particles; thus the glassy and crystalline states have nearly the same heat capacity. Glass may be regarded as a fourth state of matter. A. A. ELDRIDGE.

Determinations of mol. wt. of sparingly soluble substances in camphor. H. CARLSOHN (Ber., 1927, **60**, [*B*], 473—476).—Rast's method (A., 1922, ii, 421) does not always yield reproducible results when applied to substances, m. p. above 180°, which are sparingly soluble in camphor. A modified method is given in which the f. p. instead of the m. p. is observed. Solidification usually occurs rapidly and within 1°. If the molten mass does not solidify within 2°, it is too concentrated, and unchanged substance initially separates. In this case, the experiment is utilised for the determination of the solubility of the substance in camphor by observation of the temperature at which the residual eutectic mixture rapidly and completely solidifies. This is deduced from the formula $40\times a\times 1000/\Delta\times b=M$, in which a and b are the weights of substance and camphor, Δ is the depression, and M the supposed mol. wt. of the solute. H. WREN.

Mol. wt. of sulphur trioxide from vapour density. G. ODDO and A. CASALINO (Gazzetta, 1927, **57**, 75—82).—Measurements of the vapour density at 25° of liquid and fibrous sulphur trioxide gave the following mean values for the mol. wt., respectively: 82·68 and 83·77. R. W. LUNT.

Liquid, fibrous, and colloidal sulphur trioxide. G. ODDO (Gazzetta, 1927, **57**, 29—47).—Determinations of the lowering of the f. p. of phosphorus oxychloride produced by the addition of sulphur trioxide show that the liquid form corresponds with the formula SO_3, the ordinary fibrous form with $(SO_3)_2$, and a sample of fibrous form twelve years old with approximately $(SO_3)_5$, which is therefore termed "colloidal" sulphur trioxide. R. W. LUNT.

Weight of a normal litre and compressibility of ammonia. E. MOLES (Anal. Fís. Quím., 1926, **24**, 717—730).—The most probable value of the weight of a normal litre of ammonia, in the light of recent data, is 0·7715 g. G. W. ROBINSON.

Precipitated magnetite, with particular reference to hysteresis. L. A. WELO and O. BAUDISCH (Phil. Mag., 1927, [vii], **3**, 396—410).—A comparison of the properties of precipitated magnetite is made by the methods of Lefort (Compt. rend., 1852, **34**, 488; 1869, **48**, 179) of Kaufmann (Z. Elektrochem., 1901, **7**, 733), and of the authors (A., 1925, ii, 1071). All three magnetites are shown by *X*-ray examination to have the same structure. There is evidence of closer packing in the magnetite made according to the method of Lefort, indicating that this product is of smaller crystal size than the others. Measurements of the magnetic permeabilities and hysteresis, both of the annealed and unannealed samples, support this observation. Magnetite has been prepared in a new way, by oxidising precipitated ferrous hydroxide with nitric oxide. A. E. MITCHELL.

Magnetic susceptibilities of gases at low pressures. V. I. VAIDYANATHAN (Indian J. Physics, 1926, **1**, 183—198).—The magnetic susceptibility of carbon dioxide in the pressure range 0—700 mm. has been determined by an ingenious apparatus, described in detail, in which the motion of the gas is measured when placed in a heterogeneous magnetic field. The volume susceptibility is found to be proportional to the gas pressure $\kappa_{CO_2}=-0\cdot00092\times 10^{-6}$ ($\kappa_{air}=0\cdot0308\times 10^{-6}$). The paramagnetic susceptibilities of oxygen and air in the same pressure range were determined in a slightly modified apparatus in which the motion acquired by the gas in the field was balanced by the motion acquired by a solution of known susceptibility. The values obtained were $\kappa_{O_2}=0\cdot142\times 10^{-6}$, and $\kappa_{air}=0\cdot029\times 10^{-6}$, and were proportional to the pressure. R. W. LUNT.

Magnetic susceptibilities of oxygen and nitrogen. F. J. VON WISNIEWSKI (Z. Physik, 1927, **41**, 385—394).—On the basis of the author's model of a diatomic molecule (A., 1926, 1194) the paramagnetic susceptibility of oxygen has been calculated from Langevin's equation relating this quantity to the magnetic moment and the temperature. The value obtained, $0\cdot1399\times 10^{-6}$, is in good agreement with that observed by Bauer and Piccard (J. Phys.

Radium, 1920, [vi], **1**, 97), $0{\cdot}1407\times10^{-6}$. The diamagnetic susceptibilities of nitrogen, argon, and neon have been calculated by an extension of the author's theory, and are shown to vary as the fourth power of the circular quantum number. The values obtained are within 8% of those observed by Hector (A., 1924, ii, 854). R. W. LUNT.

Critical survey of recent advances in the study of diamagnetism. E. S. BIELER (J. Franklin Inst., 1927, **203**, 211—242).

Influence of temperature on gaseous films adsorbed on mercury and on the optical constants of mercury. J. ELLERBROEK (Arch. Néerland., 1927, III A, **5**, 42—90).—The technique developed by Haak (*ibid.*, 1922, III A, **6**, 198), and by Rceser (*ibid.*, 225) for the analysis of the elliptical polarisation produced in a beam of plane polarised light when reflected has been extended and improved. From measurements of the elliptical polarisation produced when the reflecting surface is mercury in contact with dry air or dry hydrogen, the thickness of the adsorbed film has been evaluated as 6 $\mu\mu$ and 2 $\mu\mu$, respectively, on the basis of Drude's theory (Ann. Physik, 1889, **36**, 865; 1890, **39**, 481). These results are discussed at length, and in particular are thought to support the views of Iljin (A., 1925, ii, 958) and of Polanyi (*ibid.*, 1916, ii, 474) rather than those of Langmuir.

The temperature variation of the eccentricity of the elliptic polarisation has also been determined for temperatures from 20° to 160°. At 160°, the thickness of the hydrogen or air film becomes less than 0·7 $\mu\mu$ (the limit of sensitivity of the method). The temperature variation of the principal azimuth of mercury has also been determined for 6700 and 5600 Å. It has been shown to be less than that characterising the metals of high resistivity, iron, and bismuth, in accordance with the author's theory.

R. W. LUNT.

Specific heats of gases at high temperatures and pressures. E. BURLOT (Mém. Poudres, 1926, **22**, 69—106).—A previous investigation (A., 1925, ii, 1170) showed that the pressures obtained experimentally by the combustion of certain explosives in a closed vessel disagreed with those calculated from Abel's equation $p=f\Delta/(1-\alpha\Delta)$, where α is the co-volume, Δ the density of charge, and f (the "force" of the explosive)$=P_0V_0T/273$, T being the absolute temperature of the gases at maximum pressure. This disagreement was attributed to the use of values for the specific heats of certain gases as determined by Mallard and Le Chatelier and also by Sarrau, which are appreciably too high. The values for the specific heats at high temperatures and pressures have therefore been reinvestigated, but the present communication is confined to the ratio between the specific heats at constant volume of nitrogen (c) and carbon dioxide (c'). The method employed is described in detail.

For carbon dioxide at 1890°, $V/P_1=449$ and at 2096° it is 279, the corresponding values for nitrogen being 610 and 400. It is then deduced that c'/c at 1890° is 1·36 and at 2096° 1·43. These values are considerably lower than those obtained by previous investigators. There are indications that the mean molecular heat of carbon dioxide at constant volume has been over-estimated more than that of nitrogen. The possible sources of error in this determination of the ratio c'/c are discussed and considered to be less than 6% of the value obtained. S. BINNING.

Specific heats of a highly-cooled non-condensed phase. N. DE KOLOSOVSKI (Compt. rend., 1927, **184**, 322—323).—It is pointed out that the kinetic theory enables the conclusions of Perrakis (this vol., 101) to be obtained with fewer assumptions.

J. GRANT.

Velocity of sound in steam, nitrous oxide, and carbon dioxide, with special reference to the temperature coefficient of the molecular heats. W. G. SHILLING (Phil. Mag., 1927, [vii], **3**, 273—301).—Determinations of the molecular heats of chemically pure carbon dioxide, nitrous oxide, and steam have been made over the temperature range 0—1000°. The method depends on the measurement of the velocity of sound in the gases at temperatures up to 1100°. The molecular heats at constant volume were found to be: for carbon dioxide, $6{\cdot}688+0{\cdot}00423t-0{\cdot}0_6712t^2$; for nitrous oxide, $6{\cdot}629+0{\cdot}00694t-0{\cdot}0_5241t^2$, and for steam, $7{\cdot}266-0{\cdot}00763t+0{\cdot}0_41261t^2-0{\cdot}0_8401t^3$ g.-cal. at $t°$. The molecular heats at constant pressure were found to be: for carbon dioxide, $8{\cdot}708+0{\cdot}00415t-0{\cdot}0_6650t^2$; for nitrous oxide, $8{\cdot}659+0{\cdot}00677t-0{\cdot}0_5222t^2$, and for steam, $9{\cdot}596-0{\cdot}00925t+0{\cdot}0_4148t^2-0{\cdot}0_8508t^3$ g.-cal. at $t°$. The equations apply for carbon dioxide and nitrous oxide only above 0° and for steam only above 100°. A. E. MITCHELL.

Maximum and minimum density and the heat of evaporation of helium. I. and II. J. J. VAN LAAR (Proc. K. Akad. Wetensch. Amsterdam, 1926, **29**, 1303—1316, 1317—1334).—I. Theoretical.

II. From the available experimental data for the vapour pressure of helium at very low temperatures, vapour-pressure formulæ between the temperatures 0° and 4·2° Abs., and also between 3·5° and 5·2° Abs., have been deduced. With the help of these, the values of the molecular latent heat of evaporation, L, and the internal molecular heat of evaporation, $\lambda[=L-p(v_2-v_1)]$, have been determined between 0° Abs. and the critical temperature, 5·19° Abs. L is thus found to have a maximum value at 3·5° Abs. and a point of inflexion at the temperature of maximum density 2·3° Abs., whilst λ has a minimum at 1·5° and a maximum at about 3·4°, the point of inflexion between being at 2·2° Abs. approximately. The values of L are of the same order of magnitude as those found experimentally by Onnes and Dana (this vol., 101). The appearance of a maximum can be explained naturally, and does not require the assumption of the "degeneration of energy" of the liquid at low temperatures. M. S. BURR.

Methods and apparatus used in the cryogenic laboratory. XIX. The methyl chloride and ethylene circulations. The hydrogen liquefier and circulation. The helium liquefier and circulation. H. K. ONNES (Proc. K. Akad. Wetensch. Amsterdam, 1926, **29**, 1176—1183).

Melting curve of hydrogen. H. K. ONNES and W. VAN GULIK (Proc. K. Akad. Wetensch. Amster-

dam, 1926, 29, 1184—1187).—Using the same method as for helium (Keesom, A., 1926, 893), the above curve has been examined over the range of pressure 53·5—5·2 atm., corresponding with a temperature range 15·63—14·11° Abs. J. S. Carter.

Thermal properties of gases. III. Critical constants and vapour pressure of sulphur dioxide. E. Cardoso and U. Fiorentino (J. Chim. phys., 1926, 23, 841—847; cf. A., 1923, ii, 833).—The critical temperature and pressure of sulphur dioxide have been redetermined as 157·50±0·05° and 77·79±0·05 atm., respectively; vapour-pressure data are given from 0 to 157·50°. R. W. Lunt.

Physical constants of some alkyl carbonates. P. N. Kogerman and J. Kranig (Acta Com. Univ. Tartuensis, *A*, 12, 7).—The b. p., specific gravities, and refractivities of methyl, ethyl, *n*-propyl, *iso*propyl, *n*-butyl, *iso*butyl, and *iso*amyl carbonates have been determined. iso*Propyl carbonate* was prepared for the first time, b. p. 147·2° (corr.), d_4^{20} 0·9162. The b. p. of *iso*amyl carbonate is 233°. The values found for d_4^{20} and for n for the compounds examined differ from those given in the literature. W. E. Downey.

Dynamic method for measuring vapour pressures. J. N. Pearce and R. D. Snow (J. Physical Chem., 1927, 31, 231—245).—A new modification of the dynamic method of measuring vapour pressure is described. The difficulty of measuring the large volume of air passing through the solution is eliminated by electrolytic generation of hydrogen and oxygen and the calculation of the volume of mixed gases from the weight of silver deposited in a voltameter. The number of molecules of water vapour, n_1, and the total volume of hydrogen and oxygen, n_2, are calculated from the respective weights of water absorbed and silver deposited. The vapour pressure is then given by the equation $p=n_1P/(n_1+n_2)$, where P is the corrected barometric pressure. The values for the vapour pressure of water at 25° found by this method vary from 23·745 to 23·756 mm. The mean value of eight determinations, 23·752 mm., is the same as that of Derby, Daniels, and Gutsche (A., 1914, ii, 533). Data for aqueous solutions of potassium chloride (0·2*M* to saturation) and mannitol (0·4—1*M*) at 25° are given, and the method is being extended to other aqueous solutions up to the limits of solubility. A *résumé* of the determinations made by other methods used in measuring vapour pressure is given.

L. S. Theobald.

Vapour pressures of the alkali metals. H. Rowe (Phil. Mag., 1927, [vii], 3, 534—546).—When experimental values of the vapour pressures of sodium, potassium, rubidium, and cæsium are compared with those deduced from various formulæ purporting to represent the variation of vapour pressure with temperature, many discrepancies are found. When the vapour pressures are extrapolated at various temperatures, many variations are shown in the pressures obtained from the different formulæ. It is concluded that no single formula can represent the variation of the vapour pressure of a metal with temperature, and that it is possible to arrive at an approximate value for the vapour pressure at any temperature only from a comparison of all the available data. A. E. Mitchell.

Influence of cold rolling on the rate of evaporation of metals. F. Sauerwald, H. Patalong, and H. Ratke (Z. Physik, 1927, 41, 355—377).—The velocity of evaporation of cold-rolled zinc and silver sheet has been found to exceed that of the recrystallised metal by from 40 to 450%. The m. p. and transition points are but slightly changed. These phenomena are discussed at length.

R. W. Lunt.

Expansion of liquids and heat of vaporisation. N. de Kolosovski (J. Chim. phys., 1927, 24, 56—61).—Combination of van der Waals' formula αT_c=constant, where α is the coefficient of expansion of a liquid at a given reduced temperature and T_c is the critical temperature, with Trouton's rule and the rule that the b. p.$=2T_c/3$, leads to the expression $M\rho\alpha$=constant, where $M\rho$ is the molecular heat of vaporisation. From the relation previously derived (A., 1925, ii, 646), connecting the expansion modulus of a liquid, k, and its critical temperature, the equation $M\rho=A+B/k$, where A and B are constants, may be deduced in a similar manner. If these formulæ are used to calculate $M\rho$ from expansion data, the values obtained for non-associated liquids agree satisfactorily with the experimental values. For liquefied gases, however, the calculated values are much too high.

R. Cuthill.

Mean free paths in a gas the molecules of which are attracting rigid elastic spheres. E. Condon and E. V. Van Amringe (Phil. Mag., 1927, [vii], 3, 604—614).—Mathematical. An evaluation of the mean free path in a gas the molecules of which comprise attracting rigid elastic spheres, is made on the lines of classical theory. It is shown (*a*) that the Maxwell free path is represented accurately by a formula of the type suggested by Sutherland, in which the constant C is the ratio of the energy of two molecules in contact to the gas constant per molecule, and (*b*) that the mean free path appropriate to the transfer theory of viscosity is represented approximately by the same formula, in which the constant C is about three quarters of the above ratio. The results lead to a direct method of evaluating the energy of two molecules in contact from the experimental data on the temperature coefficient of viscosity.

A. E. Mitchell.

Diffusion of oxygen through silver. F. M. G. Johnson and P. Larose (J. Amer. Chem. Soc., 1927, 49, 312—326).—The experiments previously described (A., 1924, ii, 750) have been continued with improved technique; in particular, an apparatus is described in which gases may be continuously and automatically mixed in any proportions and a constant flow of any definite mixture maintained. The results obtained with welded silver plates agree with those previously published. Richardson's equation (Phil. Mag., 1904, [vi], 7, 266) is shown to represent the diffusion of gases through metals within experimental error. The mechanism of the diffusion is supposed to consist of an initial absorption in which the gaseous molecules become atoms which are transformed into ions in presence of the metal, and a dynamic equilibrium

between atoms and ions is set up, chain-like, through the metal. The atoms, on issuing from the partition, combine to molecules, or react with other substances.

S. K. TWEEDY.

Refractive indices of mixtures calculated by the formula of Dieterici and of Lichtenecker. E. VAN AUBEL (Bull. Acad. roy. Belg., 1926, [v], **12**, 476—480).—Lichtenecker's formula for the refractive index n of a binary mixture is $\log n = \theta_1 \log n_1 + \theta_2 \log n_2$, where n_1 and n_2 are the refractive indices of the respective constituents, and θ_1 and θ_2 their percentages by volume, a correction being necessary if any contraction takes place on mixing. For mixtures of acetone and water and of sulphuric acid and water, the maximum differences between observed and calculated values of n are found to be 6×10^{-4} and 34×10^{-4}, respectively. Dieterici's formula is slightly superior, the corresponding differences being 4×10^{-4} and 29×10^{-4}, respectively.

S. J. GREGG.

Cryoscopic determinations of the solubility of gases. F. GARELLI and E. MONATH (Atti R. Accad. Sci. Torino, 1926, **61**, 4—11, 12—20).—I. Cryoscopic and analytical data having shown approximately that acetylene is unassociated when dissolved in benzene, *cyclo*hexane, aniline, and dimethylaniline, it is suggested that the solubility of acetylene in these and other solvents may be determined cryoscopically.

II. The solubility at atmospheric pressure of nitric oxide and of carbon monoxide in benzene, bromoform, nitrobenzene, and *cyclo*hexane has been derived from cryoscopic data, on the assumption that the solute is unassociated in solution. The lowering of the f. p. by nitrogen and helium is so small that these gases can be used to free the solvents from gaseous impurities.

R. W. LUNT.

Solubility of gases in *cyclo*hexanol. (MLLE.) G. CAUQUIL (J. Chim. phys., 1927, **24**, 53—55).—The solubility in *cyclo*hexanol of hydrogen, neon, argon, oxygen, carbon monoxide, carbon dioxide, ammonia, phosphine, nitrous oxide, silicomethane, methane, ethane, propane, ethylene, acetylene, and methyl chloride has been determined at 26° and under approximately 76 cm. pressure. In every case, the solubility is greater than the solubility in water.

R. CUTHILL.

Solubility effects. V. Chloral–caffeine, urotropine [hexamethylenetetramine]–antipyrine, urotropine–chloral. VI. Chemical constitution and solubility. E. OLIVERI-MANDALÀ (Gazzetta, 1926, **56**, 889—896; 896—901; cf. this vol., 237, 238).—V. The existence of the crystalline compound of chloral hydrate and caffeine hydrate (Leulier, A., 1912, i, 644) has been confirmed. The solubility of caffeine is greatly increased by the presence of chloral; the solubility coefficient varies but little with the temperature. The f.-p. depressions obtained by dissolving antipyrine in hexamethylenetetramine solutions and hexamethylenetetramine in chloral solutions are normal. The compounds obtained by Mannich and Krosche (A., 1913, i, 101), and Leulier (*loc. cit.*) are therefore apparently non-existent in solution.

VI. [With A. NERI.]—The so-called solubility coefficients have been determined for various substances dissolved in solutions of other substances. The latter are shown in parentheses. No increase in solubility is found with thiocarbamide, thiocarbanilide, or benzanilide (in antipyrine). For other combinations, the solubility coefficients increase in the following order: phenacetin (antipyrine), benzamide (antipyrine), acetanilide (sodium benzoate), acetanilide (pyramidone), aspirin (pyramidone), acetanilide (antipyrine), caffeine (chloral hydrate), quinine hydrochloride (antipyrine), caffeine (sodium benzoate). No general relation between the chemical constitution and the solubility effect is apparent.

E. W. WIGNALL.

Analogy between conjugate pairs of liquids and systems consisting of a liquid phase with a vapour phase in equilibrium with it. A. BOUTARIC (J. Chim. phys., 1927, **24**, 50—52).—If from one of a pair of conjugate solutions one component is gradually removed by means of a semi-permeable piston impermeable to the other component, the curve representing the relation between the volume of the solution and its osmotic pressure will be similar to the isotherm of a gas. In particular, the curve for the critical solution temperature will be analogous to the critical isotherm. Just as in the case of a gas it is possible to pass continuously from the gaseous state to the liquid state, so with a pair of liquids it is possible to pass continuously from one conjugate to the other.

R. CUTHILL.

Properties of bromine as solvent. W. FINKELSTEIN (J. Russ. Phys. Chem. Soc., 1926, **58**, 565—586).—The problem of electrolytic dissociation in feebly dissociating solvents is discussed. The conductivity and transport numbers of benzamide in liquid bromine were determined at 18° and 75°. Benzamide forms a solid *compound*, $Ph{\cdot}CO{\cdot}NH_2,Br_2$. The specific conductance rises sharply to a maximum of 2×10^{-2} at a concentration of 14·5% benzamide, and the molecular conductivity gives a similar maximum at $v=0{\cdot}5$, slowly sinking to $3{\cdot}4\times10^{-3}$ at $v=16$. The conductivity increases with time to a limit of almost double its original value in 3 days. Cryoscopic determinations show considerable association, the association factor being 5 at a concentration of 8% of $Ph{\cdot}CO{\cdot}NH_2,Br_2$. Transport number determinations suggest the presence of a bivalent cation $[Ph{\cdot}CO{\cdot}NH_2(Ph{\cdot}CO{\cdot}NH_2,Br_2)_5]^{++}$. The theoretical significance of the results is discussed in great detail. Liquid bromine is dissociated to a certain extent, $Br_2 \rightleftharpoons Br^+ + Br'$. The positive Br^+ ion removes two electrons from the tervalent nitrogen of the amide, and becomes a negative Br', leaving the nitrogen with a double positive charge. The ion $[Ph{\cdot}CO{\cdot}NH_2]^{++}$ combines with 6 molecules of benzamide dibromide to form the bivalent complex cation. In concentrated solutions, the dissociation of the bromine molecule is favoured, whilst dilute solutions favour dissociation of the bromine–benzamide complex.

M. ZVEGINTZOV.

Solubility of metals of the iron group and of copper in mercury. G. TAMMANN and K. KOLLMANN (Z. anorg. Chem., 1927, **160**, 242—248).—The solubilities of iron, cobalt, and nickel in mercury have

been determined by depositing the metal electrolytically in a known volume of mercury and measuring the potential of the amalgam against the calomel electrode. The potential falls, at first rapidly, and attains after a few hours a steady value corresponding with the *E.M.F.* of the saturated amalgam. The solubilities in mols. per mol. of mercury are: iron, $4{\cdot}1\times10^{-19}$; nickel, $2{\cdot}0\times10^{-5}$, and cobalt, $5{\cdot}7\times10^{-3}$, at 17°.

The same method is not applicable to the determination of the solubility of copper, owing to the slowness with which the saturated amalgam gives up its copper, but by measuring the *E.M.F.* of a series of amalgams of varying copper content, the solubility is found to be $3{\cdot}31\times10^{-3}$%, in fair agreement with Richard's value of $2{\cdot}4\times10^{-3}$. The lower value is ascribed to oxidation of the metallic copper in the latter case during filtration and to retention of the oxide in the filter. H. F. GILLBE.

Solubility of metals in mercury and the potentials of very dilute amalgams. G. TAMMANN and J. HINNUBER (Z. anorg. Chem., 1927, **160**, 249—270).—The following solubilities of metals in mercury have been determined potentiometrically: manganese, $2{\cdot}5\times10^{-4}$%; antimony, $2{\cdot}9\times10^{-5}$%; chromium, $3{\cdot}1\times10^{-11}$%; uranium, $1{\cdot}4\times10^{-4}$%; arsenic, vanadium, molybdenum, and tungsten, too small to be measured.

The solubility of metals in mercury is discussed from the point of view of the periodic classification. In general, the solubility increases as the mercury group is approached, except in the case of the alkali and alkaline-earth metals. The low-melting alkali metals are more soluble than the higher-melting alkaline-earth metals, which in turn are more soluble than the metals of the copper group. The solubility of the alkalis, zinc, and cadmium, and arsenic, antimony, and bismuth, decreases with rising m. p., the reverse being true of tin, lead, and the alkaline-earth metals. The statement that rise of m. p. is accompanied by a decrease of solubility is therefore untenable. An approximate rule is: metals having m. p. between 300° and 400° possess a solubility greater than 1%, which decreases with rising m. p.; those melting at above 1000° have a solubility not greater than 0·1%, which decreases still further with rising m. p.

Some experiments on the wetting of freshly-broken metallic surfaces by mercury are described.

The potentials of very dilute amalgams are discussed, and results are given for copper, cadmium, tin, and lead, agreeing very well with the calculated values. By plotting the *E.M.F.* of various amalgams against the logarithm of the concentration of the dissolved metal, a series of straight lines is obtained which are parallel for metals of the same valency. H. F. GILLBE.

Solubility of lanthanum hydroxide. E. SADOLIN (Z. anorg. Chem., 1927, **160**, 133—151).—Addition of a strong base to a solution of lanthanum chloride gives a colloidal precipitate of $La(OH)_{3-x}Cl_x$, where x increases with increasing chloride-ion concentration and decreasing hydroxyl-ion concentration. The p_H of the solution shows a turning point at about three equivalents of added base, at which the precipitation of the lanthanum is complete. The freshly-prepared precipitate gives no definite solubility product, on account of its chlorine content; the initial value is given by $\log L_{La(OH)_3}=18{\cdot}93$ at 18°. The solubility decreases with time for some weeks, owing to loss of chlorine. The stable end-product has a definite solubility product given by $-\log L_{La(OH)_3}=20{\cdot}98$ at 18°, a value similar to that of lanthanum oxide which has been heated at 950°. H. F. GILLBE.

Molecular association and mechanism of separation into two phases. G. N. ANTONOV (Phil. Mag., 1927, [vii], **3**, 571—580; cf. A., 1925, ii, 865; 1926, 786).—Further examination of the discontinuous variation of the physical properties of liquids with temperature and the anomalous results obtained in the regions close to the critical points lead to the conclusion that the change of state is intimately connected with the change of molecular aggregation. The association factor for liquids is not the same at different temperatures, but varies with the temperature, and may become very large at low temperatures. The presence or absence of the hydroxyl radical is not a criterion of the association of liquids. A. E. MITCHELL.

Partition of hydrogen chloride between water and benzene. R. W. KNIGHT and C. N. HINSHELWOOD (J.C.S., 1927, 466—472).—The solubility of hydrogen chloride in water and in benzene, and its distribution between the two solvents over a wide range of concentrations, have been determined at 20°. The results indicate the existence of an equilibrium between ionised and un-ionised molecules in the aqueous phase, such that the ionisation is half complete at a concentration of about 500 g./litre. Un-ionised molecules are present in appreciable amounts only at concentrations much greater than those indicated by osmotic and conductivity data to which the Debye–Hückel correction has not been applied. H. F. GILLBE.

Partition coefficients and solubility. W. K. PERSHKE (J. Russ. Phys. Chem. Soc., 1926, **58**, 495—510).—It is shown theoretically that the partition coefficient is the ratio of the solubilities of the dissolved substance in the two solvents. The partition of azobenzene between hexane and methyl alcohol, and of succinic acid between ether and water, and the changes in mutual solubility due to the third component, have been determined. The partition coefficient varies with the concentration, but is almost identical with the ratio of solubilities in a mixture of the two solvents, although it differs markedly from the ratio of the solubilities in the pure solvents. The case of the partition of a liquid between two solvents with each of which it is completely miscible is theoretically discussed, and shown to agree with the experimental results. M. ZVEGINTZOV.

Sorption of gas by charcoal as a dissolution phenomenon. J. SAMESHIMA (Bull. Chem. Soc. Japan, 1927, **2**, 1—10).—Measurements of the velocity of sorption of carbon dioxide by granular and powdered cane-sugar charcoal under constant pressure show that although the same volume of gas is absorbed in each case (54·0 c.c. at *N.T.P.*), the velocity of

absorption is greater with powdered charcoal than with granular. The volume absorbed by different kinds of charcoal is roughly the same (40—50 c.c.). These facts support the view that the sorption is due to the dissolution of the gas in the mass of the charcoal. From measurements on bamboo charcoal, it is found that Henry's law is not applicable, and that the amount of gas absorbed decreases with rise of temperature. L. L. Bircumshaw.

Adsorption at solid surfaces. I. Adsorption of gases by activated and non-activated charcoals. O. Ruff and G. Roesner (Ber., 1927, **60**, [*B*], 411—425).—The adsorption of argon, carbon dioxide, ammonia, and sulphur dioxide by activated and non-activated alder and coconut charcoal, acetylene soot charcoal, supernorite, and technical activated carbon IV has been measured. The products were freed from tar and moisture by ignition at 900° and activated by carbon dioxide. The power of adsorbing gas appears to be less dependent on the activity than on the structure of the charcoal. For any particular variety of charcoal, ignition in a vacuum or indifferent gas at temperatures above 1100° produces a parallel diminution in activity (measured towards phenol) and in the power of adsorbing gases. For the adsorption of gases, the porosity of the material (atomic spaces in material) and its form are important factors, in addition to the extent of the surface, whereas activation, which is of prime importance for many dissolved substances, is of consequence only in so far as it leads to a certain expansion of the surface and to the opening of the pores of the adsorbent. The form of the adsorption curves at 0° is such as would be expected from any of the accepted theories of adsorption. At lower temperatures, irregularities are observed with sulphur dioxide, ammonia, and carbon dioxide which may be interpreted as indications of saturation with these gases. They are not, however, sufficiently definite to permit conclusions regarding the superposition of chemical on physical adsorption. H. Wren.

Adsorption at solid surfaces. II. Specific and unspecific, particularly with regard to charcoal. O. Ruff (Ber., 1927, **60**, [*B*], 426—432; cf. preceding abstract).—A theoretical consideration of the specific adsorption of molecular-disperse dissolved substances and unspecific adsorption of gaseous substances, particularly the rare gases. H. Wren.

Adsorption. S. Mokruschin and O. Essin (Kolloid-Z., 1927, **41**, 106—107).—The authors' equation for electrical adsorption (A., 1926, 573) has been applied to the adsorption of argon and carbon monoxide by coconut charcoal, and to the adsorption of bromine, acetic acid, propionic acid, and butyric acid by blood charcoal. The equation is thus found to be valid for purely chemical adsorption. The applicability of the equation confirms the dipolar character of the molecular forces. E. S. Hedges.

Adsorption of basic colouring matters by filter-paper. S. Mokruschin and O. Essin (Kolloid-Z., 1927, **41**, 104—105).—The adsorption of the basic substances, malachite-green, diamond-green, rosaniline, safranine, and methylene-blue, was studied at a surface of filter-paper. The authors' equation for electrical adsorption (A., 1926, 573) was found to be applicable. E. S. Hedges.

Adsorption equations. E. Swan and A. R. Urquhart (J. Physical Chem., 1927, **31**, 251—276).—A review of the literature in which the various adsorption equations are collected and considered with regard to their applicability to actual adsorption systems. The general adsorption equation, the isotherm, isobar, isostere, rate of adsorption, and the heat of adsorption are dealt with, and a bibliography is appended. L. S. Theobald.

Adsorption and heat of adsorption of ammonia gas on metallic catalysts. W. A. Dew and H. S. Taylor (J. Physical Chem., 1927, **31**, 277—290; cf. Taylor and Burns, A., 1921, ii, 630; Gauger and Taylor, *ibid.*, 1923, ii, 398; Beebe and Taylor, *ibid.*, 1924, ii, 159).—The adsorption of ammonia by copper, nickel, and iron catalysts, and of hydrogen by copper and iron catalysts has been studied. In the case of ammonia, the isotherms were obtained for copper at 218°, for nickel at 110° and 0°, for iron–molybdenum at 25°, and for iron at 0°. The integral heats of adsorption of ammonia by copper and nickel at 0°, and the differential heats of adsorption by copper, nickel, and iron are recorded. Adsorption of ammonia by sodium, supported on glass beads, was also measured at 0°. L. S. Theobald.

Adsorption. XVII. Concentration of a sol and coagulation by electrolytes. S. Ghosh and N. R. Dhar (J. Physical Chem., 1927, **31**, 187—206; cf. A., 1925, ii, 386, 511, 778; 1926, 673, 1004).—The influence of change in concentration on the coagulation of sols by electrolytes has been further studied. Sols of stannic hydroxide (positive), aluminium hydroxide, vanadium pentoxide, thorium hydroxide, sulphur (Weimarn), and gold follow the rule that the greater the concentration of the sol the greater is the amount of an electrolyte required for coagulation. Sols of antimony sulphide, Prussian-blue, gum dammar, and gamboge do not follow the law when coagulated by univalent and sometimes by bivalent ions. Antimony sulphide sol behaves normally, however, when coagulated by silver nitrate, strychnine hydrochloride, quinine hydrochloride, or methylene-blue. A negative sol of manganese dioxide behaved normally on dilution towards all electrolytes except potassium hydroxide, when the precipitating values remained practically constant, an effect attributed to the adsorption of hydroxyl ions by the sol. A positive manganese dioxide sol behaved normally towards the anions Cl′ and NO_3' given by potassium chloride and potassium nitrate, respectively, but not towards those given by cupric chloride and silver nitrate, owing to the preferential adsorption of silver and copper ions by the sol. A sol of metallic silver was abnormal when coagulated by uni-univalent electrolytes on account of the highly adsorbed hydroxyl ions derived from the silver hydroxide usually present.

A uranium ferrocyanide sol has been prepared for the first time by the addition of uranium nitrate to a dilute solution of potassium ferrocyanide followed by dialysis. The Schulze–Hardy law applies to this sol,

but is only partly followed in the case of the gum dammar sol mentioned above.

The above results show that sols which do not adsorb an ion of the same charge follow the dilution rule, whilst the sols which do so are abnormal in this respect. L. S. THEOBALD.

Adsorption of dyes on silver halides. S. E. SHEPPARD (Nature, 1927, **119**, 281).—A correction (cf. this vol., 107). At saturation, one dye molecule is associated with two ions of the surface lattice of silver bromide. A. A. ELDRIDGE.

Dynamic surface tension and the structure of surfaces. O. K. RICE (J. Physical Chem., 1927, **31**, 207—215).—The theory of dynamic surface tension is developed from a new point of view. A simple thermodynamic proof is given that the dynamic surface tension is greater than the static when the surface is extended and less when the surface is contracted. The possibility that equilibrium may be established between all parts of the solvent, but not between portions of the solute near to and remote from the surface, is discussed, considering only the dynamic surface tension of extension. It is shown mathematically that the narrower the region to which adsorption is confined the larger will be this value, and if the laws for perfect solutions hold near the surface, the dynamic can never be greater than the static surface tension of the pure solvent when adsorption is positive, but when adsorption is negative, then an infinite value of the dynamic surface tension is theoretically possible.

Du Noüy's work on the surface tension of solutions of sodium oleate (A., 1925, ii, 109) is criticised. L. S. THEOBALD.

Spreading of fatty acids, fats, and proteins. E. GORTER and F. GRENDEL (Proc. K. Akad. Wetensch. Amsterdam, 1926, **29**, 1262—1274).—The spreading of fatty acids on water surfaces is highly dependent on the length of the fatty acid chain, the acidity of the water, and the temperature. With acids which have a chain of 14 or 16 carbon atoms, unimolecular spreading occurs at all temperatures, but the film may have either a condensed or an expanded form. With lower members of the series, unimolecular spreading is observed only at low temperatures and high acidities. Similar measurements with the corresponding triglycerides show the same influence of length of chain and temperature, the influence of acidity being, however, much less pronounced. Spreading occurs much more readily with fats than with the acids, a chain of six carbon atoms sufficing to render the molecule sufficiently stable to produce perfect spreading. It is believed that for certain lengths of carbon chains under appropriate conditions of temperature and acidity "colloidal spreading" occurs, *i.e.*, associated molecules have their polar groups oriented towards an outer surface and the spreading of these aggregates is due to these superficially placed groups. This behaviour is also observed when the spreading of soaps is examined. Only by the use of strongly acid media (p_H 1—2) can the association which persists at the water surface be broken. With hæmoglobin, casein, and serum-protein it is possible to obtain unimolecular spreading on media which are sufficiently acid (p_H 1—2). Such spreading is not observed with gelatin, gliadin, or peptone. This is attributed to the presence of short-chained amino-acids in these molecules. The influence of acidity on the spreading of proteins is rather complex. The proteins were dissolved in sodium hydroxide solutions, and are hence comparable with the soaps, in that molecules are associated with their polar groups turned outwards. On pure water or faintly acid media, this association remains unaltered. On increasing the acidity, protein is gradually set free and at the isoelectric point spreads in a unimolecular layer. Further increase in the acidity results in the formation of associated protein hydrochloride molecules, which spread in a unimolecular layer only when the acidity is considerably increased. J. S. CARTER.

Soap solutions. III. Effect of acids, bases, and salts on the surface tension of aqueous sodium oleate solutions. J. MIKUMO (J. Soc. Chem. Ind. Japan, 1927, **30**, 75—80).—The changes in the surface tension (at 20°) of dilute aqueous solutions of sodium oleate produced by the addition of acids, sodium salts, and sodium hydroxide have been investigated stalagmometrically. The changes produced by the hydrogen and hydroxyl ions are greater than those due to other ions. The introduction of hydroxyl ion represses the hydrolysis, resulting in a loss of acid soap and a rise of the surface tension to its maximum. Further increase of the hydroxyl-ion concentration causes the surface tension to fall until the flocculating point is reached, when the surface tension again rises very slowly. The presence of hydrogen ion decomposes the soap and depresses the surface tension very rapidly by increasing the quantity of acid soap, but beyond the critical separation point the surface tension rises suddenly, owing to the separation of free acid. These effects depend on the strengths of the bases and acids. Salt solutions which are acidic (*e.g.*, ammonium chloride) behave as acids, but acids weaker than oleic acid have but little action on the soap solution. Oleic acid also has a positive effect. The extremely low surface tension of soap solutions is mainly due to the presence of fatty acids produced by hydrolysis (perhaps acidic soaps in sol form) and concentrated in the surface layer. Slightly acidic substances, *e.g.*, boric acid, increase the lathering and detergent action of soaps by lowering of the surface tension. Dilute alkali solutions seem to act as detergents in virtue of their peptising action. K. KASHIMA.

Position of the absorption bands of potassium permanganate and uranyl nitrate in various colourless solvents. V. R. VON KURELEC (Biochem. Z., 1927, **180**, 65—84).—Five bands in the absorption spectrum of potassium permanganate and four in that of uranyl nitrate have been compared when these substances were dissolved in various solvents, many of which form homologous series. In most cases, the bands are displaced by the non-aqueous solvent towards the red with permanganate and towards the violet with uranyl nitrate. The opposite displacements are not conditioned by the fact that the bands for the two substances are at opposite ends of the

spectrum nor by a difference in charge. The extent of the displacement of the permanganate bands increases with the number of carbon atoms in the homologous series of solvents, but that of uranyl nitrate decreases. With uranyl nitrate, the position of the bands appears to depend on the specific gravity or refractive index of the medium, displacement being to the violet in media with specific gravity less than 1, but to the red if greater than 1.

P. W. CLUTTERBUCK.

Anomalous rotatory dispersion, in the ultra-violet, of aqueous solutions of tartaric acid containing boric acid. R. DESCAMPS (Compt. rend., 1927, **184**, 453—455).—The photographic spectro-polarimeter (A., 1926, 142) has been used to test the conclusions of Lowry and Austin (*ibid.*, 1922, ii, 414) in the ultra-violet region (5780—2537 A.). For solutions containing different amounts of tartaric and boric acids, it is found that the rotatory dispersion curves belong to Lowry's anomalous complex type. Straight lines are obtained for Biot's law $\alpha=k/\lambda^2$ only between the wave-lengths 5780 and 4358 Å., and 5780 and 4047 Å. for solutions which contain equi-molecular mixtures and a slight excess of boric acid, respectively. The anomaly is explained by the presence of at least two types of optically active molecules which have different dispersions. J. GRANT.

Dielectric constants of solutions of electrolytes. III. Dielectric constants of solutions of salts in acetone, benzonitrile, *o*-nitrotoluene, and methyl cyanoacetate. P. WALDEN and O. WERNER (Z. physikal. Chem., 1926, **124**, 405—426; cf. A., 1925, ii, 773).—The dielectric constants of solutions of the alkylammonium halides and picrates in the above four solvents and also of solutions of barium perchlorate, ammonium iodide, mercuric chloride, and mercuric cyanide in acetone have been measured at 20°. For tetra-alkylammonium salts and barium perchlorate in acetone, the dielectric constant falls with increase in concentration, the concentration–dielectric constant curve being rectilinear, and having the same slope for all these salts. This is assumed to mean that in these solutions the solutes are completely ionised. With the other alkylammonium picrates, the rate of decrease of the dielectric constant with increase in concentration is less, and tends to fall still further with increasing concentration. The chlorides, as also mercuric cyanide, scarcely alter the dielectric constant at all, the curve frequently possessing very flat minima and maxima, and their solutions have extremely small conductivities. The present measurements therefore yield for the acetone solutions examined results closely analogous to those of conductivity determinations (A., 1926, 1104). Solutions in benzonitrile, *o*-nitrotoluene, and methyl cyanoacetate resemble the acetone solutions in behaviour, but for solutions of triethylammonium and diethylammonium chloride in benzonitrile the dielectric constant first falls very slightly with increase in concentration, then slowly rises again, and ultimately becomes greater than that of the pure solvent. R. CUTHILL.

Preparation of metallic colloids. E. FOUARD (Compt. rend., 1927, **184**, 328—329).—A method is described for the preparation of chemically pure colloidal solutions of arsenic, iodine, tellurium, mercury, lead, bismuth, copper, antimony, and the alkaloids. A solution of a salt of the metal containing a pure organic colloid (albumin, starch, or gelatin) is electrolysed with a current of a few milliamperes. At the cathode the metal ions are neutralised by the repelled negatively-charged colloid micelles. A colloidal organo-metallic complex is thus formed. The anode is separated by immersion in a collodion cell rendered semi-permeable by precipitated copper ferrocyanide. The cathode should be a bad conductor (carbon, silicon, selenium, or arsenic), so as to reduce the frequency with which formation of the complex occurs on the cathode. The colloids are stable and present a characteristic dichroism to diffused light. They form heat-reversible gels spontaneously. J. GRANT.

Production of hydrosols. A. B. DUMANSKI, A. P. BUNTIN, and A. G. KNIGA (Kolloid-Z., 1927, **41**, 108—111).—A study was made of the formation of positively-charged hydrosols of ferric hydroxide by adding to a solution of ferric chloride a number of metallic carbonates and hydroxides in the dry state. The carbonates of the alkali metals, the alkaline-earth metals, and of magnesium, cadmium, and zinc readily gave hydrosols, whilst with carbonates of cobalt, lead, copper, and iron very slow reaction occurred, generally with formation of a gel, especially if excess of the carbonate was used. Similar results were obtained with the hydroxides of these metals. The production of sols of aluminium hydroxide from aluminium chloride was affected by the agents in a similar way, but chromic chloride gave in all these reactions unstable, easily coagulated sols. Stable, negatively-charged hydrosols of lead dioxide can be prepared in absence of a protective colloid by pouring into water a saturated solution of lead tetra-acetate in acetic acid, or of lead tetrapropionate in propionic acid. The brown sols lose their stability when freed from the organic acid by dialysis. Negatively-charged sols of the hydroxides of lead, iron, chromium, tin, and titanium were produced by dialysis of complex substances of the type $[Pb(CO_2)_2(CHO)_n,nPb(OH)_2]''2K$, formed when certain metallic hydroxides in alkaline solution act on tartaric acid. The properties of these sols and of the gels obtained therefrom are described. E. S. HEDGES.

Colloid syntheses with the aid of stannous chloride. I. and II. A. GUTBIER and B. OTTENSTEIN (Z. anorg. Chem., 1927, **160**, 27—47, 48—56).—I. Addition of stannous chloride solution to a solution of a palladium salt produces a series of colour changes resulting in the formation of a deep black precipitate. After the precipitation, which is always complete within 3 days, the solution is entirely free from palladium. It is shown that a stannous chloride solution cannot be neutralised without causing the partial formation of stannic compounds, and the conclusion is reached that an ordinary solution of stannous chloride contains a variety of substances, notably hydrated stannic oxide, SnO_2,xH_2O. The precipitate consists of colloidal palladium adsorbed on hydrated stannic oxide; no oxygen compound of the palladium

is present, and no stoicheiometric relationship exists between the constituents. It is easily peptised by ammonia, potassium hydroxide, or hydrochloric acid, giving a brown solution of fair stability, except when hydrochloric acid has been used, as this attacks the protective stannic oxide. Flocculation is brought about by much smaller quantities of electrolytes than are necessary in the case of the corresponding platinum solutions. The original precipitate is very readily acted on by the atmosphere, and after a few hours can no longer be peptised to a stable solution; it is thus similar to the platinum compound.

A very similar compound to that already described has been synthesised by mixing solutions of colloidal stannic oxide and colloidal palladium.

By mixing a strongly acid stannous chloride solution and a solution of palladium tetrachloride, a green liquid is obtained, in which the presence of colloidal palladium could not be detected by any method; a similar green solution could not be obtained by the use of any other reducing solution. The liquid rapidly turns brown and flocculates, the change being followed by conductivity measurements. The nature of this solution is discussed.

II. [With E. KESSLER.]—Addition of an acid stannous chloride solution to a solution of selenious acid produces an opalescence; after a time, the mixture becomes yellow, and on keeping or dilution with water a red precipitate is obtained, which is an adsorption compound of selenium and hydrated stannic oxide in varying proportions. The initial opalescence is due to the formation of colloidal hydrated stannic oxide, which becomes yellow as it adsorbs the colloidal selenium. In concentrated solution, the initial reaction velocity is greater than in dilute solution, but the end velocity is greater in the latter case. The supernatant liquid is always free from selenium and tin at the end of the precipitation. The precipitate when freshly prepared can be peptised easily with ammonia or hydrochloric acid, giving a red solution of colloidal selenium of great stability. Analyses of a number of the preparations are given.

Tellurium forms a completely analogous series of compounds; the peptised solution is, however, more sensitive to electrolytes. H. F. GILLBE.

Formation of colloids from complex ions. A. B. DUMANSKI, A. P. BUNTIN, S. J. DIATCHKOVSKI, and A. G. KNIGA (J. Russ. Phys. Chem. Soc., 1926, **58**, 326—346).—An electrochemical method is described for testing the authors' theory that a colloidal particle is synthesised by the successive formation of more and more complex ions. The changes in conductivity and f.-p. depression are attributed to the formation of intermediate complexes inferred from the nature of the curves. The addition of acid to sodium tungstate and sodium molybdate gives ultimately colloidal solutions of tungstic and molybdic acid. The conductivity and f.-p. depression curves show several well-defined maxima and minima corresponding with intermediate complexes. Ultramicroscopical examination shows the presence of colloidal particles only towards the end of the reaction. The mechanism $Na_2MoO_4+2HCl \longrightarrow 2NaCl+H_2MoO_4$ and $H_2MoO_4+MoO_4'' \longrightarrow H_2O+[MoO_4,MoO_3]''$ is suggested. Copper ferrocyanide, Prussian blue, and silicic acid give similar curves. Characteristic curves are also obtained with ferric hydroxide, stannic acid, and zirconium hydroxide, which readily pass into the gel form with excess of reagent. The method is extended to several other colloids, and the application of it to the comparative study of the hydrosols and hydrogels of different elements is discussed. M. ZVEGINTZOV.

Sodium urate as a colloidal electrolyte. H. FREUNDLICH and L. F. LOEB (Biochem. Z., 1927, **180**, 141—155).—Anomalous conductivity results obtained with sodium urate solutions which have been made alkaline and then neutralised or have been heated and then cooled lead to the conclusion that sodium urate is a colloidal electrolyte.

P. W. CLUTTERBUCK.

Lyophilic colloids. M. VOLMER (Z. physikal. Chem., 1927, **125**, 151—157).—Theoretical. A formula is derived which allows the numbers of particles of all sizes in a diluted colloidal solution to be determined, provided that their numerical distribution in the original solution is known. L. F. GILBERT.

Centrifugal determination of the distribution of the size of particles of suspended material. J. B. NICHOLS and H. C. LIEBE (Third Colloid Symposium Monograph, 1925, 268—284).—For lithopone, the approximate relation between the radius dividing the mass distribution curve into equal weights of material and the obscuring power depends on the amount of surface oxidation as well as on the size of the particles. CHEMICAL ABSTRACTS.

Emulsification and distribution of size of particles. A. J. STAMM (Third Colloid Symposium Monograph, 1925, 251—267).—The method of preparation of the emulsion is the prime factor in determining dispersity. Different univalent soaps show the same mass maximum and total surface of dispersed particles. Excess of alkali increases dispersity in oil-in-water emulsions without affecting the mass maximum, but decreases dispersity in the reverse type for the smaller particles. The wedge theory of emulsification is insufficient, and an electrical effect is suggested. Palmitic acid gives a mass optimum corresponding with larger particles than do soaps. Increasing benzene concentration with constant soap content shifts the mass maximum exponentially. When the ratio of soap to dispersed material is small, calculations based on the total surface of dispersed particles indicate that the interfacial films are of unimolecular thickness. CHEMICAL ABSTRACTS.

Calculation of thermodynamic properties of colloidal solutions from measurements with the ultracentrifuge. A. TISELIUS (Z. physikal. Chem., 1926, **124**, 449—463; cf. Svedberg, A., 1926, 677).—A general theory of sedimentation equilibrium in colloidal systems containing electrolytes is derived thermodynamically, using the conception of activity.

R. CUTHILL.

Particles causing scattering of light in the crystalline lens of the eye. G. I. POKROWSKI (Kolloid-Z., 1927, **41**, 146—148).—It is suggested that the scattering of light in the crystalline lens of the eye, to which the halo observed in a sudden glance at a

bright light is attributed, is due to the presence of cylindrical particles in the eye. E. S. HEDGES.

Viscosimetric investigation of cotton-yellow. WO. OSTWALD and R. AUERBACH (Kolloid-Z., 1927, **41**, 112—122).—By means of the capillary viscosimeter and the overflow-viscosimeter, using varying rates of flow of liquid, the viscosities of sols of commercial cotton-yellow containing sodium sulphate were determined at different concentrations. The curve exhibits a series of maxima and minima, the highest viscosity being recorded with a 1·2% sol. The maxima and minima are less marked on heating or cooling the solution, or when the content of salt is diminished, but the effect is enhanced by increasing the amount of sodium sulphate. Similar experiments with a mixture of gelatin and sodium sulphate gave a curve showing two well-defined maxima. Mechanical treatment lowers the viscosity of sols of cotton-yellow. E. S. HEDGES.

Ageing of gelatin. A. NAGORNY (Kolloid-Z., 1927, **41**, 123—129).—Gelatin solutions were sterilised by boiling and kept at temperatures of 6° and 37°, respectively, the variation of viscosity with age being studied over periods of 1 or 2 months. Measurements at 20° showed the viscosity of the gelatin kept at 37° to decrease with age, whilst that kept at 6° underwent an increase in viscosity with age. On the other hand, measurements at 30° showed scarcely any change in the viscosity of either. At 20°, the specimen kept at 37° approximated to Poiseuille's rule, and both specimens did so at 30°. Little difference was found in the viscosity of gum-arabic solutions kept at 6° and 37°, respectively. A specimen of gelatin aged at 37° requires more ammonium sulphate solution to effect precipitation than does a specimen kept at 6°: the latter can be separated into two portions by fractional precipitation by means of ammonium sulphate, one of which gelatinises at the ordinary temperature. It is considered that the particles of the disperse phase are larger in the colder solution and that these remain intact when the measurement is carried out at 20°, but become more finely dispersed or dissolved at 30°. The question is discussed whether the difference between the small and large particles is merely one of size, or whether chemical differences are involved. The fractional precipitation by ammonium sulphate supports the latter view. E. S. HEDGES.

***X*-Ray spectrum of the so-called Gladstone's alkali-cellulose compound (in relation to the change in *X*-ray spectrum of cellulose on swelling in concentrated solutions of alkali hydroxides). I.** J. R. KATZ (Z. physikal. Chem., 1926, **124**, 352—358).—When ramie fibres are swollen by treatment with a 14% solution of sodium hydroxide, the *X*-ray spectrogram of cellulose is replaced by a new spectrogram consisting of an "amorphous" ring, due to the alkali solution itself, within which are two equatorial bands, with the form of arcs of a circle. If the swollen fibres are dried, the amorphous ring disappears, but the bands remain. Washing out the free alkali with alcohol does not affect the bands, but there also appear new circles and segments of circles, corresponding with an orderly arrangement of the crystallites in the fibres. Fibres swollen with lithium hydroxide or potassium hydroxide give similar results. Since swelling with zinc chloride or calcium thocyanate does not alter the spectrogram of the ramie, it seems that the effects observed using alkali hydroxides are due to the formation of compounds of the cellulose with alkali. R. CUTHILL.

Behaviour of Prussian blue sol towards certain metallic hydroxides. E. WEDEKIND and HEINRICH FISCHER (Ber., 1927, **60**, [*B*], 544—545; cf. this vol., 328).—Titanic, tungstic, and tantalic acids and lead hydroxide do not adsorb Prussian blue from its colloidal solution. The hydroxides of aluminium, magnesium, lanthanum, thorium, cerium, neodymium, praseodymium, yttrium, gadolinum, and erbium adsorb the sol as readily as does ferric hydroxide, but in course of time the colour of the substrate disappears completely. Zirconium and dysprosium hydroxide and yellow mercury oxide cause slow decolorisation of the blue solution without showing visible adsorption; at 0°, the substrate becomes coloured, indicating that adsorption is the precursor of chemical change. H. WREN.

Existence of two zones of instability in the flocculation of ferric hydroxide sols by electrolytes with multivalent anions. A. BOUTARIC and [MLLE.] M. DUPIN (Compt. rend., 1927, **184**, 326—327; cf. A., 1926, 905).—A ferric hydroxide sol containing 1·6 g. per litre showed two zones of flocculation when treated with increasing concentrations of a sodium phosphate solution: (1) between the concentrations $a=207\times10^{-6}N$ and $b=530\times10^{-6}N$; (2) above the concentration $c=22\times10^{-3}N$. With more concentrated sols, a and b increase, and c decreases slightly. The limits are not affected by sulphuric acid and potassium hydroxide, but are increased by small amounts of ferric chloride, $(c-b)/b$ remaining almost constant, and $(b-a)/a$ decreasing. Stabilising colloids increase c and decrease b, whilst a varies according to the colloid used. The ratio $(b-a)/a$ decreases, but $(c-b)/b$ increases. At high colloid concentrations, the zone of flocculation between a and b disappears. J. GRANT.

Dispersion and aggregation of silk in concentrated salt solutions. P. P. VON WEIMARN (Kolloid-Z., 1927, **41**, 148—152).—Silk dissolves at ordinary pressures to form a colloidal solution in hot concentrated solutions of many very soluble, strongly hydrated salts of the alkali and alkaline-earth metals. The order of influence of the anions is as follows: $F' < SO_4'' <$ citrate $<$ tartrate $<$ acetate $< Cl' < NO_3' < Br' < I' < SCN'$. Addition of strong solutions of the fluorides of ammonium or potassium, or the sulphates of sodium, potassium, ammonium, or lithium, to a solution of silk in hot, concentrated calcium chloride causes aggregation and reprecipitation of the silk. At the ordinary temperature, the silk is reprecipitated by addition of all easily soluble salts, except lithium iodide and lithium thiocyanate. The regenerated silk generally has a thread-like structure. Simple cooling does not cause gelatinisation, but only an increase in viscosity. The silk is also regenerated by the addition of alcohol, or an aqueous or alcoholic solution of tannin. The silk reprecipitated by alcohol may be obtained as a solid block. E. S. HEDGES.

Influence of metals on thixotropic sols and gels. H. FREUNDLICH and W. RAWITZER (Kolloid-Z., 1927, **41**, 102—104).—Sols of ferric hydroxide exhibit the phenomenon of thixotropy, *i.e.*, on addition of electrolytes they set to a gel, which forms a sol once more on shaking. When the colloid is left in contact with certain metals for periods of a few days, the time of setting to the thixotropic gel is shortened, whether the contact with the metal is effected before or after addition of the electrolyte. It is definitely shown that the phenomenon is not due to cations of the metal, to adsorbed hydroxyl ions, or to the formation of hydrogen peroxide. Since a similar effect is produced by application of a direct or an alternating current, the phenomenon is supposed to be due to local currents in the metal. In confirmation of this, the effect increases with the electropositive nature of the metal. E. S. HEDGES.

Colloidal and molecular solubility and a peptisation rule. WO. OSTWALD (Kolloid-Z., 1927, **41**, 163—169).—Contrary to the behaviour of molecularly-dispersed substances, the amount of a colloidal gel dissolved (or peptised) by a medium is not independent of the amount of gel present, but generally increases with the amount of gel used. It is supposed that the gel is heterogeneous in that it exhibits "state-isomerism," the "isomerides" varying in their susceptibility to peptisation. It is admitted that this explanation cannot account for von Buzágh's results (cf. following abstract), where a maximum of peptisation was observed. E. S. HEDGES.

Theory of peptisation. I. Dependence of solubility on the amount of colloid. A. VON BUZÁGH (Kolloid-Z., 1927, **41**, 169—183).—In the peptisation of colloidal barium carbonate, casein, Congo-red acid, Congo-ruby acid, Congo-blue, and ferric hydroxide, the quantity of colloid which passes into solution is not independent of the amount of colloid taken (cf. preceding abstract). As a rule, the curve connecting these quantities exhibits a marked maximum, showing that for a given peptising agent and a given volume there is an optimum condition for sol formation when a medium amount of colloid is present. It is believed that the gels are composite, containing fractions with structural differences which are soluble in certain concentrations of the peptisation medium and insoluble at other concentrations. E. S. HEDGES.

String-formation of emulsoid particles in an alternating electric field. E. MUTH (Kolloid-Z., 1927, **41**, 97—102).—Under the influence of an alternating electric field, the particles of emulsions of milk, cream, butter, or petroleum with water arrange themselves into chains the long axes of which lie in the direction of the applied field. This resembles the effects observed by Thomson and by Whytlaw-Gray and Speakman (Nature, 1921, **107**, 520, 619) in clouds of metallic oxides dispersed from an arc. On removal of the field, the chains break up into the original primary spherical particles. An explanation is given, based on the electrical double layer existing at the colloid particle-dispersion medium interface. It is considered that an alternating polarity is here set up in rhythm with the frequency of the field. The string-formation is independent of the frequency of alternation of the field. E. S. HEDGES.

Liesegang system of "rhythmic" precipitates. R. FRICKE and O. SUWELACK (Z. physikal. Chem., 1926, **124**, 359—393).—The occurrence of periodic precipitation when a solution of ammonia is allowed to diffuse into an agar-agar jelly containing magnesium chloride has been investigated by analysing successive sections of the jelly. It is found that the product of the activities of the ions of the magnesium hydroxide increases for some distance beyond the last precipitate and then falls again. The phenomenon is due to the ordinary processes of diffusion and precipitation and is not peculiar to solutions containing substances in the colloidal state (cf. A., 1924, ii, 26). R. CUTHILL.

Cataphoresis technique. G. ETTISCH and D. DEUTSCH (Physikal. Z., 1927, **28**, 153—154).—The use of materials the resistivity of which is of the order of 10^5 ohms/cm.^{3}, such as parchment paper and unglazed porcelain, for the study of cataphoresis phenomena is described. With these materials, observations can be made in 1—5 min. R. W. LUNT.

Use of Donnan's membrane equilibrium theory for the determination of the charge of colloid particles. N. BJERRUM (Phil. Mag., 1927, [vii], **3**, 22—26).—A reply to the criticism by Rinde (A., 1926, 347) of the author's paper (*ibid.*, 1925, ii, 111). A. E. MITCHELL.

Graphical method for the calculation of the energy yield of homogeneous reactions. P. JOLIBOIS and P. MONTAGNE (Compt. rend., 1927, **184**, 323—325).—Comparison is made of the yields obtained by experiment and those calculated on the hypothesis that the effect of an electric spark on a chemical reaction is purely thermal. At constant temperature, the yield decreases when the gas pressure increases. At constant pressure, the yield attains a maximum which, with increasing pressures, is displaced towards those obtained at higher temperatures. The yield tends to become independent of pressure at temperatures above 3500° Abs. J. GRANT.

Organic acids and bases in non-aqueous solutions. II. Aliphatic acids. F. HOLZL (Monatsh., 1927, **47**, 559—600).—The conductivity method already applied to the investigation of compound formation between acetic acid and various bases in absolute alcoholic solution at 25° (A., 1926, 1206) has been extended to the investigation of each of the acids formic, butyric, and succinic with the bases ammonia, ethylamine, diethylamine, ethylenediamine, benzylamine, aniline, *p*-toluidine, mono- and di-methylaniline, α- and β-naphthylamine, *o*-, *m*-, and *p*-phenylenediamine, diphenylamine, and carbamide. As previously observed, normal salts are obtained with the stronger bases, but with the weaker bases compounds containing a larger proportion of acid are found, and detected either by maxima or inflexions in the conductivity curves. The strength and degree of association of the acid are also important factors, since, for example, phenylenediamine forms a normal salt A_2B (A=1 mol. of the acid; B=1 mol. of the base) with formic acid, but not with

butyric acid. The following is a summary of the compounds formed at the various dilutions: (1) with formic acid, ammonia, 0·42*N*, and ethylamine, 0·93*N* yield only equimolecular compounds of the type AB; ethylenediamine 0·053*N*, AB and A_2B; aniline 0·05*N*, AB, but at higher concentrations up to *N* the maxima occur at points corresponding with a larger proportion of acid; *p*-toluidine, mono- and di-methylaniline show the same phenomenon to a less extent, the concentrations at which the maxima correspond with the salt AB being, respectively, 0·1*N*, 0·05*N*, and 0·05*N*; α-naphthylamine 0·1*N*, AB; β-naphthylamine 0·1*N*, A_2B and AB; *o*-, *m*-, and *p*-phenylenediamine 0·1*N*, AB; carbamide 0·1*N*, AB. With none of the acids was there any evidence of compound formation with diphenylamine; (2) with butyric acid, ammonia, mono- and di-ethylamine, ethylenediamine, benzylamine, aniline, mono- and di-methylaniline, *m*- and *p*-phenylenediamine, and carbamide all form salts of the type AB, the weaker bases behaving in the same manner as they do with formic acid; α-naphthylamine 0·1*N*, AB and AB_2; β-naphthylamine 0·1*N*, A_2B and AB; *o*-phenylenediamine 0·1*N*, A_2B and AB: (3) with succinic acid, ammonia 0·01*N*, ethylamine 0·233 and 0·117*N*, and benzylamine 0·127*N*, all give AB and AB_2; aniline 0·2, 0·1, and 0·05*N*, methylaniline 0·1 and 0·05*N*, dimethylaniline 0·25, 0·1, and 0·05*N*, all give AB only; α- and β-naphthylamine 0·1*N*, A_2B and A_2B_3; *o*-phenylenediamine 0·1*N*, A_2B and AB; *m*-phenylenediamine 0·1 and 0·05*N*, AB; *p*-phenylenediamine 0·125, 0·1, and 0·09*N*, AB and AB_2; carbamide 0·2*N*, AB_2. J. W. Baker.

Influence of organic substances on the rate of absorption of carbon dioxide by solutions of sodium carbonate. P. Riou and P. Cartier (Compt. rend., 1927, **184**, 325—326).—The rates of absorption of carbon dioxide by solutions of sodium carbonate containing various quantities of sucrose, dextrose, and glycerol at 20° rise to maxima and then fall as the viscosity of the solutions increases. J. Grant.

Neutral salt effect. L. E. Bowe (J. Physical Chem., 1927, **31**, 291—302).—The influence of sodium chloride, bromide, and iodide (*N*—4*N*) on the rate of hydrolysis of sucrose and of ethyl acetate has been determined. Potential measurements show that the apparent hydrogen-ion concentration increases tenfold in the case of the 4*N*-sodium iodide solution, and the influence of the neutral salts, contrary to Harned (A., 1916, ii, 8), but in agreement with Arkadiev (*ibid.*, 1923, ii, 369), follows the order iodide>bromide>chloride. The percentage increase in the apparent hydrogen-ion concentration indicated by the sucrose hydrolysis agrees well with that found by the potential method. The influence of sodium chloride on the rate of hydrolysis of ethyl acetate by 0·1*N*-hydrochloric acid is less than in the inversion of sucrose, and sodium bromide produces a smaller effect than the chloride (cf. Åkerlof, A., 1922, ii, 134; Poma, *ibid.*, 1911, ii, 707). Alcohol and acetic acid had but small influence on the reaction velocity. L. S. Theobald.

Lyotropy. H. R. Kruyt and C. Robinson (Proc. K. Akad. Wetensch. Amsterdam, 1926, 29, 1244—1250).—The observations of Linderstrøm-Lang (A., 1925, ii, 30) on the influence of neutral salts on the solubility of quinol and quinone in water have been extended to *m*- and *p*-nitroaniline, *p*-phenylenediamine, and *p*-nitrophenol. The influence of salts on the solubility of quinol is dependent only on the cation. For quinone, *m*- and *p*-nitroaniline, and *p*-phenylenediamine the reverse is true. The solubility of *p*-nitrophenol is influenced by both ions. In presence of bromides, iodides, nitrates, and thiocyanates, the solubilities of the various organic substances in pure water are often exceeded. The theory of Debye (*ibid.*, 171) does not offer a satisfactory explanation of this increased solubility, nor does it suggest a specific influence of the ions. A more plausible explanation is to be found in the orientation of water dipoles in the immediate neighbourhood of the ions, *i.e.*, orientation of the water of hydration. Various physico-chemical phenomena lead to the conclusion that hydration decreases in the order: cations: $Li^{\cdot}>Na^{\cdot}>K^{\cdot}>Rb^{\cdot}>Cs^{\cdot}$; anions: $SO_4''>Cl'>Br'>NO_3'>I'>CNS'$. In general, this will be the sequence of the salting-out effect, $Li^{\cdot}$ and SO_4'' having a strong, and $Cs^{\cdot}$ and CNS' a weak effect. Since dissolution implies an electrical, attractive force between solvent and solute molecules, the water molecules, in consequence of their dipolar character, will be oriented round solute molecules. Two kinds of orientation are possible, since either the positive or the negative end of the water molecule may be turned towards the solute molecule. Postulating a polar character for the dissolved substance, one type of orientation must predominate. With anionphilic molecules (*e.g.*, quinone etc.), the orientation of dipoles round the anion favours the orientation round the organic molecules and increases their solubility. Cations will tend to decrease the solubility, but their influence is small, since they are kept far from the molecule. Hence, in addition to the usual salting-out effect, there is an actual solubility increase brought about by the anion. The feebly-hydrated thiocyanate ion lowers the solubility but little and hence the increase in solubility predominates. The sulphate ion, however, has such a powerful lowering effect that a considerable decrease in solubility results. For cationphilic substances (quinol etc.), a corresponding argument holds. J. S. Carter.

Nessler's reagent. S. M. Naudé (Z. physikal. Chem., 1927, **125**, 98—110).—The existence of the compounds $KHgI_3$ and $KHgI_3,1{\cdot}5H_2O$ is claimed from the results of an investigation of the system HgI_2–KI–H_2O. These results agree approximately with those of Dunningham (J.C.S., 1914, **105**, 368, 724). This author, however, reported $KHgI_3,H_2O$ in the place of $KHgI_3,1{\cdot}5H_2O$. Nessler's solution probably contains $KHgI_3$, not K_2HgI_4. L. F. Gilbert.

Equilibrium in binary systems containing guaiacol as a component. N. A. Puschin and B. Vaic (Monatsh., 1927, **47**, 529—535).—The f.-p. curves for mixtures of guaiacol with aniline, *o*- and *p*-toluidine, pyridine, β-naphthylamine, diphenylamine, ethylurethane, and naphthalene have been determined, and the duration of the eutectic crystall-

isation has been observed. The curves indicate the existence of equimolecular *compounds* with aniline, m. p. 17°, *o*-toluidine, m. p. 24°, *p*-toluidine, m. p. 24·3°, and pyridine, m. p. 5·6°; no compounds are formed in the other cases. The eutectic temperatures for the various systems in the order given above are, respectively, 10·3° and 12°; 15° (traced only to 80 mol.% of *o*-toluidine); 14° and 20°; −5° and −47·8°; 12°; 10°; 5°; and 18°. The eutectic mixtures contain 22 and 92; 20; 22 and 66; 31 and 92; 26; 24; 40; and 18 mol.% of the second component, respectively. J. W. Baker.

Freezing of solutions. II. Crystallisation of maleic, fumaric, and succinic compounds. G. Viseur (Bull. Soc. chim. Belg., 1926, 35, 426—450).—The f. p. of binary mixtures of the dimethyl and diethyl esters of fumaric, maleic, and succinic acids have been determined. Ethyl maleate and ethyl fumarate form an equimolecular compound which forms mixed crystals with each of the constituents. Methyl fumarate and methyl maleate, methyl succinate and methyl maleate, methyl succinate and methyl fumarate, ethyl succinate and ethyl maleate, and ethyl succinate and ethyl fumarate form mixed crystals. The f.-p. method is inapplicable to the acids and amides, as they decompose slowly at high temperatures. The m. p. of mixtures of maleic and fumaric, maleic and succinic, and fumaric and succinic acids, and of the corresponding diamides, were determined therefore by enclosing them in capillary tubes and immersing these in a series of baths at different temperatures, the temperature of "instantaneous fusion" being taken as the m. p. Mixed crystals were observed with the amides, but the results for the mixed acids had to be correlated with the results of solubility determinations in acetone before definite conclusions could be reached. It was then found that mixed crystal formation occurs only in the system succinic acid–fumaric acid.

The m. p. of the amides and acids, and the m. p., b. p., and densities of the esters are recorded. The following are to be noted: maleic acid, m. p. 241·7—241·9°; methyl maleate, m. p. 7·6°, d 1·4513; ethyl maleate, m. p. −17°. L. F. Gilbert.

Mol. wt. of sulphur trioxide in various solvents. G. Oddo and A. Casalino (Gazzetta, 1927, 57, 60—75).—Using sulphuryl chloride and ethyl chloroacetate as solvents, the molecular depression of the f. p. of the compound $SO_3,2POCl_3$ is found to be 106°. The irregular values obtained when liquid sulphur trioxide is used as solute show that solid solutions are formed; fibrous sulphur trioxide gives values corresponding with the theoretical mol. wt., 160. In sulphuric acid, the lowering produced by liquid sulphur trioxide corresponds with mol. wt. 79·8; and that produced by fibrous sulphur trioxide with mol. wt. 88, or approximately 55% $(SO_3)_2$. R. W. Lunt.

Behaviour of sulphur trioxide with phosphorus oxychloride. G. Oddo and A. Casalino (Gazzetta, 1927, 57, 47—59).—The system phosphorus oxychloride and either liquid (SO_3) or fibrous ($[SO_3]_2$) sulphur trioxide shows two eutectics corresponding with $SO_3,POCl_3$ and $SO_3,3POCl_3$. The substances are completely miscible and give a mixture of constant b. p. (111·5—111·9°/735 mm., m. p. −16·62°) corresponding in composition with $SO_3,2POCl_3$. R. W. Lunt.

Dissociation pressures of monopotassium and monosodium orthophosphates and of dipotassium and disodium dihydrogen pyrophosphates. Phosphate. IV. S. J. Kiehl and G. H. Wallace (J. Amer. Chem. Soc., 1927, 49, 375—386).—The dissociation pressures of the following systems were measured by a static method, the apparatus being a modification of that described by Johnston (A., 1908, ii, 358): $nK_2H_2P_2O_7 \rightleftharpoons 2(KPO_3)_n+nH_2O$ (165—260°); $nNa_2H_2P_2O_7 \rightleftharpoons 2(NaPO_3)_n+nH_2O$ (170—280°); nKH_2PO_4 $(KPO_3)_n+nH_2O$ (170—264°); $2NaH_2PO_4 \rightleftharpoons Na_2H_2P_2O_7+H_2O$ (110—150°). The curves show that disodium dihydrogen pyrophosphate may be prepared by heating monosodium orthophosphate in an open vessel at 150°. The corresponding potassium salt, which forms a non-deliquescent, crystalline monohydrate, cannot be prepared in this way, since its dissociation pressure at lower temperatures is higher than that of the orthophosphate–metaphosphate system under the same conditions. For this reason, the systems: $2KH_2PO_4$ $K_2H_2P_2O_7+H_2O$ and $nNaH_2PO_4$ $(NaPO_3)_n+nH_2O$ afford no equilibrium data. S. K. Tweedy.

Pseudo-ternary systems containing sulphur. II. System sulphur–benzoic acid. D. L. Hammick and W. E. Holt (J.C.S., 1927, 493—497).—Equilibria in the system sulphur–benzoic acid have been studied by the synthetic method. Discrepancies between the results and those of Kruyt are probably due to oxidation of the sulphur in the latter's experiments. On the sulphur side, the equilibrium is of Kruyt's type η, and on the benzoic acid side of the type ordinarily found for two partly miscible liquids. The clouding phenomenon noticed by Kruyt can be explained without the assumption that three liquid layers co-exist in the neighbourhood of 170°. H. F. Gillbe.

Dehydration and hydration of platinocyanides. P. Gaubert (Compt. rend., 1927, 184, 383—385).—The changes undergone by small crystals of the hydrated platinocyanides of barium, lithium, yttrium, and magnesium mounted on a slide in an inert liquid (melted paraffin, vaseline, or monobromonaphthalene) have been observed under the polarising microscope, the crystals being gradually heated. The changes corresponding with the dehydration of the crystals occur at higher temperatures than in air, according to the nature of the compound. The phenomenon is reversible and is most marked in the case of the yttrium compound. The transformations of the magnesium compound are not polymorphic. The nature of the inert liquid has little influence on the results, the liberated water being absorbed by the dehydrated product rather than by the medium. J. Grant.

Ionic equilibria. I. Equilibrium between calcium oxalate and dilute hydrochloric acid. M. Auméras (J. Chim. phys., 1927, 24, 24—49).—Desiccation of precipitated calcium oxalate at 25° indicates the existence of a hydrate, $CaC_2O_4,1{\cdot}2H_2O$. If, however, the method of dehydration at increasing

temperature recommended by Guichard (A., 1925, ii, 559) is used, the formula for the hydrate is found to be CaC_2O_4,H_2O. For a solution of calcium oxalate in dilute hydrochloric acid in equilibrium with the solid salt, it is shown that if P is the solubility product of the oxalate and C and D are the first and second dissociation constants, respectively, of oxalic acid, then $PA=D$, and $AC=B$, where $A=[H^{\cdot}]/[HC_2O_4^{\prime}][Ca^{\cdot\cdot}]$ and $B=[H^{\cdot}]^2/[H_2C_2O_4][Ca^{\cdot\cdot}]$. The value of B has been derived from determinations of the solubility of the oxalate in hydrochloric acid. Using published data for P and Chandler's value for C (A., 1908, ii, 467), the value of D is calculated from the above equations to be $5{\cdot}6\times10^{-5}$ at 13°, in good agreement with Chandler's values of $4{\cdot}1\times10^{-5}$ and $4{\cdot}9\times10^{-5}$ at 25°. If hydrobromic acid or nitric acid is used to dissolve the oxalate, instead of hydrochloric acid, similar results are obtained. The solubility at 20° of calcium oxalate precipitated from calcium chloride solutions is 0·0066 or 0·0073 g./litre of solution, according as the precipitant is oxalic acid or ammonium oxalate. R. CUTHILL.

Ternary system copper–zinc–manganese. O. HEUSLER (Z. anorg. Chem., 1926, **159**, 37—54).—An exhaustive investigation of the ternary system copper–zinc–manganese with diagrams and a short account of the magnetic properties of these alloys. M. CARLTON.

Equilibrium in the systems alkali chloride–cobalt chloride–water. H. W. FOOTE (Amer. J. Sci., 1927, **13**, 158—166).—The solubility curves at 25° have been determined for the systems sodium (potassium, rubidium, cæsium) chloride–cobaltous chloride–water. The saturated solutions for the five binary systems contain 26·50, 26·46, 48·57, 65·61, and 35·67% of salt, respectively. System $NaCl–CoCl_2–H_2O$. No double salts are formed. The solution saturated with respect to both salts contains 4·70% NaCl, 32·91% $CoCl_2$. System $KCl–CoCl_2–H_2O$. No double salts are formed. The univariant point is at 8·24% KCl, 34·10% $CoCl_2$. System $RbCl–CoCl_2–H_2O$. Two double *salts* are formed, $RbCl,CoCl_2,2H_2O$ (D_1) and $2RbCl,CoCl_2,2H_2O$ (D_2). Univariant points: 6·09% RbCl, 35·02% $CoCl_2$, solid phases, $CoCl_2,6H_2O$ and D_1; 7·68% RbCl, 34·36% $CoCl_2$, solid phases, D_1 and D_2; 38·43% RbCl, 11·50% $CoCl_2$, solid phases, D_2 and RbCl. System: $CsCl–CoCl_2–H_2O$. Three double salts exist, $CsCl,CoCl_2,2H_2O$ (d_1), $2CsCl,CoCl_2$ (d_2), $3CsCl,CoCl_2$ (d_3). Univariant points: 1·86% CsCl, 35·67% $CoCl_2$, solid phases, $CoCl_2,6H_2O$ and d_1; 5·03% CsCl, 31·09% $CoCl_2$, solid phases, d_1 and d_2; 40·56% CsCl, 8·98% $CoCl_2$, solid phases, d_2 and d_3; 65·48% CsCl, 0·25% $CoCl_2$, solid phases, d_3 and CsCl. J. S. CARTER.

System NH_4NO_3–$(NH_4)_2SO_4$–H_2O. E. JÄNECKE, W. EISSNER, and R. BRILL (Z. anorg. Chem., 1927, **160**, 171—184).—Solubility measurements of the system ammonium nitrate–ammonium sulphate–water show that no double salts other than $(NH_4)_2SO_4,2NH_4NO_3$ exist. The phase diagram for mixtures of ammonium nitrate and ammonium sulphate indicate that the double salt melts at 310°. The presence of ammonium sulphate lowers the transition temperature and raises the m. p. of ammonium nitrate. Mixed crystals of ammonium nitrate with the double salt exist.

The crystallographic and optical constants of the double salt have been determined. *X*-Ray investigation shows that the crystal unit consists of not less than two molecules of the double salt. H. F. GILLBE.

Univariant folds in salt-formation diagrams. Sodium nitrate. N. S. KURNAKOV and W. T. NIKOLAIEV (J. Russ. Phys. Chem. Soc., 1926, **58**, 548—552).—The equilibrium in the system $Na_2O–N_2O_5–H_2O$ has been examined at 25° and 65°. M. ZVEGINTZOV.

Univariant systems, isothermal surfaces, and three-dimensional ridges. W. T. NIKOLAIEV (J. Russ. Phys. Chem. Soc., 1926, **58**, 553—556).—The influence of a fourth component on the univariant equilibrium states of a ternary system has been studied in reference to the quaternary combination $Na_2O–N_2O_5–H_2O$–EtOH. Solubilities and densities for 25° are recorded. The data refer to alcohol concentrations of 0, 5, 15, and 30%. The diminution in the solubility of the salt is almost proportional to the amount of alcohol. M. ZVEGINTZOV.

Cryohydric curves of the ternary system $Na_2O–N_2O_5–H_2O$. W. T. NIKOLAIEV (J. Russ. Phys. Chem. Soc., 1926, **58**, 557—564; cf. preceding abstracts).—The eutectic temperature of sodium nitrate–ice is −18·1°, and the changes in temperature and composition caused by adding acid or alkali to the eutectic mixture (38·07% by weight of sodium nitrate) have been determined. For small additions, the changes are proportional to the quantities added. The ternary eutectics are at −46·4° (acid) and −39·1° (alkaline), where crystals of $NaNO_3$+ice+$HNO_3,3H_2O$ and $NaNO_3$+ice+$NaOH,7H_2O$ separate out, respectively. By combining these results in a triangular space model with the isothermal diagrams at 25° and 65° (cf. preceding abstract), a univariant "isochoric" fold is obtained the ridge of which lies on an "isochoric" univariant plane through the central tie-line (H_2O)–$(NaNO_3)$, which divides it into an alkaline and an acid section. By joining the three binary eutectics ice+HNO_3 (−43°), ice+NaOH (−28°), ice+$NaNO_3$ (−18·1°) and the two ternary eutectics, an "ice-field" is isolated which includes all those systems in which ice is present; this is divided into an alkaline and an acid section by the f.-p. curve of neutral solutions of sodium nitrate. M. ZVEGINTZOV.

Distillation of heterogeneous ternary mixtures. II. System ethyl alcohol–benzene–water. J. BARBAUDY (J. Chim. phys., 1927, **24** 1—23; cf. A., 1926, 578).—The b. p. at 760 mm. of a large number of mixtures of alcohol and benzene, and of homogeneous and heterogeneous ternary mixtures of alcohol, benzene, and water have been determined, and the results represented graphically. The composition of the saturated vapour was determined by the partial condensation method previously described (*loc. cit.*), and the distillates were also analysed. R. CUTHILL.

Reaction regions. XIII. Influence of size of particles of the reacting substances and of the

nature of the igniter. W. P. JORISSEN and C. GROENEVELD (Rec. trav. chim., 1927, **46**, 47—53; cf. A., 1926, 1206; this vol., 112).—Figures and curves are given showing the extension of the reaction regions of mixtures of aluminium and sulphur, iron and sulphur, and of iron, aluminium, and sulphur with increase in the power of the igniting mixture and decrease in the particle size of the constituents of the mixture. H. F. GILLBE.

Reactions in the solid state. VII. D. BALAREV (Z. anorg. Chem., 1927, **160**, 92—100).—A large number of the reactions studied by Tammann, Hedvall, and the author are shown either to be complex or to be dependent on the presence of substances in the liquid or gaseous phase. The conclusion is that all such reactions which show a thermal effect on the heating curve and are simple in nature involve a straightforward distillation process. H. F. GILLBE.

[Reactions in the solid state.] G. TAMMANN (Z. anorg. Chem., 1927, **160**, 101—106).—Polemical against Balarev (preceding abstract). H. F. GILLBE.

Specific inductive capacity of heterogeneous mixtures. J. ERRERA (Compt. rend., 1927, **184**, 455—458).—The variations of the ratio of the density of compressed powder to that of the substance in the solid homogeneous state have been studied in the case of lead chloride, lead nitrate, and potassium chloride and the changes plotted as a function of the specific inductive capacity. For densities greater than a lower limiting value, the variation is linear until the ratio=1. The value of the specific inductive capacity for potassium chloride (cubic system) when the ratio is unity is almost the same as for crystalline potassium chloride. J. GRANT.

Applications of thermodynamics. E. DENINA (Gazzetta, 1927, **57**, 3—7).—A discussion of the method of application of general thermodynamical equations most appropriate to particular types of problems. R. W. LUNT.

Activity coefficients of electrolytes. I. Limiting law for a ter-tervalent salt. V. K. LAMER, C. V. KING, and C. F. MASON (J. Amer. Chem. Soc., 1927, **49**, 363—374).—The activity coefficients of the ions of the sparingly soluble hexammine cobalt ferricyanide were determined by measuring its solubility in aqueous magnesium sulphate, potassium nitrate, and sodium chloride solutions. In solutions of the first two salts, the limiting Debye-Hückel equation is obeyed up to an ionic strength of 0·007. A slight discrepancy in the case of sodium chloride suggests that Debye and Huckel's simple concept of ionic size cannot account for the deviations from the limiting law (see following abstract). S. K. TWEEDY.

Activity coefficients of electrolytes. II. Unsymmetric valency-type effect in highly dilute solutions. V. K. LAMER and C. F. MASON (J. Amer. Chem. Soc., 1927, **49**, 410—426).—The "electric-type effect" (Bronsted and LaMer, A., 1924, ii, 306) is investigated for luteotetramminodiamminocobaltiates and luteodinitrodiammino-oxalocobaltiates by measuring the solubilities of these salts in salt solutions. When the salt solution involves a univalent anion, the Debye–Hückel theory and the Lewis and Randall principle of ionic strength are both satisfied; in other cases, abnormal results are obtained, even at the highest dilutions (0·00008*M*). These are attributed to the neglect of higher terms (z^3. . . .) in the Debye-Hückel expression for the density of electricity. A revision of the interionic attraction theory in this respect yields equations which are qualitatively in agreement with experiment and are in accord with Bjerrum's ideas on "ion association" (*v. infra*). S. K. TWEEDY.

Ionic association. I. Influence of ionic association on the activity of ions at moderate degrees of association. N. BJERRUM (Kgl. Danske Videnskab. Selsk. math.-fys. Medd., 1926, **7**. [9], 1—48).—The formula developed by Debye and Hückel (A., 1923, ii, 459, 724; 1924, ii, 386; 1925, ii, 513) for calculating activity from the concentration and dimensions of the ions is shown not to be accurate for small ions and for ions of high valency. A method for obtaining more exact values is developed. New values are tabulated for the activity coefficients of univalent ions in water for various concentrations, and these are compared with the old values. By a simple transformation they can be applied to all solutions of electrolytes. From the experimental data, the following values for the sum of the ionic radii of a number of electrolytes were determined (values in Å.): potassium nitrate, 1·57; potassium iodate, sodium iodate, 1·33; magnesium sulphate, copper sulphate, cadmium sulphate, 4·2; potassium sulphate, 3·8; barium chloride, 5·8; lanthanum nitrate, 6·4. In methyl alcohol, values of 4·1—6·5 Å., and in ethyl alcohol, 2·4—7·8 Å., were calculated. W. CLARK.

Activation of gases by adsorption. G. B. KISTIAKOWSKY (Proc. Nat. Acad. Sci., 1927, **13**, 1—4; cf. Fryling, A., 1926, 800).—On the assumption that the surfaces of metallic catalysts are composed of atoms in different states of lattice saturation (Taylor, A., 1925, ii, 562; 1926, 365), a study of the heat of adsorption in its dependence on the volume adsorbed for hydrogen and carbon monoxide on an active copper catalyst leads to the conclusion that only the unsaturated surface atoms are effective in bringing about activation of the adsorbed gas. Measurements of the heat of adsorption of hydrogen on a copper surface poisoned by a small amount of oxygen indicate that the role of oxygen is to oxidise preferentially the most unsaturated surface atoms. J. S. CARTER.

Theory of the heat of adsorption of gases. H. CASSEL (Physikal. Z., 1927, **28**, 152—153).—An extension of the author's thermodynamic theory (A., 1926, 127), which is held to be more conformable with experiment. Iljin's work (*ibid.*, 1104) is criticised. R. W. LUNT.

Change of entropy on melting. I. Variation of the entropy change of the elements with atomic number. E. KORDES (Z. anorg. Chem., 1927, **160**, 67—76).—The entropy change of the elements on melting is a periodic function of the atomic number, with maxima at the halogen elements,

subsidiary maxima at the metals of group VIII, and minima near the elements of group IV. Crompton's view that the entropy change of the metals is independent of the nature of the metal is thus untenable.

The periodicity is discussed in the light of the number of atoms composing the elementary molecule, and further investigations are in progress to correlate the periodicity with atomic structure.

H. F. GILLBE.

Ratio of the heats of combustion of benzoic acid and salicylic acid. E. BERNER (J.C.S., 1927, 338—341).—The ratio of the heats of combustion of benzoic acid and salicylic acid has been redetermined and is found to be 1·2074 (vac.). This gives 5233·7 g.-cal.^{15}/g. for the heat of combustion of salicylic acid when the value for benzoic acid is taken as 6319 g.-cal.^{15}/g. Evidence is submitted that these values are more correct than those of Verkade and Coops (A., 1926, 785). H. F. GILLBE.

Heats of combustion of the different varieties of lustre carbon; existence of amorphous carbon. W. A. ROTH and O. DOEPKE (Ber., 1927, 60, [*B*], 530—536; cf. A., 1926, 894).—Three different samples of lustre carbon with differing densities have been examined, from two of which Debye–Scherrer diagrams have been obtained. Increase in density is parallel to a strengthening of the graphite interferences and marked decrease in the heat of combustion. Attempts to base an explanation of the energy differences solely on surface change or surface tension involve the assumption either of extremely great surface tensions or particularly minute elementary units; the actual existence of amorphous carbon as a particular modification is therefore rendered more probable. A lustre carbon, *d* 2·07, had a heat of combustion greater by 195 g.-cal/g. than that of graphite, whereas a product *d* 1·86 had the value 8148 g.-cal/g., the highest value observed up to the present for pure carbon. H. WREN.

Investigations in the critical region. II. Specific heats at constant pressure of ethyl ether above and below the critical point. K. BENNEWITZ (Z. physikal. Chem., 1927, 111—134; cf. A., 1926, 1210).—An apparatus is described by means of which the specific volumes and the specific heats of ethyl ether were determined between about 33° and 215° at a constant pressure of 40 atm. The results show that the fall in the specific heat above the critical temperature is gradual and that the properties which are presumably characteristic of the substance in the state of vapour are not attained until the temperature is 10° or 15° above the critical temperature.

L. F. GILBERT.

Physical chemistry of complex salts. I. Transport numbers of copper salicylate. W. E. HAMER and C. R. BURY (J.C.S., 1927, 333—338).—The solubility of copper salicylate in water at 25° is 10·19 g./litre, and the transport number of the cation 0·628, the latter being determined by a conductotitrimetric method. In neutral solution, the salt ionises as a simple cupric salt, which is not incompatible with its behaviour as a ψ-acid in alkaline solution. H. F. GILLBE.

Hydrate problem. V. Electrolytic transport of water in *N*-solutions. H. REMY (Z. physikal. Chem., 1926, 124, 394—404; cf. A., 1926, 1201).—Determinations by the diaphragm method (A., 1926, 128) of the transport of water in the electrolysis of *N*-potassium chloride solutions yield concordant results only if no correction for possible electro-endosmosis is applied. The value so obtained agrees satisfactorily with the one obtained by the method depending on the use of a reference substance. With sodium chloride, the electro-endosmotic effect may not be entirely negligible, but in general it is undesirable to attempt to apply any correction. Values for the water transport have been obtained by the diaphragm method for *N*-solutions of the chlorides of potassium, sodium, lithium, and ammonium, of the iodides of barium, strontium, calcium, and magnesium, and of hydroxylamine hydrochloride.

R. CUTHILL.

Variable resistance. O. MAASS and J. H. MENNIE (J. Amer. Chem. Soc., 1927, 49, 451—452).—The resistance of a mercury column of constant length is varied by the insertion of a glass rod which produces a change in the cross-section of a part of the column. The advantages claimed are ease and cheapness of construction, great sensitivity (about 0·0003 ohm), low temperature coefficient, and complete absence of contact resistance. S. K. TWEEDY.

Electrical conductivity of mixtures of sulphuric and phosphoric acids. J. MEYER and A. PAWLETTA (Ber., 1927, 60 [*B*], 551—553).—A perfectly normal, mutual influence of the dissociation relationships is observed in mixtures of sulphuric and orthophosphoric acids. Contrary to Pessel (A., 1923, ii, 396), there is no evidence of chemical reaction between the acids. H. WREN.

Electrical conductivity of the system arsenious bromide–ethyl ether. M. USSANOWITSCH (Z. physikal. Chem., 1926, 124, 427—435).—The specific conductance of solutions of arsenious bromide in ether at 18° rapidly increases with increase in the bromide concentration up to 95%, after which it quickly falls to the value for the pure bromide. For high concentrations, the temperature coefficient is positive, but decreases with falling concentration, and for concentrations below about 75% is negative. This effect does not appear, however, to be due to interaction between solvent and solute. If the molecular conductivity is calculated with reference to the bromide as the electrolyte, the conductivity–concentration curve has two maxima, but if the ether is taken as the electrolyte, a normal curve results.

R. CUTHILL.

Conduction process in glass. I. Replacement of the sodium by alkali metals and ammonium. C. B. HURD, E. W. ENGEL, and A. A. VERNON (J. Amer. Chem. Soc., 1927, 49, 447—450).—Cells of the type (+) carbon|metallic salt (fused or in solution)|incandescence electric lamp (—) were investigated. The replacement of sodium by sodium in the glass of the lamp-bulb produced little or no effect; metallic sodium deposited within the lamp. Potassium penetrated readily, but fracture occurred with any considerable depth of penetration,

unless a potassium glass was used. Replacement of sodium by lithium ions was difficult. The ammonium radical readily penetrated sodium glass, sodium hydride and amide probably being formed; with sufficiently extensive replacement, however, fracture occurred. It is inferred that glass has a mesh-like structure, the mesh being more and more elastic as the temperature rises; the ease of replacement probably depends on the relative sizes of the sodium and replacing ions. S. K. TWEEDY.

Mixed electrical conduction in solid compounds. C. TUBANDT and H. REINHOLD (Z. anorg. Chem., 1927, **160**, 222—236).—The method of determining the mode of conduction through solid bodies (cf. A., 1920, ii, 279; 1921, ii 426) has been modified so that it can be employed at low temperatures. In the β-silver sulphide, previously characterised as a mixed conductor, there is a continuous exchange between ionic and electronic conduction. Increase in the current through the crystal favours electronic conduction, especially at low temperatures; as the temperature approaches the transition point (179°), the effect of change of current vanishes. Electronic conduction increases with rise of temperature, the rate of increase being the greater the smaller is the current; with greater currents, the temperature effect vanishes. An argument is developed in favour of the interchange between the two forms of conduction being bound up with the electron affinity of the ions composing the crystal. H. F. GILLBE.

Absolute values of electrode potentials. M. ANDAUER (Z. phvsikal. Chem., 1927, **125**, 135—143).—A method of measuring the *P.D.* between metals and solutions is described. A metal gauze of fine mesh (connected to earth) was placed above and parallel with the surface of the solution, and surmounted by a parallel metal plate connected to an electrometer. The air in the neighbourhood of the metal gauze was ionised by a constant radioactive source, consisting of a platinum wire coated electrolytically with polonium. The *P.D.* between the solution and the immersed electrode was determined from measurements of the changes produced in the leakage current from the charged electrometer, on connecting the electrode, plus a known variable potential placed in series with it, to earth. For calibration purposes, a second metal plate was substituted for the solution surface, and it was found that the potential at which the leakage current attained its maximum value varied with the nature of the metal. G. A. ELLIOTT.

Absolute electrolytic solution tension. II. Electrocapillary curve of mercury. K. BENNEWITZ and A. DELIJANNIS (Z. physikal. Chem., 1927, **125**, 144—150).—By plotting the surface tension of mercury in contact with mercurous nitrate against the potential of the electrode $Hg|xN\text{-}Hg_2(NO_3)_2$, the concentration of the mercurous nitrate being simultaneously varied, a parabolic curve is obtained passing through a maximum when the electrode potential has a value $\varepsilon_H=0{\cdot}475$ volt. This value corresponds with the absolute null point of the electrode potential determined by the scraping method (cf. A., 1926, 1212). H. TERREY.

General relation between *E.M.F.* and temperature. E. DENINA (Gazzetta, 1927, **57**, 8—15).—By considering the *E.M.F.* as due to contact potentials (Volta effect), a general thermodynamic expression is developed for the influence of temperature on the *E.M.F.* R. W. LUNT.

Electric potentials of ions in salt solutions. J. A. V. BUTLER (Phil. Mag., 1927, [vii], **3**, 213—215).—The electric potential at the surface of an ion due to its ion atmosphere is distinguished from the electric potential of the ion itself, and an equation is deduced which gives the *E.M.F.* of a simple concentration cell without transport and expresses the free energy of transfer of a binary electrolyte from one concentration to another. The results do not affect the general conditions of equilibrium previously obtained (A., 1926, 908). A. E. MITCHELL.

Potentials associated with adsorption and diffusion. O. BLUH (Physikal. Z., 1927, **28**, 16—22).—In a system comprising two blotting-paper electrodes partly immersed in a solution, and across which a potential of 500—600 volts *D.C.* is applied, thereby maintaining a current of 6 milliamp., determinations have been made, by electrostatic methods, of the potentials acquired by small platinum search-electrodes when placed in the solution adjacent to the blotting-paper electrodes. Solutions of simple acids, bases, and salts and of several acidic and basic dyes have been examined. The results are held to afford evidence of the diffusion of the solute due to the electric field. R. W. LUNT.

***P.D.* across a semi-permeable membrane.** N. KAMEYAMA (Phil. Mag., 1927, [vii], **3**, 235—240).—Measurements of the *E.M.F.* of the chain K-amalgam$|K_4Fe(CN)_6(m_1)||K_4Fe(CN)_6(m_2)|$K-amalgam, where $||$ was a copper ferrocyanide membrane and m_1 was constant at $0{\cdot}05M$, whilst m_2 was varied between $0{\cdot}025$ and $0{\cdot}0005M$, gave only values the magnitude of which could be explained by the decomposition of the amalgam in the weaker solution. The membrane potential is thus just balanced by the concentration cell with respect to potassium ions at the ends of the chain, and the nullity of the total *E.M.F.* is taken as a verification of the relation $Em=(RT/F)\log_e[K]_1/[K]_2$, where *Em* is the *P.D.* across a copper ferrocyanide membrane in the system $K_4Fe(CN)_6(m_1)||K_4Fe(CN)_6(m_2)$ and *K* is the activity of potassium ion. The results confirm the theory of membrane potentials advanced by Donnan (A., 1911, ii, 848) in so far as the solutions examined are not so dilute as to produce disturbing effects due to interaction of the amalgam with water. A. E. MITCHELL.

Reduction potential of sugars. E. AUBEL, L. GENEVOIS, and R. WURMSER (Compt. rend., 1927, **184**, 407—409).—The oxidation–reduction potentials of a number of dyes have been determined, and also those of a number of sugars. Dyes reduced by lævulose have a reduction potential below —0·1 volt and those not reduced above —0·1 volt. Lævulose has a potential of —0·26 volt, dextrose —0·4, lactose —0·325, and galactose —0·235, all at p_H 8·2. L. F. HEWITT.

Overpotential at antimony cathodes and electrolytic stibine formation. H. J. S. SAND, J. GRANT, and W. V. LLOYD (J.C.S., 1927, 378—396).—Overvoltages at antimony cathodes in acid and alkaline solutions have been measured by the direct method and by a commutator method by which the polarisation could be determined during intervals of 1/5000 sec. at various periods after breaking the current. It is shown that at high current densities the direct method gives inaccurate results, on account of irreversible effects, although at low *C.D.* the two methods give sensibly the same results. Extrapolation to zero time from a few measurements at various time intervals is shown to be unsound, and it is suggested that polarisations should be stated together with their time interval. Such measurements correctly represent the average potential over the interval studied.

In acid solutions, small potentials remain practically constant for periods up to 1/140 sec.; at higher *C.D.* the polarisations fall off rapidly with time, but in every case the polarisation during a given period assumes a maximum independent of the *C.D.* The direct method gives an indefinite increase of polarisation with *C.D.* The overvoltage in acid solution increases with dilution to a less extent than is required by the formula applicable to Herasymenko's experiments, which are shown, therefore, to be of a different nature. Further, it is demonstrated that Heyrovsky's theory of the intermediate formation of negatively-charged hydrogen ions during the production of molecular hydrogen, based on Herasymenko's experiments, is untenable.

In alkaline solution, the overvoltage–*C.D.* curves obtained by the direct method show an inflexion corresponding with the maximum given by the commutator method. Similar results are found for solutions containing large amounts of alkali salts, but high *C.D.* are required to establish a constant overvoltage.

No simple relationship between overvoltage and stibine evolution could be established in either acid or alkaline solution. High *C.D.* are required, and the yield appears to depend on the solubility of the cathode in the electrolyte. The best yield in alkaline solution is obtained by blowing a rapid stream of hydrogen over the surface of the cathode, as otherwise the nascent stibine is decomposed by the electrolyte, with the formation of metallic antimony.

H. F. GILLBE.

Phenomena associated with cathode sputtering. T. BAUM (Z. Physik, 1927, **40**, 686—707).—From measurements of the magnetic deflexion of the stream of particles emitted from a silver cathode in an atmosphere at 10^{-2} mm. due to a current of 25 milliamp. at 2500 volts, it is shown that the particles are uncharged silver atoms. The disintegration of the cathode surface under such conditions is discussed at length. R. W. LUNT.

Valve action of silver in aqueous solutions of potassium silver cyanide. A. GUNTHER-SCHULZE (Z. Physik, 1926, **40**, 879—882).—Silver in potassium silver cyanide does not act as a rectifier for alternating current, because it does not then form a non-conducting film, but it acts as an interrupter for direct current. E. B. LUDLAM.

Combustion of complex gaseous mixtures. III. Inflammation of mixtures of carbon monoxide and hydrogen with air in a closed vessel. G. B. MAXWELL, W. PAYMAN, and R. V. WHEELER (J.C.S., 1927, 297—310).—The application of the "law of speeds" (*ibid.*, 1922, **121**, 365) to the conditions of combustion of gaseous mixtures in closed vessels has been tested. Mixtures of air with hydrogen, carbon monoxide, and mixtures of these two gases in the proportions $3H_2+CO$, H_2+CO, H_2+3CO were exploded in a spherical bomb, with central ignition, the initial pressure being atmospheric. It is shown that the times for explosion for the full range of mixtures $3H_2+CO$ and H_2+CO with air can be calculated from the experimental values for the mixtures of air with hydrogen and the mixture H_2+3CO. The "effective" times of explosion of mixtures of carbon monoxide and air, calculated in the same way, are shown to correspond with the times of explosion when the mixtures are saturated with water vapour at 40°, the concentration of water vapour being then that which has the optimum effect on the speed of combustion of carbon monoxide. The law of speeds is shown to explain the results of Bone, Newitt, and Townend (*ibid.*, 1923, **123**, 2008), and of Fenning (Phil. Trans., 1926, **A**, **225**, 331).

W. THOMAS.

Movement of flame in closed vessels: after-burning. O. C. DE C. ELLIS and R. V. WHEELER (J.C.S., 1927, 310—322).—The movement of a flame in a closed vessel consists of two phases: in (i) the proper motion of the flame and that of the unburnt mixture in front of the flame-front have the same direction; in (ii) the direction of motion of the flame and of the mixture may be opposed, and combustion proceeds under an enhanced and increasing pressure. As (ii) begins, the explosion vessel is re-illuminated near the point of ignition, and this luminescence persists for a considerable time after the flame-front has reached the walls. These phenomena are illustrated by experiments with mixtures of carbon monoxide and air exploded within (*a*) a sphere and (*b*) a cylinder, ignition being central in each case. It is concluded that this luminescence is due to "after-burning," *i.e.*, the combination of molecules of carbon monoxide and oxygen that had escaped combustion while the flame was travelling. This is supported by the results of comparative experiments with mixtures $2CO+O_2+4Z$, in which Z is oxygen, carbon monoxide, carbon dioxide, argon, or helium, the mixtures in each case being saturated with water vapour at various temperatures. The extent to which the reactivity of carbon monoxide is dependent on the presence of water vapour is shown by the results. The duration of the after-burning is longest in the case of argon as a diluent, and its actinic effect is also greatest. W. THOMAS.

Effect of pressure on the limits for the propagation of flame in ether–air. A. G. WHITE (J.C.S., 1927, 498—499).—Limits for the horizontal propagation of flame in ether–air have been determined at pressures between 758 mm. and 90 mm. Reduction

of pressure results in two separate ranges, of which the one containing more ether, the cool flame range, diminishes rapidly, to disappear entirely before the pressure has been reduced to 360 mm. The lower limit changes little until the pressure is 300 mm., but the upper limit of the "ordinary" range decreases fairly uniformly from 500 to 90 mm. pressure.

W. THOMAS.

Detonation of gaseous mixtures of acetylene and of pentane. A. EGERTON and S. F. GATES (Proc. Roy. Soc., 1927, **A**, **114**, 137—151).—Mixtures of acetylene and of pentane vapour with the amount of oxygen required for complete combustion, and diluted with varying amounts of nitrogen, oxygen, argon, carbon dioxide, and excess of fuel, have been studied with the view of finding the position at which a detonation wave develops in a burning mixture of gases under fixed conditions, and the influence on this position of a change of concentration of the combustible gas mixture and of the nature of the diluent gas. The conditions for constancy of the position of detonation are thorough mixture of the gases, uniformity in the bore of the tube, and as little movement in the gas as possible. The degree of humidity of the gas, the method of ignition, and the presence of ions in the gas (from β-rays from radium) have no definite effect on the position. Weak mixtures give much less concordant results than stronger. Oxygen accelerates combustion, detonation occurring considerably earlier than with a similar quantity of nitrogen, and slightly earlier than with a similar quantity of argon (unless the mixture is weak). A large excess of combustible has a great delaying effect, but early detonation occurs with mixtures containing up to double the amount required for complete combustion. Carbon dioxide has a greater delaying effect than nitrogen. These results are discussed and explanations suggested. The velocity of the detonation wave is less in argon and in oxygen than in nitrogen, and greater in mixtures rich in combustible constituents. Dilution decreases the velocity. The conditions governing the establishment of a detonation wave are discussed, and it is supposed that detonation is initiated as a spontaneous explosion of a region of gas, and that, once initiated, the condition for combustion of the detonating type is more readily attained. Detonation appears to take place slightly ahead of the visible combustion front, Le Chatelier's view thus being confirmed. The addition of small quantities of the "antiknock" compounds, lead tetraethyl and diethyl selenide, does not affect the position of detonation at ordinary initial pressures and temperatures.

L. L. BIRCUMSHAW.

Detonation in gaseous mixtures at high initial pressures and temperatures. A. EGERTON and S. F. GATES (Proc. Roy. Soc., 1927, **A**, **114**, 152—160; cf. preceding abstract).—The previous investigations on detonation in acetylene and pentane mixtures have been extended to embrace higher initial pressures (up to 10 atm.) and temperatures (up to 240°). A steel explosion tube is used having glass windows through which the explosion flame may be photographed. Explosion is thus effected under conditions somewhat similar to those which hold in an internal-combustion engine. The tendency to detonate increases considerably with increasing initial pressure up to 3 atm., after which further increase in pressure has very little effect (cf. Woodbury, Canby, and Lewis, J. Soc. Aut. Eng., 1921, 8, 209). At a given initial pressure, rise of initial temperature appears to cause detonation to occur slightly later. Measurements of the velocity of the detonation wave from the slope of the start of the bands of light from the windows show that the velocity decreases with dilution, and is practically unaffected by increase in initial temperature or pressure. The phenomenon of "knocking" in internal-combustion engines is discussed. The "antiknock" lead tetraethyl is found to have no effect on the position of detonation of the mixtures investigated at high pressure, either at normal initial temperature or at 230—240°.

L. L. BIRCUMSHAW.

Gaseous reaction between hydrogen sulphide and sulphur dioxide. H. A. TAYLOR and W. A. WESLEY (J. Physical Chem., 1927, **31**, 216—230; cf. Lewis and Randall, A., 1918, ii, 159; Randall and Bichowsky, *ibid.*, 159).—The velocity of reaction of hydrogen sulphide and sulphur dioxide in pyrex tubes at temperatures ranging from 370° to 730° has been measured by a dynamic method. The velocity is proportional to the surface area of the reaction vessel, the glass acting as a contact catalyst for the reaction. The temperature coefficient decreases with a rise in temperature. At constant temperature, the velocity varies as the partial pressure of the sulphur dioxide and as the 1·5 power of the partial pressure of the hydrogen sulphide.

The mechanism of the reaction advanced is that the reactants are activated by adsorption on the glass surface, and reaction between activated molecules only then follows. Combination in the gaseous state, if any, is very slight.

L. S. THEOBALD.

Mechanism of explosive reactions. C. Z. ROSENCRANS (Univ. Ill. Eng. Exp. Sta. Bull., 1926, No. 157, 1—64).—A study of the explosion of mixtures of ethyl ether and air in a cylindrical bomb of constant volume. Differences between the theoretical and experimental flame propagation curves are ascribed to the heat loss. Usually, but not always, the flame fills the bomb when maximum pressure is attained. At the time of the flame arrest, the pressure was in general 25% of its maximum. The flame arrest is believed to be due to the great decrease in density of the gases within and behind the flame front causing a momentary extinction of the flame. The existence of after-burning and the adjustment of chemical equilibrium behind the flame front were demonstrated. An equation expressing the reaction velocity as a function of the pressure is indicated.

CHEMICAL ABSTRACTS.

Chemical action in the electric spark discharge. Ignition of methane. H. F. COWARD and E. G. MEITER (J. Amer. Chem. Soc., 1927, **49**, 396—409).—The chemical changes attending the passage of a stream of regular sparks through air containing 6·8—11·2% of methane were investigated, each spark having just sufficient energy to ignite the mixture in

its path. For a given mixture, the extent of reaction appears to be nearly proportional to the square of the current. The reaction products contain a large quantity of carbon monoxide and some hydrogen, even when an excess of oxygen is present, from which it is concluded that a methane–air flame started by a spark discharge is propagated from the vicinity of the spark by means of the heats of the reactions $CH_4+O_2=CO+H_2+H_2O$(gas); $2H_2+O_2=2H_2O$ (gas). The methane flame appears to have a small thickness, the first lamina including chiefly the formation of carbon monoxide and water vapour and the last chiefly carbon dioxide. Since the observed volumes of gas which have to be ignited in order to start general inflammation agree approximately with the known facts concerning the energy of the igniting spark and the thermal conductivity and ignition temperature of the mixture, it is concluded that the spark acts mainly, if not entirely, as a source of thermal energy in igniting a gas mixture. S. K. Tweedy.

Mechanism of the uniform movement in the propagation of flame. H. F. Coward and G. W. Jones (J. Amer. Chem. Soc., 1927, **49**, 386—396).—The flame speeds in a series of mixtures of methane with "atmospheres" of air, 20·9% of oxygen and 79·1% of argon, and 20·9% of oxygen and 79·1% of helium were measured in tubes of various diameters and positions. The important factors determining flame speeds appear to be the heat developed in the flame, the heat capacities of the burnt and unburnt mixture, and the rate of chemical reaction. Very little change in flame speed is observed when helium (which has a high thermal conductivity and low absorption for radiant energy) is replaced by argon (which has a low thermal conductivity and a higher absorption for radiant energy; cf. Lind, J.C.S., 1924, **125**, 1867). This is because the energy is carried away so rapidly. It is suggested that the temperature coefficient of the rate of oxidation of methane is relatively small at flame temperatures.

S. K. Tweedy.

Kinetics of ozonisation by the action of α-particles. W. Mund and J. D'Olieslager (Bull. Acad. roy. Belg., 1926, [v], **12**, 309—326).—The rate of production of ozone in a mixture of oxygen and radon was measured by a comparison method: two reaction vessels, one containing a small quantity of mercury, were connected to the two sides of a differential sulphuric acid manometer. In one vessel, the ozone was destroyed by the mercury as soon as formed, causing a pressure difference between the two vessels from which the rate of ozone production could be calculated. For a given intensity of irradiation, ozone is formed at constant velocity, and it is also destroyed with a velocity proportional to its concentration. The velocity of the two opposing reactions is proportional to the intensity of irradiation. The calculated velocity of the forward reaction corresponds with the formation of one molecule of ozone from each pair of ions formed. H. F. Gillbe.

Velocity of ionic reactions. J. N. Bronsted and R. Livingston (J. Amer. Chem. Soc., 1927, **49**, 435—446).—The velocities of the reactions $[CoBr(NH_3)_5]^{\cdot\cdot}+OH' \longrightarrow [Co(OH)(NH_3)_5]^{\cdot\cdot}+Br'$ and $2[CoBr(NH_3)_5]^{\cdot\cdot}+Hg^{\cdot\cdot}+2H_2O \longrightarrow 2[Co(H_2O)(NH_3)_5]^{\cdot\cdot\cdot}+HgBr_2$ were investigated in very dilute solution by colorimetric methods. The first reaction exhibits a negative, and the second reaction a positive, salt effect; both these effects are quantitatively accounted for by Bronsted's theory of ionic reaction (A., 1922, ii, 699). S. K. Tweedy.

Kinetics of the stages in the Landolt reaction. A. Skrabal and A. Zahorka (Z. Elektrochem., 1927, **33**, 42—63).—A further study has been made (cf. A., 1922, ii, 488; 1924, ii, 543) of the kinetics of the reactions (1) $IO_3'+3SO_3''=I'+3SO_4''$; (2) $IO_3'+6H^{\cdot}+5I'=3I_2+3H_2O$ (Dushman reaction); (3) $3I_2+3SO_3''+3H_2O=6I'+6H^{\cdot}+3SO_4''$, which together constitute the Landolt reaction. Other recent work on the subject, especially that of Thiel (A., 1924, ii, 750) and of Eggert (A., 1925, ii, 407), is discussed and criticised. The validity of Dushman's equation, $-d[IO_3']/dt=K[IO_3'][I']^2[H^{\cdot}]^2$, for reaction (2) and the value of the constant, K, have again been confirmed by measuring the velocity of reaction between iodide and iodate in solutions buffered with acetic acid and acetate and containing arsenious acid to prevent the liberation of iodine. Measurements were also made in solutions buffered with potassium dihydrogen arsenate and disodium hydrogen arsenate, from which the second dissociation constant of arsenic acid is calculated to be $1·6\times10^{-7}$ at 25°. Reaction (1) has been investigated in solutions of acidity ranging from p_H 0 to p_H 13, but satisfactory results were obtained only over the range p_H 4—13. Over this wide range, the results can be represented by the equation $-d[IO']/dt=0·53\times10^6[H^{\cdot}][HSO_3'][IO_3']+0·67\times10^{17}[H^{\cdot}]^2[SO_3'']^2[IO_3']$ at 25°, when concentrations are measured in g.-mol./litre and time in minutes. Two terms appear on the right-hand side of this equation, since the sulphite in solution may exist partly as sulphite ion and partly as hydrogen sulphite ion, the proportion of each depending on the acidity of the solution. Over the range p_H 4—5 (solutions of iodate and hydrogen sulphite) the second term is negligible, whilst above p_H 9 (solutions of iodate and sulphite) the first can be neglected. Within the region p_H 5—9 (solutions of iodate, sulphite, and hydrogen sulphite) both terms must be taken into account. The above equation was established from data for the kinetics of the complete Landolt reaction, as well as from measurements on the isolated reaction (1). The derivation of the relationships employed in the interpretation of the experimental results is set out in detail, and the mechanism of reaction (3), which can be regarded as instantaneous in comparison with (1) and (2), is also discussed. H. J. T. Ellingham.

Kinetics of formate formation. G. Birstein and N. Lobanov (Z. anorg. Chem., 1927, **160**, 377—386).—Measurements of the velocity constant of the reaction between formaldehyde and concentrated sodium hydroxide solutions (6·3N) in presence of methyl alcohol show that the reaction is probably termolecular, proceeding according to the equation $2H·CHO+NaOH=H·CO_2Na+MeOH$. The results, however, do not preclude the possibility that the reaction is really made up of two consecutive reac-

tions, such as $H{\cdot}CHO+NaOH=H{\cdot}CO_2Na+H_2$, and $H{\cdot}CHO+H_2=MeOH$; in presence of cuprous or silver oxides, hydrogen is evolved, but no methyl alcohol is formed. The two reaction products, methyl alcohol and sodium formate, have a marked influence on the velocity, the latter accelerating and the former retarding the reaction. The action of the formate is probably secondary, in that it prevents the retarding action of part of the methyl alcohol. A. R. Powell.

Reduction of cupric oxide by dextrose and uric acid. E. Lanyi (Biochem. Z., 1927, **180**, 85—96).—A study of the reduction by Bertrand's method of reduction of cupric oxide in alkaline solution in presence of sodium potassium tartrate by dextrose shows that if the amount of sugar used is plotted against the amount of oxide reduced for a particular time of heating, the curve gives low values for both small (20 mg.) and large (100 mg.) amounts of sugar, but shows a maximum with mean concentrations (50 mg.). The greater the time of heating the more pronounced is the maximum. As the amount of sugar increases, the relative amount of cupric oxide reduced decreases. The same general conclusion is reached when the reduction is carried out in presence of citric acid, glycerol, or dilute acetic acid in place of sodium potassium tartrate, and also when the reduction is effected by potassium urate.

P. W. Clutterbuck.

Kinematographic study of the influence of gelatin on rates of crystal growth and dissolution of copper sulphate. W. G. France (Third Colloid Symposium Monograph, 1925, 317—323).—The rate of dissolution of copper sulphate crystals in water exceeds their rate of growth from saturated solutions. Gelatin in small quantities depresses growth far more than it does dissolution.

Chemical Abstracts.

Hydrogen electrode in the study of the rate of saponification of oils and fats by aqueous alkali. J. W. McBain, H. S. Howes, and (Miss) M. Thorburn.—See B., 1927, 145.

Thermal decomposition of ozone in presence of chlorine. A. Pinkus and A. Radbill (Bull. Soc. chim. Belg., 1926, **35**, 451—459).—Kinetic and colorimetric determinations show that a sufficiently small proportion of chlorine considerably retards the rate of decomposition of ozone (cf. Kistiakovski, A., 1926, 34), but that this effect diminishes rapidly with increase of chlorine or rise of temperature, positive catalysis eventually occurring. The same amount of chlorine may therefore act as a stabiliser at one temperature and as a decomposing catalyst at a higher temperature. L. F. Gilbert.

Acid and salt effects in catalysed reactions. VI. The early stages of an auto-catalysed reaction. General form of the simple auto-catalytic catenary. H. M. Dawson (J.C.S., 1927, 458—466).—The phenomena associated with the auto-catalytic reaction of acetone with iodine in aqueous solution are interpreted in terms of the joint catalytic activity of the hydrogen and hydroxyl ions. Equations have been derived which show that the reaction velocity falls to a minimum and then increases. The constant which in terms of the simple hydrogen-ion theory appears to measure the initial hydrogen-ion concentration is found to represent the actual hydrogen-ion concentration at the point of minimum velocity, and this constant affords a means of determining the catalytic coefficient of the hydroxyl ion. The auto-catalytic catenary obtained by plotting v against p_H can be put in a general form by expressing the velocity and hydrogen-ion concentration in terms of those values which characterise the point of minimum velocity. The actual course of the auto-catalytic change is then given by $r=\cosh h$, where r is the reduced velocity and h is the natural logarithm of the reduced hydrogen-ion concentration. W. Thomas.

Catalytic properties of mineral waters. I. Behaviour of the water of Wiesbaden hot springs towards hydrogen peroxide solutions. L. Fresenius, A. Eichler, and H. Lederer (Z. anorg. Chem., 1927, **160**, 273—296).—Hydrogen peroxide solutions are decomposed fairly rapidly by fresh water from the Wiesbaden hot springs, but the rate of decomposition decreases slowly with the time that elapses after taking the water from the springs, owing to loss of carbon dioxide and a corresponding increase in the p_H value. Solutions of ferrous and manganous sulphate containing the same concentration of metal ion as the spring water have a similar catalytic action on hydrogen peroxide solutions, the activity of the manganous ion becoming greater as the p_H value of the solution is increased. In the presence of an alkali or alkaline-earth carbonate or hydrogen carbonate, the rate of decomposition is the same as in the spring water, hence it is probable that the activity of the water is due to its content of ferrous and manganous carbonates (7 parts and 1 part per million, respectively). The activity is destroyed by the addition of hydrocyanic acid, but not by ultrafiltration or by exposure to bright sunlight. The catalytic activity of the ultrafiltrate immediately after filtration is less than that of the unfiltered water, but increases rapidly in 3—4 hrs. to a maximum which is greater than that of the untreated water.

A. R. Powell.

Catalysis of hydroxylamine. III. A. Kurtenacker and F. Werner (Z. anorg. Chem., 1927, **160**, 333—346; cf. A., 1924, ii, 250).—Alkaline solutions of hydroxylamine are reduced quantitatively to ammonia by vanadyl salts, quinquevalent molybdenum salts, and ferrous sulphate. In dilute acid solutions, cuprous sulphate and molybdenum (V) sulphate have the same effect, ferrous sulphate and cuprous chloride are without action, and vanadyl sulphate causes a catalytic decomposition into ammonia, nitrogen, and nitrous oxide. In very strongly acid solutions, only the molybdenum salt has any action, causing a slow but eventually complete reduction to ammonia. Cuprous oxide induces a slow catalytic decomposition of alkaline hydroxylamine solutions, the velocity of the action increasing with the alkalinity. A. R. Powell.

Catalysis of hydroxylamine. IV. Decomposition of hydroxylamine in alkaline solution. A. Kurtenacker and F. Werner (Z. anorg. Chem., 1927, **160**, 387—394; cf. preceding abstract).—The

course of the decomposition of hydroxylamine in alkaline solutions depends on the concentration of the alkali, on the temperature, and on the nature of any catalyst present. The higher is the alkali concentration in the absence of a catalyst or in the presence of pumice, platinised pumice, or platinum gauze, the smaller is the proportion of nitrous oxide and the greater the proportion of nitrogen formed. In presence of platinum-black, obtained from platinic chloride and formic acid, the proportion of nitrous oxide formed increases slightly with a rise in the concentration of alkali. Catalysts in general cause an increase in the yield of nitrous oxide for any given conditions, platinum-black being the most efficient catalyst in this respect, giving a yield up to 36% of the weight of hydroxylamine. The mechanism of the reaction is discussed at some length, together with theories that have been suggested by other investigators. The authors' results seem to show that the reaction proceeds through the formation of the labile condensation product, hydroxyhydrazine, which may react with a further molecule of hydroxylamine, giving ammonia and nitrogen, or may decompose into ammonia and nitroxyl, the latter being converted into hyponitrous acid, which decomposes into nitrous oxide and water (cf. Hofmann and Kroll, A., 1924, ii, 546). A. R. Powell.

Catalytic minimum point. II. Iodine–acetone reaction in buffer solution. M. Bergstein (J. Physical Chem., 1927, **31**, 178—186; cf. this vol., 214).—The reactions between iodine and acetone have been studied at 25° near p_H 7 in standard sodium potassium phosphate buffer solutions and near the catalytic minimum point. The experimental curves show a break, the two portions being linear. The values of the velocity constant corresponding with the second portion show a linear relationship to the concentration of hydroxyl ion near p_H 7. These values also decrease with increasing concentration of added potassium iodide. The temperature coefficient, k_{35}/k_{25}, for the second stage of the reaction at p_H 6·813 in phosphate buffer solution is 3·61, a value which is not in conformity with the protion theory of catalysis (cf. Rice, A., 1924, ii, 98). In Walpole's standard acetate buffer solutions, the apparent catalytic minimum point is found to occur at p_H 3·85, a value which is unchanged from 25° to 40°. The reactions between iodine and acetone are complicated and the nature of the catalysis has not been fully established. L. S. Theobald.

Catalytic oxidation by complex iron salts. O. Baudisch and D. Davidson (J. Biol. Chem., 1927, **71**, 501—508).—The oxidation of sodium pentacyanoammineferroate by molecular oxygen is inversely proportional to the p_H, whilst the reduction of the corresponding ferriate by an organic compound is directly proportional to the p_H. In accordance with this, it is found that, in the catalytic oxidation of hydantoin, *iso*barbituric acid, and 5-aminouracil, in presence of the complex ferroate, oxidation is more rapid at p_H 12 than at p_H 7. whilst at a given p_H the oxidation is catalysed to an equal extent by the ferroate or ferriate, but is dependent on the concentration of catalyst. C. R. Harington.

Catalytic reduction of nitric oxide and oxidation of ammonia. IV. L. Andrussov (Ber., 1927, 60, [*B*], 536—540; cf. A., 1926, 582; B., 1926, 318; 1927, 217).—In comparison with the oxidation of ammonia at a platinum surface, the reduction of nitric oxide proceeds slowly, but by sufficiently prolonging the period of contact, ammonia may be obtained in 90% yield. At 600—650°, nitrogen is formed to an appreciable extent, which increases rapidly with rising temperature and is due mainly to thermal decomposition of the ammonia produced. It is assumed that the primary product of the change is nitroxyl, which is reduced successively to hydroxylamine and ammonia. In consequence of the relatively slow gas current, backward diffusion of the products occurs to a considerable extent. This is of less importance than in the oxidation of ammonia, since the di-imide formed from nitroxyl and ammonia is rapidly converted by the excess of hydrogen into ammonia. H. Wren.

Catalytic oxidation of ammonia. W. W. Scott and W. D. Leech.—See B., 1927, 186.

Catalytic oxidation of cyanogen to nitric oxide, and the intermediate product. S. Abe and R. Hara (J. Soc. Chem. Ind. Japan, 1927, **30**, 1—9).—Using platinum gauze as a catalyst, 90—96% of the cyanogen is oxidised by air to nitric oxide without difficulty. The effect of the reaction temperature (550—1000°), the gas velocity (20—802 c.c. per min.), and the concentration of cyanogen (1·5—15·2%) on the yield of nitric oxide is shown diagrammatically. The concentration of cyanogen is generally kept less than 4%. At 450—550°, nitric oxide is suddenly produced and a maximal yield is obtained at 700—800°. When the gaseous product is cooled in a freezing mixture, a small amount of a transparent, yellow, viscous liquid is obtained. In dry nitrogen or air, the liquid slowly polymerises into a solid of the same colour. The products are extremely reactive with moisture and have the empirical formula C_2N_2O. The catalytic oxidation of cyanogen is therefore assumed to proceed as follows, analogously to the oxidation of hydrogen cyanide (cf. Hara and Shinozaki, *ibid.*, **28**, 474): $2C_2N_2+O_2=2C_2N_2O$ and $2C_2N_2O+3O_2=4CO+4NO$. K. Kashima.

Methane equilibrium. III. R. C. Cantelo (J. Physical Chem., 1927, **31**, 246—250; cf. this vol., 204).—The catalytic decomposition of ethylene is most effectively accomplished by the nickel catalyst specially prepared from nickel oxide (cf. this vol., 20) At 300°, and above, methane is found in the decomposition products, the percentage of methane following one passage over the catalyst, increasing with rise of temperature. Repeated passage of the gaseous products over the catalyst showed that, contrary to Sabatier (A., 1900, i, 534), ethane was stable in presence of a nickel catalyst up to 360°. The constants for the methane equilibrium, obtained by repeated passage of the products of decomposition of ethylene over the catalyst, are in general agreement with those of Mayer and Altmayer (A., 1907, i, 457). L. S. Theobald.

Methane equilibrium. IV. R. C. Cantelo (J. Physical Chem., 1927, **31**, 417—418; cf. preceding

abstract).—The free energy decrease accompanying the synthesis of methane from amorphous carbon and hydrogen is calculated to be 14,500 g.-cal.

L. S. THEOBALD.

Surface adsorption and velocity of chemical action at gas–solid interfaces. F. H. CONSTABLE (Proc. Camb. Phil. Soc., 1927, **23**, 593—606).—For small rates of flow of alcohol vapour over copper, the velocity of catalytic dehydrogenation increases with increase in the rate of flow. This is due to the circumstance that the products of reaction are present in amounts comparable with that of the alcohol, and by being adsorbed on the catalyst reduce its active surface. Increase of the velocity of passage of the vapour above a certain critical value produces no further increase in the rate of reaction. The relation previously deduced (A., 1926, 582) between the partial pressure of the reactant in a mixture and the fractional reaction velocity has been verified for mixtures of alcohol vapour with water, acetone, and benzene. An expression is derived for the effect of mixture of vapours on the temperature coefficient of reaction. The temperature coefficient is increased or reduced according as the heat of desorption of the reactant is less or greater than that of the diluent. Water present in alcohol proves to have little effect on the temperature coefficient of the reaction.

R. CUTHILL.

New method of measuring the absolute surface area of a metallic catalyst. F. H. CONSTABLE (Nature, 1927, **119**, 349).—If S is the surface area of the metal forming M g. of oxide spread over the china-clay support (cf. A., 1926, 1195), C is the electrical conductivity of the film, q the equivalent air thickness of the oxide film, μ the refractive index of the oxide, ρ the density of the oxide, k_c the initial value of the constant in the parabolic law for the fall in conductivity, and k_q the initial value for the equivalent air thickness, then $S/M=\mu\sqrt{k_c/k_q}/\rho C$. For an activated copper film (k_c and k_q being measured at 210°): $k_c=1{\cdot}52\times10^{-2}$; $k_q=2{\cdot}50\times10^{-10}$; $\mu=2{\cdot}85$; $C=0{\cdot}64$; $\rho=6{\cdot}3$, whence $S/M=6900$ cm.^{2} per g. of film, the corresponding area of the support being 3200 cm.^{2} Reduced copper has a surface activity at least 8000 times as great as that of electrolytic copper.

A. A. ELDRIDGE.

Chemical yield in the decomposition of carbon dioxide at low pressure by the condensed spark. P. JOLIBOIS, H. LEFEBVRE, and P. MONTAGNE (Compt. rend., 1927, **184**, 522—525).—The decomposition of carbon dioxide at low pressures by the condensed spark increases with the voltage, and is influenced by the size and shape of the containing vessel and the position of the electrodes. The yield rises to a maximum and falls as the capacity of the discharge circuit decreases, and for a particular capacity the maximum yield falls off slightly as the pressure increases. These results agree with the authors' theoretical conclusions (this vol., 19), the yields indicating that the electrical energy is only partly used as chemical energy.

J. GRANT.

Electrolytic production of copper acetate. V. PAVLOV and B. BROUNSE (Ukraine Chem. J., 1926, **2**, 311—320).—Copper acetate is formed as an intensely dark green powder, deposited on the anode, by the electrolysis of sodium acetate, which must be absolutely neutral. A larger concentration of the latter increases the yield. The best results are obtained when a current density of 16—20 amp. per dm.^{2} is used. Addition of sodium chloride to the solution increases the yield of copper acetate at first, but if too much is added, a double salt, probably CuCl,NaCl, is deposited. By these methods, up to 95% of the copper dissolved during electrolysis is deposited as the salt $Cu(CH_3{\cdot}CO_2)_2,H_2O$.

E. ROTHSTEIN.

Electrolytic deposition of chromium from aqueous chromic acid solutions. E. LIEBREICH (Z. Elektrochem., 1927, **33**, 69—72).—Polemics arising out of a comparison of results obtained by Müller (A., 1926, 913) with previous work by the author (*ibid.*, 1921, ii, 678; Z. Elektrochem., 1923, **29**, 208).

H. J. T. ELLINGHAM.

Electrolytic deposition of chromium from aqueous chromic acid solutions. E. MÜLLER (Z. Elektrochem., 1927, **33**, 72—76).—Reply to Liebreich (cf. preceding abstract).

H. J. T. ELLINGHAM.

Separation of bismuth by rapid electrolysis in acid solution. A. JILEK and J. LUKAS (Chem. Listy, 1927, **21**, 49—55).—Electrolysis may be carried out at 1·6—2·4 volts and with a current of 0·1 amp. in a platinum crucible with a rotating anode, if the solution contains specified quantities of fluoboric acid and sucrose. Directions are given for preparing solutions from the chloride, sulphate, and nitrate; the nitrate gives the best results. The bismuth is deposited as a coherent, lustrous layer, which may be dried and weighed in the usual manner.

S. I. LEVY.

Action of electrolysis. R. SAXON (Chem. News, 1927, **134**, 118).—Pyrites immersed in a solution of ammonium chloride and sulphate subjected to electrolysis, the pyrites being in contact with the carbon cathode, loses weight, iron passing into the solution and copper sulphide being deposited.

S. I. LEVY.

Chemical method for the standardisation of ultra-violet light. J. E. Moss and A. W. KNAPP (Brit. J. Actinotherapy, 1927, reprint).—The authors' "uroxameter" is described. The photolysis of oxalic acid sensitised by uranium acetate serves as a measure of the intensity of ultra-violet radiation below 320 μμ, and quantitative determinations can be carried out with permanganate (cf. B., 1925, 906; J. Amer. Chem. Soc., 1925, **47**, 718). Recent alternative methods are discussed (Lancet, 1924, 745; 1925, 1205). The evidence concerning the decrease in ultra-violet output of mercury-vapour lamps with time is reviewed and found to be very conflicting. The decrease in intensity of ultra-violet light from three atmospheric-pressure mercury-vapour lamps has been measured in terms of the photochemical reaction described above. The results obtained are so divergent that it is obvious that photochemical work should be controlled by a calibrated actinometer.

It is shown that a thickness of 2·2 mm. of the reacting solution absorbs all rays shorter than 321 μμ,

and evidence is quoted that the method provides a means of determining the efficacy of a light source in respect of either the "stimulative" region (280—330 μμ) of the spectrum or the "bactericidal" region (below 300 μμ). The method has been applied to testing the fastness of coloured papers to light, with the result that fading and uroxameter titrations increased proportionately. The transparency of glasses to ultra-violet radiation has been tested and the following percentage transmission of ultra-violet light obtained: with no cover 100, with silica 0·11 inch thick 85·7, with "vitaglass" 0·065 inch thick 20·8—24·4, with window glass 0·082 inch thick 3·1, with "calorex" glass 0·208 inch thick 0, and with non-actinic glass 0·2 inch thick 0·4. These results bear out the claims made for the materials.

R. A. MORTON.

Kinetics of the photochemical formation of hydrogen chloride. N. THON (Z. physikal. Chem., 1926, **124**, 327—351).—The rate of photochemical combination of hydrogen with chlorine in mixtures containing a considerable excess of one reactant and also in mixtures containing oxygen has been measured. Bodenstein and Dux's empirical expression for the reaction velocity, $d[HCl]/dt=k[Cl_2]^2[H_2]/([H_2]+n[Cl_2])$, (A., 1913, ii, 1039) expresses the results satisfactorily, n having the value 0·1. For mixtures containing oxygen, k is inversely proportional to the oxygen concentration, whilst n remains unchanged, from which it is concluded that the rate of reaction is given by $d[HCl]/dt=k_1[Cl_2]^2[H_2]/\{([H_2]+k_2[Cl_2])[O_2]\}$, where $k_1=k[O_2]$, and $k_2=n$. From the form of this expression it appears probable that the reaction is brought about by chlorine atoms or Cl_3 molecules rather than by activated normal molecules. This view is supported by the fact that no reaction occurs in yellowish-orange or orange-red light, *i.e.*, light of wave-lengths for which there is no question of the dissociation of molecules into atoms. For gas mixtures containing a considerable excess of hydrogen, the Bodenstein–Dux expression reduces to the simpler form $d[HCl]/dt=k[Cl_2]^2$. Even if the gases are in approximately the stoicheiometric proportions, the simplified formula still holds, although the order with respect to chlorine is less than 2. No evidence of a retarding effect of a considerable excess of hydrogen such as Chapman has described (J.C.S., 1923, **123**, 3062) has been observed.

R. CUTHILL.

Photochemical influence of bromine on ethyl maleate and ethyl fumarate. F. WACHHOLTZ (Z. physikal. Chem., 1927, **125**, 1—48; cf. Eggert, A., 1924, i, 368).—In carbon tetrachloride solutions containing bromine, the number of molecules, φ, of ethyl maleate transformed into the fumarate per quantum of energy absorbed is independent of the concentrations of the bromine and ester; for light of wave-length 4360 Å. it is 295 at 21°. It is independent of the light intensity, but varies with the wave-length, *e.g.*; between 15° and 24° $\varphi_{4360}=1{\cdot}85\varphi_{5370}$, approximately. φ is influenced by temperature, *e.g.*; $\varphi_{25°}-2\varphi_{21.5°}$, approximately. Mercuric bromide and mercurous nitrate and perchlorate also sensitise the photochemical change of maleic to fumaric esters. The additive reaction ethyl fumarate or maleate + bromine + $h\nu$ ⟶ dibromodiethyl succinate has also been studied. Here α, the number of added molecules of bromine per quantum absorbed, is 8·2 at 21° for light of wave-length 4360 Å. in presence of 0·1*N*-bromine. It is independent of light intensity and of ester concentration and also of the ratio present of fumaric to maleic ester. α varies with the wave-length ($\alpha_{4360}=2\alpha_{5370}$, approximately) and with the temperature ($\alpha_{24.5°}=2\alpha_{15°}$, approximately). These results are in accordance with theoretical considerations.

L. F. GILBERT.

Photochemical decomposition of potassium persulphate. II. J. L. R. MORGAN and R. H. CRIST (J. Amer. Chem. Soc., 1927, **49**, 338—346; cf. this vol., 216).—Absorption data for aqueous solutions of sulphuric acid, potassium persulphate, sulphate, and hydroxide are given; with the exception of the hydroxide, the absorbed regions do not appreciably overlap the regions absorbed by the persulphate solutions. The wave-length most effective in producing photochemical decomposition of the latter is at about 230 mμ; the calculated value is 1 μ. The velocity of the decomposition is proportional to the intensity of the light, and the temperature coefficient is about 1·18, independent of any small acidity or alkalinity. These facts indicate that the reaction is purely photochemical and is unaccompanied by side or intermediate reactions.

S. K. TWEEDY.

Photolysis of potassium nitrate. D. S. VILLARS (J. Amer. Chem. Soc., 1927, **49**, 326—337).—The quantum efficiency of the decomposition of potassium nitrate solutions in ultra-violet light ($KNO_3=KNO_2+O$) is very small for wave-lengths greater than 280 μμ; for λ254 μμ, it increases regularly with increasing p_H until p_H 9·9 is attained, after which it remains constant. Contrary to the statement of Anderson (A., 1924, ii, 408), the decomposition of potassium nitrate in polychromatic light proceeds at a rate which gradually diminishes with time, and there is no evidence of the attainment of equilibrium; complete decomposition can be obtained. Warburg's iodometric titration of nitrites (Z. Elektrochem., 1919, **25**, 334) gives good results if the solution is rendered completely alkaline before aeration with carbon dioxide.

S. K. TWEEDY.

Chemical actions of radiations. P. VILLARD (Compt. rend., 1927, **184**, 309—312).—The phenomena recorded by de Moncetz (this vol., 218) may be due to the diffusion into the spectrograph of a few rays of the ultra-violet region capable of destroying the *X*-ray image. Up to a point, the infra-red rays compensate for this and produce the effect of protection, but beyond this they react on the plate in an almost normal fashion. This neutralising effect between red and violet rays is supported by experimental evidence, except that here silver bromide is modified by *X*-rays in place of ordinary light-sensitive silver chloride or bromide.

J. GRANT.

Chemical actions of radiations. P. VILLARD (Compt. rend., 1927, **184**, 352—354; cf. preceding abstract).—Experiments are described illustrating the different natures of the latent images produced by *X*-rays and by ordinary light. These images may

co-exist and vary in their properties according to the atomic level influenced by the radiation, the frequency of which is the determining factor. A gelatin-silver bromide plate solarised by light is not solarised for high-frequency radiations, and retains a considerable portion of its sensitiveness for the latter.

J. GRANT.

Photographic action of β-rays. C. D. ELLIS and W. A. WOOSTER (Proc. Roy. Soc., 1927, **A**, **114**, 266—276).—Investigation of the blackening, D, of Ilford X-ray plates by beams of practically homogeneous particles taken from the continuous β-ray spectrum shows that the blackening is independent of the time of exposure, t, when the product It (I= intensity) is constant. Thus the reciprocity law holds for homogeneous β-rays, as for heterogeneous (cf. Bothe, Z. Physik, 1922, **8**, 243). Independently of the time of development or the velocity of the β-particles, D is connected with It by the equation $D=C \log (It/\tau+1)$, where C and τ are constants. This formula is identical with that holding for the blackening by X-rays. The effect of varying either the time of development or the velocity of the particles is only to alter the constants; it appears, moreover, that C is determined only by the time of development, and τ by the velocity of the particles. The fact that the characteristic curve is linear only up to a density of about 0·3, whereas Bothe (*loc. cit.*) obtained a curve linear up to $D=1$, is discussed. L. L. BIRCUMSHAW.

Nature of base exchange. E. BIESALSKI (Z. anorg. Chem., 1927, **160**, 107—127).—A very full discussion is given of the group of phenomena classed as base exchange. Four main divisions are recognised: (1) Purely chemical; it is shown experimentally that the exchange of base of negatively-charged substrates of non-zeolitic nature is of this nature. (2) Ionic exchange, *e.g.*, permutites; the possibility of anion exchange is demonstrated. (3) "Sorption exchange." (4) Pure adsorption.

H. F. GILLBE.

Lixiviation of copper minerals with ammonia and preparation of arsenical compounds of copper. G. FESTER and F. BERTUCCI.—See B., 1927, 143.

Existence of silver hydroxide in the solid state. H. L. RILEY (Phil. Mag., 1927, [vii], **3**, 459—464).—Precipitated silver oxide, even after prolonged desiccation, contains about 0·3% of water. Silver oxide which has been subjected to prolonged drying will combine with carbon dioxide to the extent only of about one twentieth of the equivalent. On the basis of Baker's work with dry substances, this is taken as an indication that the water present in the silver oxide cannot be free, but must be present as silver hydroxide, which probably exists as a surface film on the grains of silver oxide, and has the probable formula $3Ag_2O,2AgOH$. This view is in accord with theories of crystal structure. A. E. MITCHELL.

Sodium aurous thiosulphate. J. K. GJALDBÆK (Dansk Tidsskr. Farm., 1927, **1**, 251—297).—Sodium aurous thiosulphate, $Na_3Au(S_2O_3)_2,2H_2O$, is best prepared by a modification of the method of Fordos and Gelis, which is based on the reaction $4Na_2S_2O_3+AuCl_3=Na_3Au(S_2O_3)_2+3NaCl+Na_2S_4O_6$. A solution of hydrochloroauric acid is treated with sufficient N-sodium hydroxide solution to furnish an excess of 0·1 mol. of sodium hydroxide after the whole of the acid has been converted into the sodium salt; a greater excess of alkali is to be avoided, as it causes the product to be contaminated with sulphate, from which it is difficult to free it subsequently. The resulting solution is added in small portions to a solution of sodium thiosulphate containing an excess of 5% above the theoretical amount required by the equation. The addition of each portion of gold solution produces a brown coloration (probably due to the transitory formation of an auric sodium thiosulphate), which slowly disappears on keeping; decolorisation must take place before further portions of gold solution are added. The speed of the reaction can be accelerated by the addition of sodium iodide as a catalyst, the effect being due to the formation of aurous iodide as intermediate compound. Sodium aurous thiosulphate can also be prepared directly from aurous iodide and sodium thiosulphate, but the preparation of the former substance in a pure state is difficult. Solid sodium aurous thiosulphate (97—99% pure) is obtained in 95% yield by diluting the above solution until it contains 4—5% of the salt and adding four times its volume of 96% alcohol. The product can be further purified by dissolving in water, adding a little sodium thiosulphate, and reprecipitating with alcohol as before. In order to remove sulphate, 50 g. of the salt dissolved in 800 c.c. of water are treated with sufficient barium chloride to precipitate the sulphate, and thereafter with N-sodium carbonate, added 2 c.c. at a time, until a filtered portion gives no test for barium. From 2 to 5% of sodium thiosulphate are added to the filtrate and the salt is precipitated with 96% alcohol. The solid salt, especially if prepared by precipitation from a slightly alkaline solution containing a 5% excess of sodium thiosulphate, is quite stable. The water of crystallisation contained in the salt is completely expelled at 150—160°. Its aqueous solution is ionised almost entirely into $Na^{\cdot}$ and $Au(S_2O_3)_2'''$ ions; further dissociation into S_2O_3'' and $Au^{\cdot}$ ions takes place only to a very small extent. No metallic gold can be precipitated by ferrous sulphate, oxalic acid, or stannous chloride, but hydrogen sulphide and alkali sulphides precipitate aurous sulphide. Attempts to determine the p_H value of the solution gave results varying from 7·5 to 5·6, the irregularities being ascribed to the presence of impurities.

H. F. HARWOOD.

Formation in the unstable state of two hydrates of magnesium platinocyanide. P. GAUBERT (Compt. rend., 1927, **184**, 527—529; cf. this vol., 312).—Crystals of the hydrates of magnesium platinocyanide containing two and seven molecules of water have been prepared. The former, which are colourless, appear inside a drop of solution on the edges of which the latter are forming as a result of rapid crystallisation below 30°. The dihydrate takes up water to form the red heptahydrate, and the action is reversed in presence of a drying agent. The absence of colour from solutions of platinocyanides may be due to the presence of the dihydrate.

J. GRANT.

Soluble alkaline-earth aluminates. H. T. S. Britton (J.C.S., 1927, 422—424).—The hydrogen-ion concentration curves of the reactions between solutions of alkaline earths and aluminium salts show that these earth solutions dissolve aluminium hydroxide in exactly the same way as does sodium hydroxide to form soluble aluminates the compositions of which may be represented $M(AlO_2)_2$. The delayed precipitation of aluminium hydroxide from chloride solutions is due to the tendency of chlorides to promote the formation of colloidal solutions. The data are discussed in connexion with the presence of aluminium in soil solutions. W. Thomas.

Volatility of the compounds formed by heating barium sulphate with sulphuric acid. F. Krauss. —See B., 1927, 139.

Formation of mercuric cobaltothiocyanate ($Hg[Co(CNS)_4]$) in presence of nitric acid as a qualitative test for mercury. B. Ormont (Z. anal. Chem., 1927, 70, 308—310).—One part of mercury in 1250 parts of water can be detected by the blue coloration or precipitate of mercuric cobaltothiocyanate (Orlov, A., 1906, i, 406) produced when there are added to 2 c.c. of the solution 2 c.c. of concentrated nitric acid and 2 c.c. of a solution of potassium cobaltothiocyanate. This latter solution is prepared by dissolving 10 g. of cobalt nitrate hexahydrate and 10 g. of potassium thiocyanate in 30 c.c. of water. Copper and lead interfere and bismuth may cause the precipitate to be violet in colour. R. Cuthill.

Volatility of borax. I. M. Kolthoff (Nature, 1927, 119, 425—426).—Although it is now admitted that fused borax is volatile (cf. A., 1926, 813; Briscoe, Robinson, and Stephenson, A., 1925, ii, 619; 1926, 1007) the loss of sodium oxide is negligible if the heating is not continued for more than 2 hrs.

A. A. Eldridge.

Anhydrous borates of silver, barium, and zinc. F. De Carli (Atti R. Accad. Lincei, 1927, [vi], 5, 41—47).—Investigation of the temperatures of devitrification of systems composed of boric anhydride mixed with either silver oxide, or barium oxide, or zinc oxide demonstrates the existence of the following anhydrous borates: $Ag_2O,4B_2O_3$; BaO,B_2O_3; $BaO,2B_2O_3$; $BaO,3B_2O_3$; $BaO,4B_2O_3$; $2ZnO,B_2O_3$, and ZnO,B_2O_3. T. H. Pope.

Cobaltiboroammine. C. Duval (Compt. rend., 1927, 184, 333—334).—On subjecting a solution of cobalt acetate, boric acid, and ammonium acetate to a current of air and adding ammonia, the non-electrolyte *cobaltiborotriammine*, $[CoBO_3,(NH_3)_3]$, is obtained as a violet, insoluble powder. The compound, for which μ is lower than for cobaltinitrotriammine, is very stable; at 120°, it loses ammonia to form cobalt oxides and cobaltous borate.

E. W. Wignall.

Action of acids and alkalis on fuller's earth. F. Weldes.—See B., 1927, 127.

Europium compounds. M. P. B. Sarkar (Bull. Soc. chim., 1927, [iv], 41, 185—189).—Some new salts of europium have been prepared. The *oxalate*, $Eu_2(C_2O_4)_3,10H_2O$, is converted into a pentahydrate at 100°; the *nitrate* melts in its water of crystallisation ($6H_2O$) at 85°; *normal tartrate*, $Eu_2(C_4H_4O_6)_3,5H_2O$; *acid tartrate* is $HEu(C_4H_4O_6)_2,2H_2O$, corresponding with the analogous bismuth and gadolinium compounds. The *acetate* ($4H_2O$) loses $1H_2O$ when kept over sulphuric acid; it is more soluble in water than the corresponding gadolinium salt. The *cyanoplatinate* is $Eu_2[Pt(CN)_4]_3,21H_2O$; the amount of water of crystallisation is characteristic of the yttrium group, but the colour (yellow, with pale blue fluorescence) is characteristic of the cerium group. When kept in a vacuum, the salt loses $3H_2O$ and forms an unstable red salt with a green fluorescence, characteristic of the yttrium group. Prolonged desiccation produces $Eu_2[Pt(CN)_4]_3,H_2O$. The following compounds were also prepared: *citrate* ($+5H_2O$); *acetylacetonate*, $Eu(Me\cdot CO\cdot CH_2\cdot CO\cdot Me)_3,3H_2O$; *iodate* ($+5\cdot5H_2O$); *carbonate* ($3H_2O$); *orthophosphate* ($+4H_2O$); and double *potassium europium oxalate*, $KEu(C_2O_4)_2,2H_2O$. S. K. Tweedy.

Electrometric study of the precipitation of silicates. H. T. S. Britton (J.C.S., 1927, 425—436).—The reactions between silicic acid and sodium hydroxide and the alkaline earths in solution and those between solutions of metallic salts of typical bases and sodium silicate have been investigated by means of the hydrogen electrode. The reactions of silicic acid with the strong bases have a pronounced effect on the hydrogen-ion concentration of the solutions. The precipitates obtained by the interaction of a solution of sodium silicate, $Na_2O,2\cdot16SiO_2$, and metallic salts, except that from calcium chloride, contain less silica than that required to form the metasilicates. The hydrogen-ion concentration at which these silicate precipitates begin to be formed in solutions of p_H less than 7 are approximately those at which their corresponding hydroxides separate. The silicate precipitates obtained from alkaline solutions appear when the hydrogen-ion concentrations have not been reduced to the extent required by their respective hydroxides. The results are discussed in relation to the question of soil acidity.

W. Thomas.

Separation of metals from the gas phase. A. E. van Arkel (Chem. Weekblad, 1927, 24, 90—96).—Metals of high m. p., of which easily dissociated volatile compounds are known, can be obtained in a pure coherent form by heating a filament of the metal in an atmosphere of the vapour of the compound. The best results are obtained if the compound be prepared in the evacuated apparatus in which the metal is to be deposited; for this purpose, an excess of the (impure) metal is enclosed with the other element of the compound to be employed, which thus acts merely as a carrier to convey the metal from the impure powder to the pure deposit. Titanium, zirconium, hafnium, thorium, molybdenum, tungsten, iron, and nickel are readily purified in this way. By suitable modification, nitrides, carbides, and alloys may also be prepared. S. I. Levy.

Constitution of titanium peroxide. R. Schwarz and W. Sexauer (Ber., 1927, 60, [*B*], 500—502).—Titanium peroxide is prepared by the cautious addition of titanium sulphate solution to a mixture of potassium sulphate and hydrogen peroxide at 0°,

and precipitation with alcohol followed by treatment of the precipitate with ice-cold water. The product is dehydrated by the successive action of acetone, absolute ether, and light petroleum at 0°. Determinations of titanium dioxide, active oxygen, and water indicate the constitution $(OH)_2TiO{\cdots}O_2H_2$ or $(OH)_2Ti{:}O{<}^{(}_{OH}$ for the peroxide. H. WREN.

Action of acetic acid on red lead. Formation of basic lead peracetate. C. BRUCKNER.—See B., 1927, 139.

Complex salts of lead iodide and alkali halides. L. J. BURRAGE (Chem. News, 1927, **134**, 85—86).—Unlike the analogous double chloride and bromide, the iodide $KI,PbI_2,2H_2O$ (cf. A., 1926, 908) is very soluble in acetone. Addition of ether to the solution causes the separation of a yellow oil which coagulates to a flocculent precipitate. The latter, like the original compound, deepens in colour on keeping over calcium chloride, presumably through loss of part of the water of crystallisation; no iodine is liberated on fusion at 300°. The double *salts* $PbI_2,NH_4I,2H_2O$ and $PbI,NaI,2H_2O$, behave similarly. S. K. TWEEDY.

Oxidation of ammonium sulphide. M. P. APPLEBEY and J. A. LANYON.—See B., 1927, 131.

Oxidation of phosphorus vapour at low pressures. M. BODENSTEIN (Z. Physik, 1927, **41**, 548—550).—The experimental work of Chariton and Walta (this vol., 122) is discussed briefly, with particular reference to the significance of pressure measurements. R. W. LUNT.

Formation of phosphorus sulphides from phosphine. L. DELACHAUX (Helv. Chim. Acta, 1927, **10**, 195—197).—If phosphine is heated with more sulphur than is necessary to convert the whole of the hydrogen into hydrogen sulphide, the reaction can be represented by the equation $2PH_3+nS=3H_2S+P_2S_{n-3}$, and above 450° the ratio of the pressure, P, to the temperature (Abs.), T, is constant, indicating that at this temperature the reaction is complete. With smaller relative amounts of sulphur, the ratio P/T continues to increase for some time, even at 500°, and the gaseous phase consists of a mixture of hydrogen sulphide and phosphine, and the solid phase of phosphorus, which is gradually covered with phosphorus sulphide formed by interaction between the constituents of the gas phase. The reaction between hydrogen sulphide and phosphine does not occur with any appreciable velocity below 320°, and above this temperature the ratio P/T increases continuously with the time, no equilibrium being reached. The products are hydrogen and a variable mixture of phosphorus sulphides. R. CUTHILL.

Pervanadic acid. J. MEYER and A. PAWLETTA (Z. physikal. Chem., 1927, **125**, 49—97).—The action of hydrogen peroxide on acidified solutions of vanadic acid has been studied by colorimetric, conductometric, and titration methods. Acidification of solutions of "*iso*polyvanadic acid" (formed by decomposing the hydrogen peroxide in a solution of vanadic acid in the former substance) results in the formation of a pale yellow solution of VOX_3, in which vanadium acts as a cation. The further action of hydrogen peroxide causes the formation of a red solution of the salt VO_2X_3, in which the oxygen atoms are bound to the vanadium atom by the peroxide linking; this reaction is slow. A bright yellow solution of maximum conductance in the system *iso*polyvanadic acid+hydrogen peroxide contains the *ortho*-acid, $H_3[V(O_2)O_3]$, where again two of the oxygen atoms are joined to the vanadium atom by the peroxide linking. The sensitivity of the hydrogen peroxide–vanadic acid colour test is discussed (cf. A., 1926, 1020). The evidence of previous authors for the existence of "pervanadic acid," HVO_4, is adversely criticised. L. F. GILBERT.

Activation of oxygen (especially during the oxidation of aldehydes). W. P. JORISSEN and P. A. A. VAN DER BEEK (Rev. trav. chim., 1927, **46**, 42—46).—A brief discussion of the mode of activation of oxygen during various oxidation reactions. H. F. GILLBE.

Oxidation of bivalent chromium in aqueous solution in absence of air. A. ASMANOW (Z. anorg. Chem., 1927, **160**, 209—221).—Pure stable salts of bivalent chromium may be prepared as follows: an aqueous solution of chromic sulphate is reduced electrolytically at a lead cathode in an atmosphere of hydrogen. When reduction is complete, the chromous sulphate is precipitated by alcohol, washed with alcohol and ether, and dried in a current of hydrogen. The product is stable in dry air.

In presence of platinum as catalyst, the solution oxidises with evolution of hydrogen, the reaction being unimolecular. Sulphuric acid accelerates the reaction, but to a less extent than does hydrochloric acid. In absence of platinum, there is no measurable evolution of hydrogen with sulphuric acid present even in concentrations up to 10*N*, although the reaction takes place to some extent in presence of hydrochloric acid. In the latter case, the oxidation is accelerated by ammonium chloride.

Very rapid oxidation takes place in ammonia solution, especially in presence of ammonium salts, which prevent the precipitation of chromous hydroxide. The reaction is then no longer unimolecular, but is autocatalysed by the chromic ion. H. F. GILLBE.

Reactions of chromates at high temperatures. II. The system CaO–Cr_2O_3–O_2. K. S. NARGUND and H. E. WATSON (J. Indian Inst. Sci., 1926, **9A**, 149—167; cf. B., 1924, 670).—The dissociation pressures of calcium chromate between 900° and 1030° are recorded. At 1030° and less than 20 mm. pressure, the *compound* $Cr_2O_3,CrO_3,3CaO$ is obtained; at about 2 mm., the *compound* $3Cr_2O_3,2CrO_3,8CaO$; at lower pressures, the final *product* is $2Cr_2O_3,CrO_3,5CaO$, which has no appreciable dissociation pressure at 1030°. The dissociation pressure of chromium trioxide increases very rapidly between 210° and 250°, exceeding 400 mm. at 250° (cf. Simon and Schmidt, A., 1926, 697). In presence of lime, calcium chromate forms a *basic chromate*, $2CrO_3,3CaO$, which is comparatively easily decomposed, yielding the *compound* $Cr_2O_3,6CrO_3,12CaO$, which has a dissociation pressure of 270 mm. at 910°, and decomposes

to the *compound* $Cr_2O_3,4CrO_3,9(?)CaO$, dissociation pressure 22 mm./920°. The latter is also formed when the oxide and chromate are heated together in air; it is black, and soluble in dilute acids, and decomposes to the *compound* $Cr_2O_3,3CrO_3,6CaO$, which has no measurable dissociation pressure at 1030°. Mixtures of calcium chromate and chromic oxide yield the *compound* $Cr_2O_3,2CrO_3,2CaO$, dissociation pressure 150 mm./1030°, the final product of dissociation being a chromite. Mixtures of lime and chromic oxide heated in a vacuum yield the *chromite*, $2Cr_2O_3,2CaO$, from which treatment with acid removes lime, yielding the *compound* $2Cr_2O_3,CaO$. Mixtures of calcium oxide and chromic oxide absorb oxygen rapidly on heating, the gas being afterwards liberated at the same temperature; it is suggested that an intermediate compound is formed and decomposed. S. I. Levy.

Chlorides of bivalent molybdenum, tungsten, and tantalum. V. Tritantalum hexachloride or tantalum trichloride? K. Lindner (Z. anorg. Chem., 1927, **160**, 57—63).—The formula of Ruff and Thomas (A., 1925, ii, 1187) for the oxychloride $Ta_3Cl_7O,3H_2O$ requires the tantalum to function as a tervalent element; the author's formula for the same compound, prepared in the same manner, is $H(Ta_3Cl_7,H_2O),3H_2O$, the tantalum being bivalent. Analogous oxychlorides are not found among the complexes formed by other elements in groups V and VI, and the analytical figures are more in favour of the aquo-chloro-acid formula. Although a large amount of evidence for the latter formula is put forward, the question of the valency of the tantalum in this compound cannot be regarded as settled. H. F. Gillbe.

Complex chlorides of tervalent molybdenum. W. R. Bucknall, S. R. Carter, and W. Wardlaw (J.C.S., 1927, 512—521).—The ammonium, potassium, rubidium, and cæsium salts of the types R_3MoCl_6 and R_2MoCl_5,H_2O have been prepared and the above formulations confirmed. From solutions of low acid concentration a complex salt of molybdenyl monochloride, $KMoOCl_2,3H_2O$, was prepared. By the action of liquid ammonia on diammonium molybdenum pentachloride, a very unstable monoammine was isolated, $(NH_4)_2[MoCl_5,NH_3],H_2O$. Conductivity measurements and the preparation of the molybdenyl disalicylate, phthalate, and oxalate have been carried out to study the hydrolysis of the complex chlorides. The compound $MoCl_2OH$ is one of the products of the hydrolysis. W. Thomas.

Reduction of alkali tungstates. W. T. Spitzin (J. Russ. Phys. Chem. Soc., 1926, **58**, 474—490).—A brief *résumé* of former work on the preparation and properties of the alkali tungstate "bronzes." In the present work, the reduction by hydrogen of normal sodium tungstate, $Na_2WO_7,2H_2O$; sodium bitungstate, $Na_2W_2O_7$; paratungstate, $Na_{10}W_{12}O_{41},28H_2O$; tetratungstate, $Na_6W_7O_{13}$; metatungstate, $Na_2W_4O_{13},10H_2O$, and pentatungstate, $Na_2W_5O_{16}$, and the conditions governing the formation and decomposition of the blue, violet, red, and yellow sodium tungstate "bronzes" were investigated. The reduction of the acid tungstates occurs in two stages: between 600° and 700° excess of oxygen present as tungstic oxide (WO_3) is quantitatively removed, and sodium tungstate and metallic tungsten are left. At 900°, this is further reduced, all the sodium and oxygen being volatilised. These reactions can be employed for the quantitative analysis of complex tungstates. The various bronzes can be obtained by cautiously heating the corresponding acid tungstate in hydrogen, when an atom of oxygen is removed. On further heating in hydrogen at 550°, the blue bronze loses successively 3 mols. of tungstic oxide, giving in turn the violet, red, and yellow bronzes. The theoretical equations for the various reactions are found to agree closely with the quantitative experimental results. M. Zvegintzov.

True and pseudo-halides. A. Hantzsch and H. Carlsohn (Z. anorg. Chem., 1927, **160**, 5—26).—The halogens form true and pseudo-salts comparable with ordinary true and pseudo-acids and salts. The class to which a particular salt belongs depends on the position of the metal in the ionisation potential series. Stable pseudo-halide salts are recognised by their indifference to sulphuric acid, whereas unstable pseudo-salts react chemically in the same manner as true salts, although their physical properties are those of pseudo-salts. Metals of variable valency probably form only pseudo-salts. The limit of the ionisation potential between true and pseudo-chlorides of the univalent metals lies between sodium and lithium chlorides, whilst for iodides, and probably also for bromides, the limit is lower, on account of the greater tendency of hydriodic acid towards salt formation. The limit for iodides lies below lithium. For halides of bivalent metals, the limit is below manganese, and possibly between calcium and magnesium. Little is known with certainty about the alkaline-earth metal halides. The most positive of the tervalent metals, aluminium, and probably all ter- and multi-valent metals form exclusively pseudo-halides. Only sodium, potassium, rubidium, and cæsium give exclusively true salts. A study of the change from pseudo- to true salt in the case of the cobalt halides shows that the change is dependent on the nature of the solvent, the halogen, and the salt concentration. Of all the solvents investigated, acetone shows the least tendency to bring about the change from pseudo- to true salt. H. F. Gillbe.

Reactivity of manganese dioxide in the solid state. F. de Carli (Atti R. Accad. Lincei, 1926, [vi], **4**, 577—581).—Heating curves, obtained by means of the apparatus previously used (A., 1924, ii, 758), are given for mixtures of manganese dioxide with other oxides. The curve for the pure dioxide shows (1) a slight retardation beginning just above 400° and ending with a pause at 530°, and (2) a halt at 930—940°. Mixtures of 1 mol. of barium, strontium, and calcium oxide with 1, 2, or 3 mols. of the dioxide exhibit indications of exothermic reactions beginning at 150—250°. Of oxidisable oxides, cuprous oxide begins to react with manganese dioxide at 380° and stannous oxide at 180°. Chromium sesquioxide does not react, but the behaviour of other anhydrides towards the dioxide is similar to that towards lead dioxide. Magnesium, zinc, cupric,

cadmium, and lead oxides are without influence on the decomposition of manganese dioxide. From these results, together with those obtained with lead dioxide and by Hedvall with barium dioxide (A., 1919, ii, 26), it is evident that these three dioxides are able to react in the solid state with a large number of varied compounds. T. H. POPE.

Influence of high temperatures on metallic sulphides in a carbon-tube furnace. M. PICON (Bull. Soc. chim., 1927, [iv], 41, 189—191).—Sulphides of iron (FeS), manganese (MnS), and chromium (CrS) are more resistant to the action of carbon in a vacuum at high temperatures than the corresponding oxides. Ferrous sulphide loses its sulphur completely at 1600°; the influence of the presence of carbon on the reaction was not verified (Bogitch, B., 1926, 194). Manganese sulphide volatilises unchanged at 1375° and will dissolve up to 15% of graphite without apparent change. When this sulphide is prepared in a vacuum furnace by Mourlot's method (A., 1899, ii, 747), a product contaminated with metallic carbide is obtained; the pure substance may be obtained by the action of hydrogen sulphide on the oxide at 900°. Chromium sulphide melts with dissociation at 1550°.
S. K. TWEEDY.

Behaviour of precipitated ferric hydroxide towards hydrocyanic acid; a case of differences in reaction connected with several stages of ageing in a metallic hydroxide. E. WEDEKIND and HEINRICH FISCHER (Ber., 1927, 60, [*B*], 541—544; cf. Wedekind and Albrecht, A., 1926, 1196).—Freshly-precipitated ferric hydroxide gradually becomes black in contact with 4% hydrocyanic acid, whilst the liquid acquires an intense reddish-violet colour, the cause of which has not been ascertained. With increasing age of the ferric hydroxide, the colour becomes less intense, and is scarcely perceptible with a preparation 20 days old. With specimens which have been preserved during 5—6 weeks, the blackening of the solid or violet colour of the solution is not observed. The black precipitate consists of a mixture of Prussian blue and ferric hydroxide; it is also formed when freshly-prepared ferric hydroxide is brought into contact with Prussian blue. The ageing of the hydroxide affects only the first phase of the change, viz., the reduction of ferric to ferrous hydroxide by hydrocyanic acid.
H. WREN.

Existence and structure of the disulphides NiS_2 and CoS_2. W. F. DE JONG and H. W. V. WILLEMS (Z. anorg. Chem., 1927, 160, 185—189).—A discussion of the existence and structure of CoS_2 and NiS_2. H. F. GILLBE.

Reduction of ruthenium trichloride by sodium amalgam. H. REMY and T. WAGNER (Ber., 1927, 60, [*B*], 493—499; cf. Remy, A., 1921, ii, 209).—During the reduction of ruthenium trichloride in hydrochloric acid solution by sodium amalgam, a green coloration is observed between the initial sepia-brown and ultimate dark blue, which is more pronounced as the acidity of the solution is increased. This point corresponds with the absorption of one equivalent of hydrogen for each ruthenium ion (when allowance is made for the quantity used in the subsidiary reduction of trichloride to metal), and thus points to the existence of the dichloride in solution. Further addition of sodium amalgam causes the production of dark blue ruthenium monochloride, reaction being incomplete in strongly acid solution, but quantitative in more dilute solution. It thus appears that bivalent ruthenium as free ion and in weak complexes is very unstable and readily passes into the univalent condition, and that ruthenium dichloride, in itself colourless or feebly coloured, gives a dark green additive compound with hydrochloric acid. H. WREN.

Dehydration of the crystallohydrates of metallic salts. M. A. RAKUSIN and D. A. BRODSKI.—See B., 1927, 187.

Preparation of pure hydrogen for hydrogen electrodes. E. BILMANN and A. L. JENSEN (Bull. Soc. chim., 1927, [iv], 41, 147—151).—The hydrogen is prepared by the electrolysis of 4*N*-sodium hydroxide solution, a gold cathode being used; the gas contains 0·129 vol.-% of oxygen, which is removed by passing over platinum gauze at 400°. If the gauze is replaced by platinised asbestos, the hydrogen is contaminated with silicon hydride. The presence of the latter probably explains some of the "active" hydrogens which have been prepared.
S. K. TWEEDY.

Preparation of small quantities of potassium, rubidium, or cæsium. J. H. DE BOER, P. CLAUSING, and G. ZECHER (Z. anorg. Chem., 1927, 160, 128—132).—A new method is described for the preparation of small quantities of potassium, rubidium, or cæsium which does not involve heating at high temperatures in metal vessels. In the usual method of preparation, by distilling a mixture of a salt of the required metal with calcium or magnesium, the product is always contaminated with the alkaline-earth metal. Barium azide, prepared by distilling azoimide into barium hydroxide solution, decomposes below 200°. By mixing solutions of barium azide and the chloride of the required alkali metal, evaporating to dryness in a vacuum, and heating the solid residue, the pure alkali metal distils over. A simple type of apparatus is described, by the use of which contamination of the distillate by barium may be avoided.
H. F. GILLBE.

Manufacture of Glauber's salt and of anhydrous sodium sulphate from residue left after the concentration of potassium salts. K. KOELICHEN.—See B., 1927, 186.

Preparation and m. p. of pure phosphorus di- and tri-iodides. F. E. E. GERMANN and R. N. TRAXLER (J. Amer. Chem. Soc., 1927, 49, 307—312).—Pure crystalline phosphorus tri-iodide, m. p. 61·0°, may be prepared by the interaction of the requisite amounts of white or red phosphorus and iodine in a carbon disulphide solution from which all free sulphur has been removed. In a similar way, using white phosphorus, the di-iodide, m. p. 124·5°, may be obtained. When free sulphur is present, the products have low m. p., probably owing to the presence of a compound which may be $P_4S_3I_2$ (cf. A., 1925, ii, 1087). S. K. TWEEDY.

Quantitative spectral analysis. H. KONEN (Ver. Ges. deut. Naturforsch. Aerzte, 1926, **19**, 1108—1114).—A critical review. Quantitative spectral analysis may be carried out in three general ways: (*a*) measurements of relative intensities for one or more emission or absorption lines, (*b*) the variability of single known lines in respect of breadth and symmetry under defined conditions, (*c*) the influence of foreign substances on the spectrum of a specified element under defined conditions. The methods proposed are reviewed in some detail, and the author sees little reason to abandon the view set forth in Kayser's "Handbuch" that quantitative spectral analysis is beset with pitfalls. Many procedures have been proved to be trustworthy by actual trial, but great caution needs to be shown in attempts to extrapolate outside the tested range of validity. The great advantages and some disadvantages of the Hartley–de Gramont method of using the "ultimate" lines are pointed out. Quantitative spectral analysis still lacks a general scientific basis, although its value in practical control is emphasised.

R. A. MORTON.

Calibration in quantitative spectral analysis. A. REIS (Ver. Ges. deut. Naturforsch. Aerzte, 1926, **19**, 1114—1116).—The spark spectra above solutions of lead nitrate were photographed and the intensities of the persistent lines determined. The darkening of the plate by these lines was measured by a registering photometer, and the results were plotted against the lead content of the solutions. A series of fairly straight lines was obtained in this way in respect of the rays 4057, 3639, 2613, 2662, 3738 Å. A similar calibration showed that the conditions of excitation (which are specified) yield trustworthy information on the lead content of gold and of gold–copper alloys.

R. A. MORTON.

Quantitative *X*-ray spectral analysis. P. GUNTHER (Ver. Ges. deut. Naturforsch. Aerzte, 1926, **19**, 1118—1124).—A review of methods and achievements. The method of *X*-ray quantitative analysis is still of specialised application, but the diverse nature of the materials for which it has been adapted makes the outlook promising. R. A. MORTON.

Solutions for colorimetric standards. I. Spectral transmission curves for some aqueous solutions containing organic indicators or inorganic salts. M. G. MELLON and F. D. MARTIN (J. Physical Chem., 1927, **31**, 161—177).—The transmittancies of various aqueous solutions have been determined, and the percentage transmittancy–wave-length curves are given for the following cases: aqueous solutions (containing 1% of hydrochloric acid) of cupric sulphate, ferric chloride, and cobaltous chloride at concentrations $M/4$, $M/8$, $M/16$, and $M/32$; aqueous solutions (containing 2·8% of ammonia) of ammonium chromate, tetramminocupric sulphate and chloropentamminocobaltic chloride, and of potassium dichromate, all in various concentrations; and aqueous solutions of the commercial indicators, methyl-orange, thymol-blue, bromophenol-blue, methyl-red, bromocresol-purple, bromothymol-blue, phenol-red, cresol-red, 2 : 4-dinitrophenol, *m*- and *p*-nitrophenols, phenolphthalein, cresolphthalein, chlorophenol-red, bromophenol-red, chlorobromophenol-blue, and bromocresol-green at various p_H values.

A discussion of the data is reserved for a future communication. L. S. THEOBALD.

Flocculation of troublesome precipitates in analysis. W. CLAYTON (Analyst, 1927, **52**, 76—77).—Such diverse systems as calcium carbonate in saturated sodium chloride solution, talc and clay suspensions in water, certain solids in strongly acid and alkaline media, and precipitates such as mercuric tungstate will give coarse flocs which settle readily if a small quantity of starch solution (1 part per 250 parts of flocculated dry solid), which is adsorbed by the floc, is added. So-called soluble starch is not suitable. Where alkalinity is not objectionable, an alkaline starch solution is recommended.

D. G. HEWER.

Qualitative chemical analysis by the dry method. D. MIGLIACCI and C. CRAPETTA (Annali Chim. Appl., 1927, **17**, 66—74).—Descriptions are given of the distinctive colorations obtained when salts of each of 32 elements are mixed with nitrate of either cobalt, nickel, or chromium and a strip of filter-paper is immersed in the mixed solution, dried, and burnt. This method of carrying out the test is preferred to that in which a stick of charcoal is used.

T. H. POPE.

Precise volumetric analysis. K. O. SCHMITT (Z. anal. Chem., 1927, **70**, 230—235).—The use of weighing burettes and weighing tubes for measuring the reacting substances and of colorimetric methods for determining the exact end-point of a titration is described, and the magnitude of, and means of correcting errors introduced by weighing in air are discussed. A. R. POWELL.

Change of p_H in buffer mixtures at varying temperatures. I. M. KOLTHOFF and F. TEKELENBURG (Rec. trav. chim., 1927, **46**, 33—41).—The p_H of a large number of acid and alkaline buffer mixtures has been determined at various temperatures between 10° and 60°. The p_H of ordinary buffer mixtures does not change appreciably over this range, except in the case of glycine–sodium hydroxide and boric acid–sodium hydroxide mixtures. H. F. GILLBE.

Influence of sodium chloride on the colorimetric determination of p_H. L. B. PARSONS and W. F. DOUGLAS (J. Bact., 1926, **12**, 263—265).—The salt error of the sulphonephthalein series of indicators has been measured at 1, 2, and 3M-salt concentrations. By subtracting 0·3 unit from the observed colorimetric p_H values, results may be obtained for solutions containing 6—18% of salt which conform with electrometric data.

CHEMICAL ABSTRACTS.

Analytical investigation of water samples from the Dead Sea. R. KOEFOED and G. HAUGAARD (Compt. rend. Lab. Carlsberg, 1926, **16**, No. 9, 3—51).—Samples from the same depth have approximately the same composition, but the values of d and solute contents appear to vary periodically during the 24 hrs. The halogen, calcium, magnesium, and potassium contents are each linear functions of d; they increase very slowly as the depth increases up to

about 20 m., then very rapidly indeed (halogen expressed as silver equivalent in g. per litre from about 380 to about 505) up to 33 m., then more slowly but more regularly (silver equivalent about 2 g. per m. depth) as the depth increases again. This supports the earlier hypothesis that the level of the lake has been slowly rising during the last century. The sulphate content increases slowly up to about 24 m. depth, and then falls rapidly; the calcium content, on the other hand, rises regularly, and the water is saturated with respect to calcium sulphate, which is precipitated towards the bottom. The water is almost saturated with oxygen near the surface; hydrogen sulphide has a maximum value (1·25 c.c. per litre) at about 25 m. depth. A single bottom sample (83 m. depth) was found to contain much solid calcium carbonate, some gypsum, and a few well-developed sodium chloride crystals.

S. I. Levy.

[Determination of water in glycerol by measuring the] conductance of potassium chloride in glycerol. N. Kameyama and T. Semba (J. Soc. Chem. Ind. Japan, 1927, **30**, 10—14).—The conductance of potassium chloride in glycerol–water mixtures increases with the increasing water content in a simple manner. To glycerol (n_D^{15} 1·4716, 98·3%) a certain definite amount of potassium chloride is added; increasing amounts of water, corresponding with n c.c. of water per 100 c.c. of the original glycerol, are added step by step, and the specific conductance, K, is measured at 25°. The electrodes are of smooth platinum. For example, when the amount of potassium chloride is 471 mg. per 100 c.c. the values of n, $K\times10^5$ (found), and $K\times10^5$ (calc.) are, respectively, 0, 2·14, 2·24; 0·24, 2·50, 2·33; 0·47, 2·61, 2·42; 1·18, 2·73, 2·71; 2·12, 3·14, 3·10; 3·30, 3·58, 3·63; 4·24, 4·03, 4·08; 5·09, 4·52, 4·50; 6·36, 5·14, 5·17; 7·06, 5·54, 5·55; 8·24, 6·23, 6·23; 9·41, 6·94, 6·94; 10·59, 7·73, 7·66, and 11·77, 8·53, 8·49. The formula $K\times10^5=2\cdot24+0\cdot38n+0\cdot0127n^2$ represents the experimental values within 1·5% from $n=1$ c.c. onwards. The value of the first term and the coefficient of n in the second term are larger when the amount of potassium chloride is larger, within the range of the investigation. K. Kashima.

Determination of bromates in presence of chlorates. F. Fichter and W. F. Tschudin (Helv. Chim. Acta, 1927, **10**, 267—275).—For the determination of relatively large amounts of bromate in presence of chlorate, Barnebey's method (A., 1916, ii, 261) is satisfactory, but if the quantity of bromate is small, it is preferable to use Junck's method (B., 1913, 1130). Reduction of the bromate with formic acid, hydrazine, or hydroxylamine with subsequent titration of the bromide formed is satisfactory only when the quantities of bromate and chlorate are approximately equivalent. If chromate is present, it should be precipitated as barium chromate before the iodometric determination of the bromate. Amounts of bromate in chlorate greater than about 0·1% can also be determined by reducing the solution at the b. p. with metallic cadmium and acetic acid and titrating electrometrically with silver nitrate.

R. Cuthill.

Iodometric titrations. III. Reaction between atmospheric oxygen and acid iodide solutions. K. Bottger and W. Bottger (Z. anal. Chem., 1927, **70**, 209—213; cf. this vol., 222).—Addition of an equal volume of hydrochloric acid (d 1·19) to an iodide solution exposed to the air results in the liberation of iodine in an amount which depends on the concentration of the iodide and on the time of action. The rate at which the iodine is liberated is considerable during the first 15 min., but then rapidly decreases. For analytical operations, using iodide in strongly acid solutions, both acid and water, therefore, should be freed from air by boiling and an atmosphere of carbon dioxide be maintained in the apparatus in which the titration is carried out.

A. R. Powell.

Microchemical analysis. V. Delicate reaction of sulphites. L. Rosenthaler (Mikrochem., 1927, **5**, 27).—The solution is rendered neutral to phenolphthalein by addition of acid or alkali. A few drops of a 1% formaldehyde solution then produce a red colour, due to the liberation of alkali hydroxide by the reaction $H\cdot CHO+Na_2SO_3+H_2O=H\cdot CH(OH)(SO_3Na)+NaOH$. A distinct rose colour is produced in the presence of 0·1 mg. of sulphite in 0·5 c.c. of 0·1N-thiosulphate solution.

A. R. Powell.

Determination of sulphurous acid and sulphites. J. Bicskei (Z. anorg. Chem., 1927, **160**, 64—66).—The ordinary iodometric determination of sulphurous acid gives inaccurate results in concentrated solution owing to atmospheric oxidation and loss of sulphur dioxide. By employing a more powerful oxidising agent, these errors may be reduced. Standard sodium hypochlorite solution is added to the sulphurous acid and the excess of hypochlorite titrated with iodine. The method is applicable to solutions of high sulphur dioxide concentration.

H. F. Gillbe.

Volumetric determination of sulphates. M. Talenti (Giorn. Chim. Ind. Appl., 1926, **8**, 611—612).—Extended use of Muller's method of determining sulphates (A., 1902, ii, 425) is recommended, especially for rapid industrial controls. The benzidine solution is prepared by gently heating and shaking an approximately 2% aqueous suspension of pure benzidine, adding sufficient concentrated hydrochloric acid to give the solution a 0·25N acidity, and filtering the deep chestnut liquid thus obtained. The acidity of the filtrate is determined exactly by titration with sodium or potassium hydroxide in presence of phenolphthalein. Precipitation of the sulphate and titration of the filtrate with alkali, as described by Muller, is recommended, and when a heavy metal is present, this should be previously removed by suitable precipitation and filtration. T. H. Pope.

[High values for potassium dichromate in determinations of thiosulphate.] G. Bruhns (Z. anal. Chem., 1927, **70**, 128). W. Bottger (*Ibid.*, 311).—Polemical. R. Cuthill.

Determination of nitrogen in nitrates. A. Pizzarelli.—See B., 1927, 187.

Determination of small quantities of nitrate by means of "fornitral." W. Mestrezat and M.

DELAVILLE (Bull. Soc. Chim. biol., 1926, 8, 1217—1218).—Small quantities of nitric acid may be determined by the addition of nitron formate ("fornitral") in presence of dilute sulphuric acid. The precipitate, which separates quantitatively, is collected, washed with a saturated solution of nitron nitrate, dried, and weighed. W. O. KERMACK.

Assay of phosphoric acid and the sodium phosphates. A. F. SHIREMAN (J. Amer. Pharm. Assoc., 1926, **15**, 267—276).—Theoretically, trinitrobenzene should be a satisfactory indicator, but its colour change is too gradual. The use of calcium chloride (to precipitate $CaHPO_4$, liberating hydrogen chloride) and phenolphthalein at 55—70° is preferred. CHEMICAL ABSTRACTS.

Iodometric determination of arsenic acid. B. ORMONT (Z. anal. Chem., 1927, **70**, 310—311).—A reply to Rosenthaler's criticisms (A., 1926, 702). R. CUTHILL.

Toxicity of arsenobenzenes. I. Determination of arsenic. G. SENSI.—See B., 1927, 171.

Determination of boric acid in silicates. R. SCHMIDT.—See B., 1927, 189.

Determination of carbon monoxide by titration with silver solution. W. MANCHOT and O. SCHERER (Ber., 1927, **60**, [*B*], 326—332).—The mixture of gases is agitated with a mixture of 0·1*N*-silver nitrate (50 c.c.) and 0·15*N*-sodium hydroxide (50 c.c.) to which pyridine (50 c.c.) has immediately been added, thereby giving a clear solution. After contact with the reagent at about 65° during 0·5 hr. with frequent shaking, the solution is cooled, diluted somewhat, acidified with acetic acid (20%), and filtered. The filtrate is strongly acidified with nitric acid and the unused silver is titrated by ammonium thiocyanate in presence of ferric alum. The results are usually slightly low, probably owing to slight dissolution of the precipitated silver in the acetic acid. Carbon monoxide may be determined in this manner in its mixtures with air, hydrogen, methane, or ethylene.

Carbon monoxide reacts quantitatively with gold chloride at 60—70°, according to the equation $2AuCl_3+3CO+3H_2O=2Au+3CO_2+6HCl$, and may therefore be determined either by weighing the precipitated gold or reduction of the unused gold by ferrous sulphate, followed by titration of excess of the latter by permanganate in presence of phosphoric acid. The method is applicable in presence of methane. Ethylene, however, reduces the gold chloride solution, whereas hydrogen restricts the action of carbon monoxide. H. WREN.

Determination of cyanides and thiocyanates. J. BICSKEI (Z. anorg. Chem., 1927, **160**, 271—272).—Excess of standardised sodium hypochlorite solution quantitatively oxidises a solution of cyanide or thiocyanate to cyanate or cyanate and sulphate, respectively; the excess of hypochlorite is titrated with standard iodine solution. H. F. GILLBE.

Determination of potassium by the aid of electrometric titration. A. RAUCH (Z. anorg. Chem., 1927, **160**, 77—91).—The potassium is precipitated from a neutral or slightly alkaline solution containing about 30% of alcohol by the addition of an excess of calcium ferrocyanide solution, as the sparingly soluble potassium calcium ferrocyanide. The excess of calcium ferrocyanide is titrated electrometrically with zinc sulphate solution, which is standardised against a solution of known potassium content. The method is applicable in presence of sodium, calcium, magnesium, chloride, and sulphate ions, but cannot be employed when there are present ammonium or barium salts, nitrates, or any substances which form sparingly soluble ferrocyanides or bring about oxidation of the ferrocyanide. H. F. GILLBE.

Diphenylbenzidine as internal indicator for the titration of zinc with potassium ferrocyanide. W. H. CONE and L. C. CADY (J. Amer. Chem. Soc., 1927, **49**, 356—360).—Diphenylbenzidine may be used as an internal indicator in the titration of zinc salts by ferrocyanides. The latter must contain a small amount of ferricyanide. The blue oxidation compound formed in presence of zinc salts is immediately decomposed when an excess of potassium ferrocyanide is added; this end-point is very sharp. The titration is rapid, and back-titrations may be carried out. No correction is necessary for the amount of indicator present. Diphenylamine may also be used, but in this case a small correction must be applied. S. K. TWEEDY.

Qualitative micro-analysis and quantitative micro-analysis of cobalticyanides. I. Potassium cobalticyanide as a reagent for the detection of zinc and bismuth. II. The Vanino-Treubert reaction for bismuth. A. BENEDETTI-PICHLER (Z. anal. Chem., 1927, **70**, 257—288, 288—297).—The microchemical method of detecting zinc proposed by Emich ("Lehrbuch der Mikrochemie," Wiesbaden, 1911, p. 102) is best carried out as follows. By addition to the solution of potassium cobalticyanide, the zinc is precipitated as the cobalticyanide, and this is converted into Rinman's green by heating in a current of carbon dioxide. In this way, 0·08 μg. of zinc may be detected. If other metals of the ammonium sulphide group are present, the green colour may be masked. In this case, the zinc is separated by passing hydrogen sulphide into the acetic acid solution, treating the nitric acid solution of the precipitate with bromine and potassium hydroxide, and either electrolysing the alkaline solution or adding to it ammonium sulphide. Alternatively, if large quantities of chromium are not present, the original solution may be treated with an equal volume of a 30% solution of potassium hydroxide, and the centrifugate heated with bromine water, the clear solution finally being electrolysed.

Bismuth salts in nitric acid solution, and in absence of any considerable quantity of chloride ions, give a characteristic crystalline precipitate with potassium cobalticyanide, which, unlike the somewhat similar silver cobalticyanide and the flocculent mercurous salt, is not darkened by a 10% solution of potassium hydroxide, and is distinguished from the corresponding cadmium and zinc compounds in being blackened by an alkaline stannite solution. This test will detect 0·01 μg. of bismuth in absence of large

quantities of other metals. Free sulphuric acid, and mercuric, stannous, calcium, magnesium, and especially lead salts, may alter the crystalline form of the precipitate, and frequently "somatoid" forms (cf. Kohlschütter and Egg, A., 1925, ii, 1035) are produced, these being probably solid solutions. The bismuth may be separated from the mercury, lead, copper, and cadmium by a method resembling the one ordinarily used, except that, instead of precipitating the lead as sulphate, it is precipitated as hydroxide along with the bismuth, and the nitric acid solution of the hydroxides is either tested for the two metals separately, or the bismuth is separated from it as basic nitrate.

II. The separation of metallic lead when solutions containing lead are tested for bismuth with an alkaline stannite solution can be avoided if the reagent is prepared by adding to 5 c.c. of a 10% solution of potassium hydroxide 2 or 3 large drops of a freshly-reduced 15—20% solution of stannous chloride. Even then the test is uncertain if a very large excess of lead is present.

For quantitative micro-determinations, bismuth and lead may be separated from cobalt by precipitation with hydrogen sulphide, the bismuth being separated from the lead as basic nitrate and weighed as trioxide, and the lead weighed as sulphate. R. CUTHILL.

Volumetric determination of copper. D. KOSZEGI (Z. anal. Chem., 1927, **70**, 297—300).—To 50 c.c. of the neutral aqueous solution of the copper salt, which should correspond with not more than 0·15 g. of copper, are added 10 c.c. of a solution of 4 g. of arsenious oxide in 100 c.c. of a 3% potassium carbonate solution. Sufficient of a 10% solution of potassium hydroxide just to dissolve the resulting precipitate is then added. On boiling the solution, cuprous oxide is quantitatively precipitated according to the equation $4CuO+As_2O_3=2Cu_2O+As_2O_5$, and after 5 min. is collected and dissolved in a warm ferric sulphate solution, which is finally titrated with permanganate. R. CUTHILL.

Use of liquid amalgams in volumetric analysis. VIII. Determination of copper and tin by reduction with bismuth amalgam. K. SOMEYA (Z. anorg. Chem., 1927, **160**, 404—408).—Agitation of a solution of stannic chloride in 5—12*N*-hydrochloric acid for 10—15 min. at 45° with bismuth amalgam effects complete reduction of the tin to the stannous condition. After removing the amalgam and adding manganous sulphate solution, the stannous chloride may be titrated directly with permanganate. The presence of much sodium chloride causes slightly low results to be obtained, whereas ammonium chloride gives high results. A similar procedure is available for the determination of copper, the cuprous chloride obtained by the reduction being titrated with dichromate, using diphenylamine as internal indicator. All operations should be conducted in an atmosphere of carbon dioxide. A. R. POWELL.

Spectrographic detection and determination of impurities in aluminium and its alloys. R. ADAM.—See B., 1927, 143.

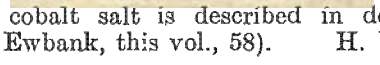
Volumetric determination of aluminium in aluminium salts. F. G. GERMUTH.—See B., 1927, 187.

Determination of alumina in silicate analysis. F. STEINBRECHER.—See B., 1927, 141.

Determination of manganese in rich alloys. E. DE LUISI.—See B., 1927, 191.

Interaction of manganese salts and permanganates. I. Action of potassium permanganate on manganese sulphate and determination of manganese. J. G. F. DRUCE (Chem. News, 1927, **134**, 145—147).—A review of the literature.

Standardisation of permanganate with electrolytic iron. L. MOSER and W. SCHONINGER (Z. anal. Chem., 1927, **70**, 235—247).—Iron deposited electrolytically from solutions containing organic compounds, such as oxalates, invariably contains carbon. Pure, smooth, silver-white deposits may, however, be obtained from a solution containing 100 g. of ferrous chloride crystals, 180 g. of sodium chloride, and 5 g. of boric acid per 100 c.c. The electrolysis is carried out at 90° with a current density of 0·9—1·0 amp./dm.^{2} at 2 volts, using a perforated platinum disc as cathode, separated by a parchment-paper diaphragm from a soft iron anode. Care must be taken that the electrolyte contains no trace of copper, arsenic, lead, manganese, or zinc, or the deposit will be contaminated. Before weighing the iron for standardising the permanganate, the cathode is washed in water, then in 0·05*N*-potassium hydroxide, and finally in alcohol; drying is effected by waving it over a small flame. A. R. POWELL.

Sensitive reaction for bivalent iron. F. KROHNKE (Ber., 1927, **60**, [*B*], 527—530).—0·01*N*-Disodium phosphate solution is added gradually with intermittent shaking to a dilute neutral solution of a ferrous salt floating on a solution of oximinoacetophenone in chloroform (1·49 g. in 100 c.c.). The aqueous solution rapidly becomes clear and colourless, whilst a blue coloration develops in the chloroform, which is stable if the supernatant liquid is not too alkaline or acidic. The presence of 0·03 mg. of iron in a litre of water may thus be detected. Cobalt, nickel, manganese, copper, zinc, cadmium, lead, and mercury impart, respectively, reddish-yellow, brown, brown, brown, yellow, yellow, reddish-yellow, and yellow colorations to the chloroform. The cobalt complex salt is distinguished by unusual stability towards acetic acid, so that nickel and cobalt can be detected in the same solution, since initially the brown nickel coloration predominates, but gives place after addition of 25% acetic acid to the reddish-yellow tint of cobalt. The complex salts have the constitution  (X=Fe$^{\cdot\cdot}$ etc.). The cobalt salt is described in detail (cf. Taylor and Ewbank, this vol., 58). H. WREN.

Iodometric titrations. IV. Determination of iron. K. BOTTGER and W. BOTTGER (Z. anal. Chem., 1927, **70**, 214—226; cf. this vol., 330).—The iodometric method for determining ferric salts given in the German Pharmacopœia gives results which are 1—2% too high, owing to the action of the air on the iodide during the long period before titration (1 hr.). Using air-free solutions and working in an atmosphere of carbon dioxide, the reaction between the ferric salt

and the iodide is completed within 15—20 min., no extra iodine is liberated, there is no after-bluing, and accurate results are always obtained. Addition of copper salts does not accelerate the reaction, but leads only to disturbing side-reactions. Thiosulphate is not oxidised under any conditions to sulphate when used for titrating acid iodine solutions, but if an excess is added and this is titrated with iodate, dichromate, or permanganate, a certain amount of sulphate is formed. A solution of chloroamine, which has been recommended as a substitute for iodine in volumetric analysis, slowly loses its strength on keeping.

A. R. Powell.

Separation of iron, chromium, nickel, manganese, tungsten, and silicon. P. Wenger and (Mlle.) E. Rogovine (Helv. Chim. Acta, 1927, **10**, 242—244).—The determination of the above metals when present together in alloys has been studied. If the metal can be reduced to fine shavings, the following method is applicable. The alloy is fused with sodium peroxide in a silver crucible and the product taken up with water. Manganates or permanganates are decomposed by warming with hydrogen peroxide and the solution is filtered. The iron is separated from the nickel and manganese in the hydrochloric acid solution of the precipitate by the acetate method and determined volumetrically with permanganate, and the nickel is precipitated as the glyoxime, whilst the manganese is precipitated as mangano-manganic oxide by boiling with ammonia and bromine. Silica and tungstic oxide in the filtrate are rendered insoluble in the usual way and separated with ammonia, and chromium is precipitated from the final filtrate as the hydroxide, after reduction with alcohol. If the alloy cannot be reduced to fine shavings, the above procedure must be modified as follows. The metal is treated with aqua regia, and any insoluble portion is then fused with sodium carbonate, taken up with hydrochloric acid, and added to the aqua regia solution. Silicon and tungsten are determined as before. Iron, nickel, and manganese are precipitated as the hydroxides by heating the alkaline solution with bromine, and are separated as described above. Chromium is determined in the filtrate in the usual manner.

R. Cuthill.

Analysis of steels. W. Singleton.—See B., 1927, 191.

New reagent for cobalt. P. Falciola (Giorn. Chim. Ind. Appl., 1926, 8, 612).—When added either as solid or solution to a strongly ammoniacal cobalt salt solution, sodium hyposulphite produces a yellow, orange, ruby-red, or dark red coloration, or a brownish-black precipitate, according to the concentration of the cobalt. One part of cobalt per 100,000 parts of solution is thus detectable. The blue colour of an ammoniacal nickel solution is unchanged by this reagent, but when much cobalt is present, together with nickel, the ammoniacal liquid is violet-blue, and, after treatment with hyposulphite, is decolorised by formaldehyde, which may cause the green colour of the nickel ion to reappear. When the cobalt is accompanied by any of the common metals or by molybdenum, uranium, vanadium, tungsten, titanium, etc., addition of hyposulphite to the ammoniacal solution and subsequent filtration yield a reddish-yellow liquid, which is deepened in colour by fresh addition of hyposulphite.

T. H. Pope.

Use of liquid amalgams in volumetric analysis. VII. Oxidimetric determination of chromium. K. Someya (Z. anorg. Chem., 1927, **160**, 355—365; cf. A., 1926, 1116).—In 0·3—2·5*N*-hydrochloric acid solution, chromic chloride is completely reduced to chromous chloride by shaking with zinc amalgam in an atmosphere of carbon dioxide. The amalgam is removed in three portions, shaking between each operation, and the solution titrated with ferric chloride, potassium permanganate, or potassium dichromate. For the simultaneous determination of iron and chromium in the same solution after reduction with zinc amalgam, the liquid is titrated with ferric chloride, using thiocyanate as indicator, then with dichromate, using diphenylamine as indicator; the first titration gives the chromium figure and the second the sum of the iron and chromium. For the determination of chromium in steel by the above method, the steel is dissolved in hydrochloric acid, the solution reduced with zinc amalgam, and the chromous chloride titrated directly with methylene-blue. In the method previously described for the determination of chlorate (A., 1926, 1117), the titanium tetrachloride solution recommended may be advantageously replaced by potassium dichromate. Lead amalgam also quantitatively reduces chromic chloride, but only in highly concentrated acid solutions.

A. R. Powell.

Spectrographic identification of certain elements and the possibility of determining them by the arc spectrum. IV. Tungsten. A. Donati (Annali Chim. Appl., 1927, **17**, 14—26).—In admixture with silica, 0·01% of WO_3 is detectable with certainty by means of the region of the carbon arc spectrum of wave-lengths 4700—3800 Å. The sensitiveness of this method for detecting tungsten is diminished somewhat in the case of a high-speed steel. A five-fold reduction in sensitiveness is caused by the presence of oxides of manganese. If the material is mixed with trimanganic tetroxide and made into a paste with silica, a more regularly coloured arc is obtained. In this way, samples of Sardinian pyrolusite have been examined qualitatively and the tungsten in them has been determined.

T. H. Pope.

Determination of tin and lead in solder and of tungsten in ferrotungsten by calculations on the Archimedean principle. Koch.—See B., 1927, 143.

Standardisation of titanous sulphate solutions. W. M. Thornton, jun., and A. E. Wood.—See B., 1927, 187.

Separation of titanium from uranium. A. Angeletti (Annali Chim. Appl., 1927, **17**, 53—54).—Cupferron (ammonium salt of nitrosophenylhydroxylamine) precipitates titanium, but not uranyl salts (cf. A., 1921, ii, 524). In determining titanium and uranium present together, the liquid is rendered acid, but not excessively so, by means of sulphuric or hydrochloric acid, and the former metal precipitated by excess of the cupferron. The precipitate is collected,

washed with cold water under slight suction, dried, ignited, and weighed as titanium dioxide. The uranium is determined by precipitation of the filtrate with ammonia solution. T. H. POPE.

Detection of thorium in the filaments of prepared electric vacuum lamps. P. SELENYI (Z. anorg. Chem., 1927, **160**, 318—322).—If the glass bulb of an electric lamp of the vacuum type is coated with tin-foil and then heated at 150° while a potential of 300 volts is maintained between the foil and the filament, the foil being the positive pole, a stream of electrons will pass from the glass towards the filament, thereby introducing into the lamp a small quantity of metallic sodium derived from the electrolytic decomposition of the glass. This sodium acts as a "getter" for the minute traces of oxygen still in the lamp, so that when the lamp is subsequently burnt with 30—40% of its specified voltage while the tin-foil is connected to the positive lead-in wire of the filament through a galvanometer, a current of several milliamp. will flow through the instrument if the filament contains thorium, owing to the electronic emission of the thoria. Non-thoriated filaments give only the slightest trace of emission under these conditions. A. R. POWELL.

Spectrographic identification of certain elements and the possibility of determining them by means of the arc spectrum. III. Vanadium. C. PORLEZZA and A. DONATI (Annali Chim. Appl., 1927, **17**, 3—14).—Application of the method employed previously for uranium (this vol., 124, 184), to mixtures of vanadium pentoxide with silica shows that, for the region of the arc spectrum from 4730 to 3795 Å., the spectrographic sensitiveness of vanadium is greater than that of uranium, two of the lines being visible when the concentration of the vanadium is only 0·001%. Quantitative application of the method to a sample of Colorado carnotite containing 5·09% of vanadium pentoxide gave the result about 5%. T. H. POPE.

Iodometric determination of the antimonic ion. A. TRAVERS and JOUOT (Compt. rend., 1927, **184**, 605—606).—The determination of the antimonic ion according to the reaction $Sb_2O_5+4HI \rightleftharpoons Sb_2O_3+2I_2+2H_2O$ cannot be rendered complete by the addition of excess of hydriodic acid (produced by the action of potassium iodide and an acid solution of antimonic chloride), since the compound $SbCl_3,3KI,1{\cdot}5H_2O$ is formed, which dissolves in the dilute hydrochloric acid to produce a brilliant yellow colour and renders the titration of the iodine impossible. The addition of tartaric acid to form tartar emetic is effective but slow. The addition to the solution of potassium iodide (about five times the amount required for the reaction) and about 15% of hydrochloric acid produces the complex $SbCl_n,x$HCl. This inhibits the reversal of the reaction and gives results rapidly and in good agreement with the electrolytic method. Type metal may be attacked by hydrochloric acid containing 13% of bromine. J. GRANT.

Micro-determination of bismuth. R. STREBINGER and E. FLASCHNER (Mikrochem., 1927, **5**, 12—15).—The nitric acid solution of bismuth nitrate is treated with ammonia until a faint opalescence is produced, solid pyrogallol is added, and the mixture heated for 15 min. on the water-bath. The precipitate is collected in a filter-tube, washed alternately with water and benzene to prevent creeping, dried at 110°, and weighed (cf. Feigl and Ordelt, A., 1925, ii, 442). A. R. POWELL.

Volumetric determination of bismuth, and rapid gravimetric determination of bismuth in ores. G. G. REISSAUS (Z. anal. Chem., 1927, **70**, 300—308).—Metallic bismuth is precipitated from its sulphuric acid solution by means of zinc, then dissolved in ferric sulphate solution and sulphuric acid, and the ferrous sulphate formed titrated with permanganate. Alternatively, the metal may be precipitated from solution in hydrochloric acid, not more than 15 g. of bismuth being present in 1000 c.c. of solution, by boiling with copper in an atmosphere of carbon dioxide, the reaction being: $BiCl_3+3Cu=3CuCl+Bi$. The cuprous chloride solution is then titrated hot with potassium bromate, using methyl-orange as indicator. Instead of titrating in this way, the metallic bismuth may be dissolved off from the unchanged copper with hot 30% nitric acid, precipitated with ammonium phosphate, and weighed as bismuth phosphate. The advantage of these methods lies in the convenience of the separation from lead. R. CUTHILL.

Electrotitration of platinum metals. W. D. TREADWELL and M. ZÜRCHER (Helv. Chim. Acta, 1927, **10**, 281—285).—Experiments have been performed on the potentiometric titration of solutions of salts of the platinum metals with a slightly acid 0·01*N*-titanous chloride solution. With a solution of palladous chloride containing free chlorine there are sharp *P.D.* changes corresponding with the conversion of the free chlorine into chloride ion, and with reduction to the metal. If auric chloride is also present, there is an intermediate change due to the reduction of the auric ion to the metal. For solutions containing platinic and palladous chlorides, the reduction of the two metals separately is not indicated. The curve for hydrochloroplatinic acid shows the reduction to the metal clearly, and also gives some signs of the reduction to the platinous state, these latter being more pronounced if an alkali iodide is added to the solution. Auric chloride can be titrated in presence of hydrochloroplatinic acid if the two are present in comparable amounts. R. CUTHILL.

Test for platinum. F. DURDIK.—See B., 1927, 193.

Combustion furnace with electric heating. C. GASTALDI (Annali Chim. Appl., 1927, **17**, 82—83).—In a furnace of the Heraeus type having a trough 93 cm. long, the use of three movable heating elements with a total length of 76 cm. permits of the regulation of the heating of the combustion tube. T. H. POPE.

Laboratory gas-generating apparatus. W. R. JEWELL (Chem. Eng. Min. Rev., 1926, **19**, 78). CHEMICAL ABSTRACTS.

Device for adjusting the levelling bulb on a gas-analysing apparatus. A. M. MCCOLLISTER and C. R. WAGNER.—See B., 1927, 127.

Electromagnetic separator for laboratory use. C. J. KSANDA.—See B., 1927, 144.

Still for the purification of mercury. H. S. BOOTH and N. C. JONES.—See B., 1927, 193.

Nephelometric apparatus. H. KLEINMANN (Biochem. Z., 1926, **179**, 301—303).—An improvement in the nephelometer previously described (A., 1923, ii, 429) is effected by using wider glasses which are optically matched. J. PRYDE.

New type of thermometer for cryoscopy of aqueous solutions. H. MENZEL (Z. Elektrochem., 1927, **33**, 63—69).—A description of a mercury-in-glass thermometer graduated in "molar degrees" (1 molar degree=1·860°), designed to simplify work on cryoscopy of aqueous solutions. The zero is fixed at 0° and the scale extends from +0·1 to −3·0 molar degrees. The construction, calibration, and correction of the thermometer are discussed, and results obtained with aqueous solutions of hydrogen peroxide, potassium chloride, and magnesium chloride are tabulated. H. J. T. ELLINGHAM.

Sublimation apparatus. L. BENVEGNIN (Ann. Chim. Analyt., 1927, [ii], **9**, 38—39).—The metal container is held in place by the heating plates (copper plates separated by asbestos) and the weighed watch glass over it is covered by a refrigerator with a concave lower surface the same shape as the watch-glass. Two screws keep the apparatus firmly together. Heating should be so regulated that sublimation is complete in 20 min., or too much water may condense on the sides of the watch glass. D. G. HEWER.

Apparatus for measuring the diffusion of gases and vapours through membranes. E. E. SCHUMACHER and L. FERGUSON (J. Amer. Chem. Soc., 1927, **49**, 427—428).—The membrane is held in a combined mechanical clamp and mercury seal. S. K. TWEEDY.

Automatic low-temperature thermostat. O. MAASS and W. H. BARNES (J. Amer. Chem. Soc., 1927, **49**, 360—363).—The light petroleum cooling-bath previously described is improved by the addition of a simple device which automatically adds liquid air to the bath when necessary. Any temperature between that of the room and that of liquid air may be maintained to within 0·1° or less. S. K. TWEEDY.

Simple, automatic cryostat. A. SIMON [with O. FISCHER, R. GLAUNER, and L. EHLING] (Ber., 1927, **60**, [*B*], 568—576).—An apparatus is figured and described by means of which any desired temperature between +20° and −195° may be maintained constant over a long period by means of a liquid boiling under suitably adjusted pressure. For temperatures between +20° and −30°, ether is used, whereas from −30° to −70° ammonia is employed. Methyl chloride can be used to −95°. Acetone and carbon disulphide are unsuitable. The b. p.–pressure curves for all the solvents are given. H. WREN.

Thermal properties of gases. IV. Apparatus for determination of densities of co-existing vapour and liquid phases. E. CARDOSO. **V. Densities of co-existing phases of sulphur dioxide.** E. CARDOSO and E. SORRENTINO (J. Chim. Phys., 1927, **24**, 65—76, 77—82).—IV. The apparatus consists essentially of a calibrated capillary tube having a small bulb at the end containing a piece of iron which can be agitated by a solenoid outside; the calibrated capillary is sealed on to ordinary capillary tubing, which is bent into the form of a U some distance from the calibrated piece, and finally terminates in a large reservoir fitted with a three-way tap. Two such systems are placed side by side, and by means of the taps are connected to the same gas generating apparatus; by taking a pressure reading, the quantity of gas present in each system is determined, and the mercury is then brought to a definite point on the calibrated capillary. The mercury in the U-portions of tubing is now frozen by immersing them in a bath of solid carbon dioxide and alcohol, fluctuations in the position of the mercury meniscus due to slight temperature variations of the reservoir thus being avoided. The calibrated capillaries are now surrounded by a constant-temperature bath, and the volumes of liquid and vapour in each tube read off. Then if P and P_1 are the weights of substance in the respective tubes, V and V_1 the volumes of liquid, and v and v_1 the volumes of vapour, the liquid density $D=(v_1P-vP_1)/(v_1V-vV_1)$ and the vapour density $d=(VP_1-V_1P)/(v_1V-vV_1)$.

V. The densities of the co-existing liquid and vapour phases have been determined at temperatures between 13·5° and 157·3°, and the rectilinear diameter so obtained shows no sudden point of inflexion near the critical temperature, as previous workers have supposed, but only a very slight curvature. By extrapolation, the critical density of sulphur dioxide is found to be $0{\cdot}5240\pm0{\cdot}0005$. S. J. GREGG.

Mineralogical Chemistry.

Density measurements of the Tyrrhenian Sea. J. THOULET (Compt. rend., 1927, **184**, 385—386).—Systematic density measurements of the Tyrrhenian Sea have shown the existence of four straits communicating it with neighbouring seas, the principal current being that from the Strait of Gibraltar. The Mediterranean Sea is a flooded basin the bed of which consists of active volcanic material constantly producing fresh or slightly salt water, carbon dioxide, and sulphuric acid. The carbon dioxide is most abundant on the bed of the ocean. J. GRANT.

Fusion of diabase with calcium carbonate. A. S. GINSBERG and X. S. NIKOGOSIAN (Bull. Acad. Sci. Leningrad, 1926, [vi], 679—696).—Various mixtures of diabase from Lake Onega with calcium carbonate have been fused and the resulting mass has been examined on solidification. With small pro-

portions of calcium carbonate, vitreous masses were obtained, but the 1 (carbonate) : 3 (diabase) mixture yielded a glassy basio mass filled with inclusions of acicular diopside. Further increase in the proportion of the carbonate resulted in the crystallisation of melilite, particularly with the 2 : 3 mixture; this corresponds closely in composition with certain melilites and may be represented as a mixture of 53·73% akermanite, 27·97% sarcolite, 17·06% gehlenite, and 1·26% enstatite. With the help of the diagrams of Buddington (A., 1922, ii, 155) and Scheumann (Centr. Min., 1922, 512), showing the relation between the optical properties of melilites and their compositions, the masses obtained give data agreeing closely with the actual constants for the crystals developed. Further increase in the proportion of calcium carbonate to diabase in the mixture leads to the formation of the skeleton form of melilite, anorthite (?), and rosary-like granules of a highly refractive mineral of olivine character. Commencing with the 8 : 5 mixture, the fused masses, which are homogeneous liquids at 1500°, disperse into powder on solidification, the possibility of the formation of the γ-modification of Ca_2SiO_4 being thus indicated.

Hence enrichment of a diabasic magma with limestone may lead, as Daly ("Igneous Rocks and their Origin," 1914, 29) suggests, through an intermediate nepheline phase, which reacts with augites (cf. Bowen, J. Geol., 1922, **30**, Suppl. to No. 6), to the formation of melilite layers, paragenetic, and in nature often connected with nepheline and calcium olivine formations.

T. H. Pope.

Oxidation of sulphides. F. Carmichael (Univ. Toronto Studies, Geol. Series, 1926, 29—36).—The amount of sulphur and metals oxidised when powdered minerals (10 g.) are agitated for 13 days with water (500 c.c.) and oxygen (760 mm., 2100 c.c.), expressed as a percentage of the original mineral, is polydymite 18·50, chalcocite 0·65, pyrrhotite (Cream Hill mine) 0·38, troilite 0·37, marcasite 0·29, pentlandite 0·26, pyrrhotite (Hybla, Ontario) 0·18, pyrite 0·13, stibnite 0·07, sphalerite 0·06, chalcopyrite 0·02, bornite 0·01, galena 0·01.

Chemical Abstracts.

Formulæ of certain Vesuvian silicates. G. Cesàro (Bull. Acad. roy. Belg., 1926, [v], **12**, 350—368).—The analyses of chondrodite, humite, and clinohumite, whilst not entirely accounted for by the mol. formulæ hitherto assigned, may be explained on the assumption that, besides MgF and MgOH, the group Mg_2O enters into the mol. composition. Analyses of nepheline accord with the assumption that this mineral is a basic metasilicate.

C. H. D. Clark.

Corundum rocks of Val Sessera (Biellese Foot-alps). F. Millosevich (Atti R. Accad. Lincei, 1927, [vi], **5**, 22—31).—The constitutions of various rocks of the Biellese district are described. The white veins of Monte Foggia consist of a corundum plagioclase very similar to plumasite and are associated, besides with pyrites, with an amphibole gabbro containing corundum which is termed *sesseralite* and has the composition:

SiO_2.	TiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MgO.
43·18	0·51	28·40	0·98	4·15	4·07
CaO.	Na_2O.	K_2O.	H_2O-.	H_2O+.	Total.
13·82	3·07	0·80	0·27	1·21	100·46

T. H. Pope.

Pyrargyrite and proustite from Sarrabus (Sardinia). M. Fenoglio (Atti R. Accad. Sci. Torino, 1926, **61**, 357—363).—Pyrargyrite from Sarrabus, occurring in groups of blackish-grey or deep red crystals of adamantine metallic lustre, often embedded in calcite, d^{17} 5·80, gave on analysis: Ag 59·61, S 17·89, Sb 22·24, As 0·15, total 99·89%. Proustite from the same district, found in vermilion crystals associated with galena and calcite, d^{17} 5·61, gave: Ag, 65·35; S, 19·49; As, 14·99; total 99·83. Crystallographic measurements were made on both minerals.

T. H. Pope.

Organic Chemistry.

Action of the silent discharge in olefines. N. J. Demjanov and N. D. Prianishnikov (J. Russ. Phys. Chem. Soc., 1926, **58**, 462—473).—Under a potential of 12,000—13 000 volts, ethylene yielded a yellow, mobile oil, 0·8360, n_D^{17} 1·4580, average mol. wt. 215, consisting of unsaturated hydrocarbons, from C_6H_{12} upwards, which reacted with bromine and dissolved in concentrated sulphuric acid, together with saturated compounds. *iso*Butylene gave a product of mol. wt. 140, d_4^{20} 0·822, $n^{5\cdot5}$ 1·4730, containing chiefly the hydrocarbons C_8H_{16} and $C_{12}H_{24}$, with a fraction of b. p. 30—42° consisting, probably, of the compound C_5H_{10}.

M. Zvegintzov.

Catalytic hydrogenation of compounds with conjugated double linkings. G. Vavon and M. Jakes (Bull. Soc. chim., 1927, [iv], **41**, 81—94).—A more detailed account of work already published (A., 1926, 934).

Use of Grignard reagents in attempted syntheses of asymmetric allene bases. C. D. Hurd and C. N. Webb (J. Amer. Chem. Soc., 1927, **49**, 546—559).—3-Pyridyl methyl ketone is obtained in 60% yield by hydrolysis of ethyl nicotinoacetate (cf. Pinner, A., 1900, i, 409; 1901, i, 176). When treated in ethereal solution with magnesium phenyl bromide, it yields *α-phenyl-α-3-pyridylethylene*, b. p. 204—210°/23 mm., m. p. 78—82°. Treatment of α-phenyl-α-*p*-tolylethylene with bromine in carbon disulphide affords *β-bromo-α-phenyl-α-p-tolylethylene*, b. p. 195—202°/20 mm. The action of magnesium on ethereal β-bromo-α-phenyl-α-1-naphthylethylene, with subsequent addition of *p*-dimethylaminobenzophenone, affords α-phenyl-α-1-naphthylethylethylene, together with unchanged reactants and a *product*, m. p. 94—105°. The preparation of the above Grignard reagent is greatly accelerated if a magnesium–copper alloy (12·75% Cu) is substituted for the pure

magnesium. When treated with 3-pyridyl methyl ketone, the Grignard reagent yields *γ-hydroxy-α-phenyl-α-1-naphthyl-γ-3-pyridyl-Δ$^{\alpha}$-butene*, m. p. 159—161°. This could not be dehydrated by heating at 160—170°, and the action of acetic anhydride afforded a mixture, m. p. 55—75°, from which a definite compound could not be isolated. Preparation of the Grignard reagent from β-bromo-α-phenyl-α-*p*-anisylethylene is accompanied by the formation of *αδ-diphenyl-αδ-di-p-anisyl-Δ$^{\alpha\gamma}$-butadiene*, m. p. 218·5—219·5°. Treatment of the Grignard reagent with 3-pyridyl methyl ketone appears to yield the corresponding vinylcarbinol or its dehydration product, the substituted allene, but this could not be purified. β-Bromo-α-phenyl-α-*p*-tolylethylene and magnesium yield analogously *αδ-diphenyl-αδ-di-p-tolyl-Δ$^{\alpha\gamma}$-butadiene*, m. p. 207—210°. The Grignard reagent does not react with 3-pyridyl methyl ketone. Treatment of α-bromo-β-phenyl-Δ$^{\alpha}$-propene with magnesium yields *s*-dimethyldiphenylbutadiene, α-phenyl-Δ$^{\alpha}$-propene, *as*-phenylmethylacetylene, and solid products. β-Bromo-αα-diphenylethylene and magnesium afford the corresponding Grignard reagent in 68% yield.

F. G. Willson.

Derivatives of Δ$^{\alpha\gamma\epsilon}$-hexatriene. C. Prévost (Compt. rend., 1927, **184**, 458—460).—Phosphorus tribromide reacts with Δ$^{\alpha\epsilon}$-hexadiene-γδ-diol to form the *αζ-dibromo-Δ$^{\beta\delta}$-hexadiene*, m. p. 85°, b. p. 128°/12 mm., described as the αγ-dibromide by Griner (cf. A., 1893, i, 241). From the dibromide, a *diacetate*, m. p. 25°, b. p. 155°/12 mm., is obtained, and this, on hydrolysis, gives the corresponding *glycol*, m. p. 106·5°, b. p. 161°/12 mm. Δ$^{\alpha\gamma\epsilon}$-Hexatriene, when brominated, yields the above dibromide (cf. Romburgh and Dorssen, *ibid.*, 1906, i, 722).

B. W. Anderson.

γ-Phenylpropinene and the preparation of true acetylenes with sodamide. M. Bourguel (Bull. Soc. chim., 1927, [iv], **41**, 192—193).—A reply to Bert and Dorier (this vol., 47). The lower density recorded by the author for γ-phenylpropinene (A., 1923, i, 430; 1925, i, 770) cannot be due to contamination with unchanged halogen compound. Purification by means of the copper derivative is unsatisfactory, and the operation is unnecessary if the reaction is performed in a solvent (light petroleum) which commences to distil at 100°/12 mm. After decomposition of the solid reaction product with ice, about one fifth of the solvent is distilled off in a vacuum. The hydrocarbon is then liberated and distilled (b. p. 63°/12 mm.). A third hydrocarbon, d^{15} 0·938, which is also regarded as a true phenylpropinene, has recently been obtained.

R. Brightman.

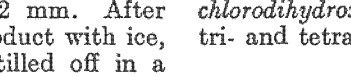
Diacetylenic acyclic hydrocarbons, $C_{13}H_{20}$ and $C_{20}H_{34}$. M. Lespieau (Compt. rend., 1927, **184**, 460—462).—An ethereal solution of magnesium in heptamethylene bromide was added slowly to ethereal βγ-dibromo-Δ$^{\alpha}$-propene, yielding a *dibromide*, $CH_2{:}CBr{\cdot}[CH_2]_3{\cdot}CBr{:}CH_2$, b. p. 180—183°/16 mm., d^{21} 1·274, n 1·497. Alcoholic potassium hydroxide converted this into Δ$^{\alpha\lambda}$-*tridecadi-inine*, b. p. 115·5°/12 mm., m. p. −2° or −3°, d^{21} 0·8262, n 1·454 (*copper* and *silver* compounds). Distillation of the tailings of the dibromide yields another *dibromide*, b. p. 210°/12 mm. (impure), from which a diacetylenic *hydrocarbon*, $C_{20}H_{34}$, m. p. 54—56° (*silver* derivative), was obtained.

B. W. Anderson.

Configurational relationship of *d*-butan-β-ol to *d*-lactic acid. P. A. Levene, A. Walti, and H. L. Haller (J. Biol. Chem., 1927, **71**, 465—469).—*d*-Butane-αγ-diol (*diphenylcarbamate*, m. p. 127—129°, $[\alpha]_D$ +53·24 in alcohol), gave, with hydrogen iodide, *α-iodobutan-γ-ol*, b. p. 58—60°/0·4 mm., and, with hydrogen bromide, d-*α-bromobutan-γ-ol*, b. p. 72—76°/20 mm., $[\alpha]_D^{20}$ +2·53°. The iodo-derivative, on reduction, yielded d-*butan-β-ol*, b. p. 99—104°, $[\alpha]_D^{20}$ +3·54°; *phenylcarbamate*, m. p. 62°, $[\alpha]_D^{20}$ +8·1° in alcohol. (*l*-Butan-β-ol gave a *phenylcarbamate*, m. p. 64—65°, $[\alpha]_D^{20}$ −16·76° in alcohol.) Since *d*-butane-αγ-diol has already been shown (A., 1926, 937) to be configurationally related to *d*-lactic acid, the latter must therefore be similarly related to *d*-butan-β-ol.

C. R. Harington.

Action of thionyl chloride on polyhydric alcohols. R. Majima and H. Simanuki (Proc. Imp. Acad. Tokyo, 1926, **2**, 544—546).—By gently boiling ethylene glycol with 8 parts of thionyl chloride for 15 hrs. there is formed glycol sulphite, b. p. 169—172° or 64—66·5°/12 mm., and a little ethylene dichloride. αγ-Dihydroxypropane gives under the same conditions mainly trimethylene dichloride and a little *trimethylene sulphite*, b. p. 74—76°/14 mm. α-Monochlorohydrin sulphite (α-chloro-βγ-propylene sulphite), b. p. 100°/16 mm., from glycerol, and *i*-erythritol hydrogen sulphite, m. p. 94—95°, from *i*-erythritol, are described. *l*-Arabitol and *d*-dulcitol give chloroform-soluble products which could not be isolated. From *d*-mannitol there is obtained in good yield a solid *trisulphite*,



or, in the presence of pyridine after 1·5 hrs., *tetrachlorohexylene sulphite*, $C_6H_8Cl_4{:}SO_3$, m. p. 50·5°, b. p. 170—180°/4·5—6 mm., from which by hydrolysis with cold sodium carbonate solution is obtained *tetrachlorohexylene glycol*, m. p. 67—68° (+0·5H_2O), $[\alpha]_D^{18\cdot5}$ +5·9°. Inositol is unattacked by thionyl chloride alone, but in presence of pyridine it gives *chloropentahydroxycyclohexane*, decomp. 248°, *tetrachlorodihydroxycyclohexane*, m. p. 186—187°, and tri- and tetra-chloro-benzenes and -phenols.

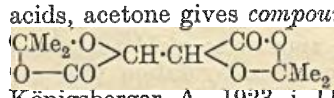
C. Hollins.

Aliphatic polysulphides. D. Twiss (J. Amer. Chem. Soc., 1927, **49**, 491—494).—Treatment of potassium *O*-ethyl thiocarbonate, in ethereal suspension or concentrated aqueous solution, with sulphur dichloride affords *ethyl formate trisulphide*, $S_3(CS{\cdot}OEt)_2$, decomp. 120—125°. Sulphur monochloride yields similarly the *tetrasulphide*, decomp. 120—125°. Potassium *O*-ethyl dithiocarbonate is converted analogously into *ethyl thioformate trisulphide*, decomp. 135°, and *tetrasulphide*, decomp. 135°. Condensation of ethyl chlorodithioformate with potassium ethyl trithiocarbonate in ethereal suspension yields *ethyl dithioformate monosulphide*, decomp. 100—110°, whilst oxidation of potassium ethyl trithiocarbonate with iodine (cf. Welde, A., 1877, ii, 314) affords the *disulphide*, decomp. 100—

110°. The *tri-* and *tetra-sulphides*, decomp. 100—110°, are obtained by the action of sulphur dichloride and monochloride, respectively, on potassium ethyl trithiocarbonate. All the above sulphides are non-distillable oils. The tri- and tetra-sulphides of ethyl formate gradually deposit sulphur, with formation of the disulphide. The sulphides of ethyl thioformate are stable, but the tri- and tetra-sulphide are slowly oxidised in air. When heated, they yield carbonyl sulphide and *O*-ethyl dithiocarbonate, but Debus' observations on the decomposition of the disulphide (Annalen, 1852, **82**, 253) could not be confirmed. The solubility of the sulphides of ethyl dithioformate decreases considerably with increase in the number of sulphur atoms. The tri- and tetra-sulphides are slowly oxidised by air. When distilled in a vacuum, the tetrasulphide yields the trisulphide and sulphur. The remaining sulphides decompose when heated, mainly with formation of ethyl polysulphides and carbon disulphide. The action of alcoholic ammonia on the sulphides of ethyl formate yields ammonium *O*-ethyl thiocarbonate and ethyl urethane. The ethyl thioformate derivatives yield, similarly, ammonium xanthate and xanthamide, the latter then yielding ammonium thiocyanate. The dithioformate derivatives yield, with ammonia, chiefly ethyl polysulphides and ammonium thiocyanate, the tetrasulphide yielding the trisulphide intermediately.

F. G. Willson.

Compounds of bivalent carbon. II. Sodium-oxyethoxymethylene and carbon monoxide diethylacetal [diethoxymethylene]. H. Scheibler (Ber., 1927, **60**, [*B*], 554—557; cf. A., 1926, 711).—Contrary to the observations of Adickes (this vol., 228), the product of the action of ethyl formate on sodium ethoxide is not a uniform substance, $CH(OEt)_2 \cdot ONa$, but a mixture of this compound with sodiumoxyethoxymethylene and unchanged sodium ethoxide, which by alternate treatment with ethyl formate and evacuation at 40° loses alcohol and yields homogeneous sodiumoxyethoxymethylene, characterised by hydrolysis to carbon monoxide, sodium hydroxide, and ethyl alcohol. The compound is transformed by ethyl bromide into ethylene, carbon monoxide, and ethyl alcohol. Its transformation into diethoxymethylene by the successive action of phosphoryl chloride and sodium ethoxide (*loc. cit.*) depends on the presence of hydrogen chloride in the former reagent and a sufficient interval before the use of the second reagent. Pure phosphoryl chloride followed immediately by sodium ethoxide converts sodiumoxyethoxymethylene into ethyl phosphate. Adickes' observation that the "primary product" [?$CH(OEt)_2 \cdot ONa$, see above] is converted by water into diethoxymethylene could not be confirmed. H. Wren.

Preparation of *iso*propylidene ethers by means of acetone and zinc chloride. H. O. L. Fischer and C. Taube (Ber., 1927, **60**, [*B*], 485—490).—A solution of anhydrous zinc chloride in dry acetone may frequently be used with advantage for the preparation of *iso*propylidene ethers. It possesses surprising solvent power towards hydroxy-compounds, and may be used at the ordinary temperature or at the b. p. Isolation of the product affords no difficulty if the ether is insoluble in water, but is not easy when this is not the case, and the compound dissolves with difficulty in organic media; removal of the zinc chloride from its acetone solution by ammonia or pyridine is then helpful. Ethers prepared in this manner are more stable than those obtained with the aid of acids. *iso*Propylidene ethers of dihydroxyacetone, mandelic and quinic acids, mannitol, lævulose, and galactose are readily prepared, but the behaviour of dextrose is abnormal. With the tartaric acids, acetone gives *compounds*,  (cf Willstätter and Königsberger, A., 1923, i, 1172), that from the *d*-acid having m. p. 102°, $[\alpha]^{17}$ +63·3° in *s*-tetrachloroethane, from the *l*-acid m. p. 102°, $[\alpha]^{18}$ −62·6° in *s*-tetrachloroethane, from the *r*-acid, m. p. 88·5°, and from the *meso*-acid, m. p. 96—97°. Dihydroxyacetone is readily isolated from technical glycerose by means of the reagent. H. Wren.

Ethers of diacetone alcohol. A. Hoffman (J. Amer. Chem. Soc., 1927, **49**, 530—535).—Ethers of diacetone alcohol are obtained as the result of a reversible addition of alcohol to the double linking of mesityl oxide when mixtures of mesityl oxide, an alcohol, and a mineral acid, preferably sulphuric acid, are kept for 10 days at the ordinary temperature. They are isolated by neutralisation of the reaction mixture, followed by distillation. Their probable constitution is $CMe_2(OR) \cdot CH_2Ac$. The following are described: *methyl diacetone ether*, b. p. 155—157°/760 mm.; *ethyl*, b. p. 164—166°/760 mm. (*oxime*, b. p. 103°/7 mm.; *semicarbazone*, m. p. 163—164°); *propyl*, b. p. 182—183°/760 mm. (*semicarbazone*, m. p. 139—140°); *butyl*, b. p. 198—199°/760 mm., b. p. 81—84°/7 mm. (*semicarbazone*, m. p. 134—135°); iso*butyl*, b. p. 85—87°/15 mm. (*semicarbazone*, m. p. 145°); iso*amyl*, b. p. 85—88°/6 mm. (*semicarbazone*, m. p. 142—143°); and *benzyl diacetone ether*, b. p. 153—157°/12 mm. (*semicarbazone*, m. p. 138—139°). Reduction of ethyl diacetone ether in ethereal solution with sodium and aqueous boric acid affords *δ-ethoxy-δ-methyl*-n-*pentan*-*β-ol*, b. p. 160—173°, d_{23}^{25} 0·868, which could not be further purified, and, when heated with concentrated sulphuric acid, yields δ-methyl-$\Delta^{\beta\delta}$-pentadiene. Oxidation of butyl diacetone ether with cold aqueous hypobromite affords chiefly *β-butoxyisovaleric acid*, b. p. 140—143°, d^{20} 1·053.

F. G. Willson.

Reactivity and stability of linking of organic radicals. II. Hydrolysis of esters, addition of hydrogen sulphide to nitriles, and conversion of alkyl chlorides into ethers. K. Kindler [with A. Treu and W. Fürst] (Annalen, 1927, **452**, 90—120; cf. this vol., 55).—An extension of previous work. New members are added to the series of comparative radical tenacities as measured by the rate of hydrolysis of substituted benzoic esters; the tenacity of $X \cdot C_6H_4$ to CO_2Et increases as X is changed thus: *p*-Cl < *m*-MeO < *p*-Ph < H < *p*-MeS < *p*-Me < *p*-Et < 3 : 4-CH_2O_2 < *p*-MeO. The value for the radical *p*-diphenyl agrees well with that found by Schönberg (A., 1925, i, 557). The tenacity of *m*-$MeO \cdot C_6H_4$ is very much less than that of *p*-$MeO \cdot C_6H_4$. The great

variations in the recorded relative tenacities of methyl and ethyl (Meerwein, A., 1920, i, 2; Skraup and Moser, *ibid.*, 1922, i, 574; cf. von Braun, *ibid.*, 1924, i, 632) are probably due to the difference in nature of the groups to which they are attached. The present results agree with those of von Braun; in both methods a negative group is used.

The tenacity of substituted alkyl radicals towards CO_2Et increases in the order $Ph{\cdot}CH_2<Me<Ph{\cdot}[CH_2]_2<Et<Ph{\cdot}[CH_2]_3<Pr^{\alpha}$; in the substituted aromatic series, $-Cl{\cdot}C_6H_4{\cdot}CH_2<p\text{-}MeO{\cdot}C_6H_4{\cdot}CH_2<p\text{-}Cl{\cdot}C_6H_4{\cdot}[CH_2]_2<p\text{-}MeO{\cdot}C_6H_4{\cdot}[CH_2]_2$. A table is given showing the effect of the various substituents of the original series on the tenacity of Ph, $Ph{\cdot}CH_2$, $Ph{\cdot}[CH_2]_2$, and $Ph{\cdot}CH{:}CH$ towards CO_2Et. This effect is greatest with benzoic esters, least with phenylacetic esters; the same order in the series holds for all four types.

When the tenacity towards CO_2Et, determined by hydrolysis, is compared with that towards CN, determined by addition of hydrogen sulphide, or towards Cl, determined by conversion into an ethoxy-derivative by sodium ethoxide, the same order again holds. The effect of substituents is much greater with chlorides.

The increasing tenacity of alkyl radicals is compared with the decreasing dissociation constants of the corresponding acids, and that of aryl radicals with the increasing dissociation constants of the phenols.

Velocity coefficients for hydrolysis by about $N/40$-sodium hydroxide were determined for the following ethyl esters: *m*-methoxybenzoate; p-*methylthiolbenzoate*, m. p. 28° (corr.), b. p. 168°/15 mm.; p-*ethylbenzoate*, b. p. 129—130°/15 mm., *p*-phenylbenzoate, acetate, propionate, butyrate, valerate, hexoate, heptoate, octoate, phenylacetate, *p*-methoxyphenylacetate, *p*-chlorophenylacetate, *p*-nitrophenylacetate, β-phenylpropionate, β-*p*-methoxyphenylpropionate, b. p. 165°/14 mm., β-3 : 4-methylenedioxyphenylpropionate, β-p-*chlorophenylpropionate*, b. p. 158—159°/15 mm., γ-phenylbutyrate, cinnamate, *o*- and *p*-methoxycinnamates, 3 : 4-methylenedioxycinnamate, *p*-methylcinnamate, *o*- and *p*-chlorocinnamates, *o*-, *m*-, and *p*-nitrocinnamates.

Velocity coefficients are given for the addition of hydrogen sulphide to phenylacetonitrile, β-phenylpropionitrile, γ-phenylbutyronitrile, *p*-chlorophenylacetonitrile, propionitrile, butyronitrile. γ-*Phenylthiolbutyramide*, m. p. 62° (corr.), p-*chlorophenylthiolacetamide*, m. p. 128—129° (corr.), and *thiolbutyramide*, a reddish-brown oil, are described.

Velocity coefficients are given for the replacement of chlorine by ethoxyl by means of sodium ethoxide (cf. von Braun, *loc. cit.*) in benzyl, *p*-chlorobenzyl, β-phenylethyl, and γ-phenylpropyl chlorides.

E. W. WIGNALL.

***iso*Erucic acid.** T. J. MIRCHANDANI and J. L. SIMONSEN (J.C.S., 1927, 371—378).—Oxidation of ethyl *iso*erucate with ozone yields a complex product in which the dibasic acids present are identified as decane-ακ-dicarboxylic acid and dodecane-αμ-dicarboxylic acid. These acids are also obtained together with *n*-octoic acid when methyl *iso*erucate is oxidised in acetone solution with potassium permanganate. Hence *iso*erucic acid is a non-homogeneous substance, consisting of an inseparable mixture of Δ^{λ}-docosenecarboxylic acid and Δ^{ν}-docosenecarboxylic acid (cf. Mascarelli, A., 1917, i, 195). From the yields of the oxidation acids, the two acids are apparently present in approximately equal amount. Apparent homogeneity is also found in certain derivatives of *iso*erucic acid (*methyl* ester, m. p. 24—26°, resolidifying at 22°; *ethyl* ester, b. p. 243°/8 mm.; *anilide*, m. p. 77—78·5°; p-*toluidide*, m. p. 85—86°; *zinc* salt, m. p. 109°). The dibromo-derivative, however, has the appearance of a mixture, and the m. p. is not sharp (cf. Macbeth and Stewart, P., 1912, 18, 68).

M. CLARK.

Synthesis of θ-, ι-, κ-, λ-, and μ-hydroxystearic acids. C. G. TOMECKO and R. ADAMS (J. Amer. Chem. Soc., 1927, 49, 522—530).—Δ^{κ}-*Undecenoyl bromide*, b. p. 103°/4 mm., n_D^{20} 1·4638, 1·0295, obtained by treating the corresponding alcohol with phosphorus tribromide in toluene, is converted, successively, into the *nitrile*, b. p. 117—119°/4 mm., n_D 1·4462, d_{20}^{20} 0·8405, and Δ^{κ}-*dodecenoic acid*, b. p. 143—144°/3 mm., n_D^{20} 1·4510, d_{20}^{20} 0·9030 (*methyl* ester, b. p. 121—123°/3 mm., 1·4414, d_2^{20} 0·8805). Ozonisation and subsequent hydrolysis of the ester affords *methyl* Δ^{ι}-*aldehydodecoate*, n_D^{20} 1·4430, d^{20} 0·9594 (*semicarbazone*, m. p. 114—115°). Treatment of ethyl sodiomalonate with undecenoyl bromide yields *ethyl* Δ^{κ}-*undecenoylmalonate*, b. p. 154°/2 mm., n_D^{20} 1·4450, d_{20}^{20} 0·9411, from which the corresponding *acid*, m. p. 112—113°, is obtained on hydrolysis. When heated at 150°, the latter loses carbon dioxide, with formation of Δ^{λ}-*tridecenoic acid*, m. p. 38—39°, b. p. 192°/20 mm., b. p. 162°/3 mm., from the *methyl* ester of which, b. p. 133°/3 mm., n_D^{20} 1·4438, d_2^{20} 0·8819, *methyl* κ-*aldehydoundecoate*, m. p. 16°, b. p. 154°/5 mm., n_D 1·4458, 0·9504, is obtained through the ozonide. Synthesis of the following methyl hydroxystearates was effected by condensing the above aldehydo-esters with Grignard reagents according to the method of Noller and Adams (A., 1926, 712), the corresponding acids being obtained by hydrolysis: θ-*hydroxystearic acid*, m. p. 74—75° (*methyl* ester, m. p. 45—46°, b. p. 212—216°/4 mm.); ι-*hydroxystearic acid*, m. p. 81—82° (*methyl* ester, m. p. 53—54°, b. p. 213—217°/4 mm.); κ-*hydroxystearic acid*, m. p. 76—77° (*methyl* ester, m. p. 49—50°, b. p. 204—206°/4 mm.); λ-*hydroxystearic acid*, m. p. 78—79° (*methyl* ester, m. p. 50—51°, b. p. 202—204°/4 mm.); and μ-*hydroxystearic acid*, m. p. 77—77·5° (*methyl* ester, m. p. 52—52·5°, b. p. 185—189°/2 mm.). *n*-Nonyl alcohol, b. p. 205—207°, obtained by reduction of *n*-nonaldehyde, yields n-*nonyl bromide*, b. p. 88°/4 mm., n_D^{20} 1·4533, d_{20}^{20} 1·0183, when boiled with concentrated hydrobromic and sulphuric acids.

F. G. WILLSON.

Optically active compounds of aluminium. W. WAHL [with M. ANDERSIN] (Ber., 1927, 60, [*B*], 399—406).—The conception that aluminium compounds are complex substances and not double salts is established by the isolation of them in optically active forms.

The water content of ammonium and potassium aluminotrioxalates, $[Al(C_2O_4)_3]R_3$, cannot be established analytically on account of the readiness and irregularity of their efflorescence. Treatment of a

cold, saturated solution of the ammonium salt with a similar solution of strychnine sulphate or nitrate leads to the separation of *strychnine aluminotrioxalate*, $[Al(C_2O_4)_3](H,C_{21}H_{22}O_2N_2)_3,12H_2O$, $[M]_D$ −281° in water. Attempts to separate this salt into fractions of differing specific rotation by crystallisation from hot water failed, owing to such extensive racemisation that the first, sparingly soluble fraction was optically inactive. The end is, however, attained by fractional extraction with water, whereby the extreme values observed for the strychnine salts of the *l*- and *d*-acid are $[M]_D$ −281·2° and +173·1°. When preserved in the solid, moist condition, the preparations undergo marked racemisation. The strychnine salts are transformed into the corresponding ammonium salts by trituration with the calculated quantity of ammonium iodide and a little water, filtration of the strychnine hydriodide, and addition of the filtrate to a large excess of absolute alcohol. The highest value of $[M]_D$ observed for the dextrorotatory salt is +81·2°; in aqueous solution, the salt suffers autoracemisation.

H. WREN.

Thermal decomposition of heterocyclic oxygen rings. M. D. TILITCHEEV (J. Russ. Phys. Chem. Soc., 1926, **58**, 447—461; cf. A., 1923, i, 1173).—The thermal decomposition of glyceryl oxalate gives a 60% yield of allyl alcohol, and no trace of *cyclo*propanol. Ethylene succinate gives mainly succinic anhydride and acetaldehyde, with some ethylene and carbon dioxide (38%). *Trimethylene oxalate*, m. p. 82—84°, prepared in 78% yield by cautiously heating methyl oxalate and trimethylene glycol, is converted by distillation in a vacuum into an *isomeride*, m. p. 186—187°. It decomposes when heated at 240—265°, evolving 46% of carbon dioxide and 54% of carbon monoxide. The residue contained propaldehyde, acraldehyde, and trimethylene glycol. *Ethylene malonate*, prepared in 95% yield as an oil by heating ethyl malonate with ethylene glycol, passes on distillation in a vacuum into a solid isomeride, m. p. 159—160°. At 205° it yields carbon dioxide (48%), acetaldehyde, ethyl acetate, ethylene acetate, and an unidentified *ester*, b. p. 148—153°/4 mm., d_4^0 1·2033, 1·4681. If the decomposition took place at 225—240°, a solid *product*, $C_9H_{10}O_5$, m. p. 108—108·5°, was also obtained.

M. ZVEGINTZOV.

Preparation of crystalline *d*-talonic acid. O. F. HEDENBURG and L. H. CRETCHER (J. Amer. Chem. Soc., 1927, **49**, 478—481).—*d*-Galactonolactone monohydrate (80 g.), pyridine (36 g.), and water (500 c.c.) are heated in a closed vessel at 100° for 115 hrs., whereby galactonic and talonic acids are obtained, which are separated from one another as their cadmium salts. Pure *d*-talonic acid has m. p. 125°, and crystallises with $0{\cdot}5H_2O$. It has $[\alpha]_D$ +16·73° in freshly-prepared 4% aqueous solution, changing to −21·57° in 240 hrs., when the solution contains 28% of acid, the remainder being present as the lactone, $[\alpha]_D$ −41°. The phenylhydrazide has m. p. 159°, $[\alpha]_D^{\delta}$ −25·43° (cf. Levene and Meyer, A., 1917, i, 631).

F. G. WILLSON.

Lactone formation of lacto- and malto-bionic acids and its bearing on the structure of lactose and maltose. P. A. LEVENE and H. SOBOTKA (J. Biol. Chem., 1927, **71**, 471—475).—Both lacto- and malto-bionic acids when preserved in aqueous solution showed a small increase in specific rotation which was complete in 2—3 hrs., and the titration values remained constant. In view of the results of Levene and Simms (A., 1926, 1025), this indicates that these acids form only lactones with six-membered rings. Support is therefore afforded to the view that in lactose and maltose the δ-position is occupied by the linking between the two hexoses.

C. R. HARINGTON.

Synthesis of α-bromoaldehydes. A. KIRRMANN (Compt. rend., 1927, **184**, 525—527).—The author considers that the products obtained by Nef (A., 1905, i, 6) and Etard (*ibid.*, 1892, 809) were impure. The method now used consists in brominating the methyl- or ethyl-acetals by phosphorus dibromotrichloride, $CH_2R{\cdot}CH(OR')_2 + 2PCl_3Br_2 \longrightarrow CHRBr{\cdot}CHO + 2R'Br + HBr + POCl_3 + PCl_3$. In the case of propaldehyde and butaldehyde, the main reaction is accompanied by the formation of αα-dibromoaldehydes, and isolation is difficult, but the higher acetals react more smoothly. In general, the methyl-acetals are unstable and regenerate the unbrominated aldehyde. Ethyl bromide was isolated in the case of the ethylacetals.

The α-bromoaldehydes are colourless liquids, which may be kept for some time without darkening, form hydrogen sulphite compounds, and give Schiff's reaction. The following are described, and densities and molecular refractions are given: *α-bromopropaldehyde*, b. p. 109—110°, or 52—54°/80 mm. (cf. Nef, *loc. cit.*); *α-bromo-n-butaldehyde*, b. p. 33°/15 mm.; *α-bromo-n-valeraldehyde*, b. p. 49°/12 mm.; *α-bromoisovaleraldehyde*, b. p. 43—44°/14 mm.; *α-bromo-n-heptaldehyde*, b. p. 80°/11 mm.

J. M. GULLAND.

Crystalline glyceraldehyde and its transformation into dihydroxyacetone. H. O. L. FISCHER, C. TAUBE, and E. BAER (Ber., 1927, **60**, [*B*], 479—485).—Bimolecular glyceraldehyde is transformed in boiling pyridine into dihydroxyacetone, the highest yield observed being 49%. The reaction is most readily explained by assigning to the aldehyde the constitution $\left(\begin{matrix}O-\\ |\\ CH(OH)\end{matrix}\!\!>CH{\cdot}CH_2{\cdot}OH\right)$. This conception is in harmony with the behaviour of the crystalline aldehyde when distilled in a high vacuum, with the non-success attending attempts to transform it into its *iso*propylidene ether, with the difficulty with which it adds hydrocyanic acid, and, in particular, with the indifference of its acetate towards phenylhydrazine. In contrast with the aldehyde, the corresponding acetal reacts readily with acetone in presence of copper sulphate. Lactaldehyde does not appear to be isomerised to hydroxyacetone in pyridine solution.

The following compounds are described: dibenzoxyacetone, m. p. 120·5°, and its *phenylhydrazone*, m. p. 69—70°; *di-p-nitrobenzoxyacetone*, m. p. 197·5° (decomp.); *dibenzoate*, m. p. 231°, *di-p-nitrobenzoate*, m. p. 247°, and *diacetate*, m. p. 154°, of *bimolecular glyceraldehyde*; *glyceraldehydediethylacetal* *isopropylidene ether*, $\begin{matrix}CMe_2{\cdot}O\\ |\\ O-CH\end{matrix}\!\!>CH{\cdot}CH(OEt)_2$, b. p. 90—

91°/20 mm., 0·9897, n^{17} 1·4208; *bimolecular lactaldehyde acetate*, $\left(\begin{matrix}O\text{——}\\ CHMe\end{matrix}\!>CH\cdot OAc\right)_2$ m. p. 185·5°. H. WREN.

Dioximes. XXXIX. G. B. SEMERIA and B. BOCCA (Atti R. Accad. Sci. Torino, 1926, **61**, 364—376).—See this vol., 135.

Optical enantiomeride of natural rhamnose. E. VOTOCEK and F. VALENTIN (Chem. Listy, 1927, **21**, 7—10).—See A., 1926, 940.

Oxidative decomposition of dextrose. B. BLEYER and W. BRAUN (Biochem. Z., 1927, **180**, 105—116).—Dextrose (1 mol.), when oxidised in alkaline solution with sodium *p*-toluenesulphonchloroamide, uses eight equivalents of oxygen and gives rise to 2 mols. of acetic acid and 2 mols. of carbon dioxide. It is supposed that 1 mol. of dextrose is decomposed hydrolytically into 2 mols. of methylglyoxal, which on oxidation gives 2 mols. of pyruvic acid, and on further oxidation 2 mols. each of acetic acid and carbon dioxide. P. W. CLUTTERBUCK.

Role of heavy metals in the autoxidation of sugars. H. A. KREBS (Biochem. Z., 1927, **180**, 377—394).—The rate of oxidation of lævulose by oxygen in feebly alkaline solution is much greater in ammoniacal solution than in phosphate or hydrogen carbonate solutions of the same hydroxyl-ion concentration. The velocity is proportional to the concentration of lævulose, ammonia, and hydroxyl ions, but is independent of the partial pressure of oxygen. The rate is increased as much as tenfold by the addition of salts of calcium and, to a less extent, of strontium or barium. Heavy metal salts (those of copper and manganese being the most effective) accelerate the autoxidation and hydrocyanic acid, pyrophosphate and hydrogen sulphide inhibit it. The effects of calcium and of the heavy metals are additive. Dextrose, mannose, galactose, and maltose are subject to the same effects at less rapid rates. The oxidation of sugars in faintly alkaline solution is attributed to the catalytic activation of oxygen by traces of heavy metals. R. K. CANNAN.

Behaviour of sugars in alkaline solution. II. Dextrose and sodium hydroxide. J. GROOT (Biochem. Z., 1927, **180**, 341—352).—The velocity constants for the rate of decline of optical rotation of dextrose in solutions of sodium and of potassium hydroxides are of the same order, increasing with the concentration of alkali up to a maximum value corresponding with the presence of alkali and dextrose in approximately molecular proportions. The temperature coefficient of the maximum velocity constant is 4·13 for a rise of temperature of 10°. The immediate depression in the rotation of dextrose produced by increasing concentrations of these hydroxides also attains a maximum value for molecular proportions of dextrose and alkali, when it amounts to 22% of the rotation of dextrose in neutral solution. The acid dissociation constant of dextrose has been determined electrometrically as $8{\cdot}6\times10^{-13}$. It is shown that the velocities above studied were directly proportional to the concentration of metallic glucosate present. It is suggested that the effects of alkali on dextrose may be attributed to enolisation of the glucosate molecule. R. K. CANNAN.

Crystallisation of sucrose. I. A. KUKHARENKO and M. E. VERKENTIN (Zapiski [Russia], 1926, **3**, 244—254).—At a supersaturation lower than the critical (which is 1·027, 1·031, and 1·030 for 0·5, 1·0, and 2·0% of calcium chloride, respectively), calcium chloride is a negative paralyser, the speed of crystallisation increasing with the concentration of calcium chloride in the mother-liquor. At supersaturation above the critical point, calcium chloride is a positive paralyser. CHEMICAL ABSTRACTS.

Saponin and allied substances. XVII. *Gypsophila* saponin and its hydrolysis products. Gypsogenin and saccharides. A. W. VAN DER HAAR (Rec. trav. chim., 1927, **46**, 85—96).—Electrodialysis of *Gypsophila* saponin by the method of Kofler and Dafert (cf. B., 1924, 73) yields free saponin together with calcium and magnesium compounds of saponin which cannot be separated by this method, but separation by means of methyl alcohol yields free saponin (ash content 0·2%) and the calcium–magnesium compound of saponin (ash content 3%). Both on hydrolysis yield the same sapogenin and saccharides. Free saponin contains water 7·2%, ash 0·2%, and on hydrolysis yields *l*-arabinose 12·2%, rhamnose hydrate 22·2%, dextrose 13·2%, *d*-galactose 17·3%, and sapogenin 21·8%. *d*-Mannose, xylose, and aldehydic acids are not produced, and only a very small quantity of lævulose was detected. The formula and m. p. 274° previously given for *Gypsophila* sapogenin (Karrer, Fioroni, Widmer, and Lier, A., 1924, i, 1091, who called it albasapogenin) are confirmed. The author assumes that free saponin is converted into the calcium–magnesium compound, in which the same sugars are combined with an altered, amorphous sapogenin, which in turn yields polysaccharides and ultimately monosaccharides. J. W. BAKER.

Structural problems of the associated lactolides and their relation to the chemistry of higher carbohydrates. M. BERGMANN (Annalen, 1927, **452**, 121—135).—A theoretical paper in which the differences between associated and polymerised molecules are examined and the criteria applied to a discussion of earlier results on the structure of ethylglycoloside, inulin, and other polysaccharides. J. W. BAKER.

Lichohexosan and lichenin. M. BERGMANN and E. KNEHE (Annalen, 1927, **452**, 151—158).—Mainly a reply to Pringsheim and Routala (this vol., 136). The authors prefer the name lichohexosan to lichosan, which is employed by Pringsheim, since the latter nomenclature suggests that it is an anhydride of the hypothetical sugar "lichose." The pure hexosan exhibits no rotation in a 2·5% aqueous solution at 20°, but at 70°, when, according to Pringsheim, deassociation is complete (M=162), it has $[\alpha]_D^{20}$ +8·7° (constant). Hence the optical inactivity cannot be due to the compensation of the activity of the aldehydic carbon atom by that of the four remaining carbon atoms, as assumed by Pringsheim, Knoll, and Kaston (A., 1925, i, 1385), but must be due to association. Pure lichohexosan triacetate prepared from

the hexosan has $[\alpha]_D$ −18·9° to −19·5° in chloroform (Pringsheim and Routala, *loc. cit.*, give −21·8° for "lichosan acetate"), whilst lichenin acetate prepared from lichenin either by the action of pyridine and acetic anhydride or sodium acetate and acetic anhydride at 60° (thus avoiding the drastic conditions employed by the other authors, *loc. cit.*), has $[\alpha]_D^{19}$ +35·6° in chloroform. Hence lichohexosan and lichenin cannot be identical, and the assumption that lichosan is the unit substance of lichenin (Pringsheim, Knoll, and Kaston, *loc. cit.*) cannot be upheld.

J. W. Baker.

Individual group of amylose from potato starch. M. Bergmann and E. Knehe (Annalen, 1927, 452, 141—150).—Acetylation of pure amylose prepared from potato starch by the method of Ling and Nanji (J.C.S., 1923, 123, 2666) with pyridine and acetic anhydride for 6—7 days at the ordinary temperature yields *amylose triacetate*, $C_6H_7O_5Ac_3$, $[\alpha]_D^{16}$ +176·7°. Further treatment of the product with pyridine and acetic anhydride for 7 days does not change its composition, and on hydrolysis with 0·5*N*-alcoholic potassium hydroxide it yields the original amylose, which can be reconverted into the same triacetate. The authors therefore conclude that amylose is composed of associated glucose anhydride units in the same manner as cellulose (cf. Hess, Weltzien, and Messmer, A., 1924, i, 142), and, contrary to the conclusion of Kuhn (*ibid.*, 1925, i, 636), believe that the production of maltose occurs through the secondary union of dextrose radicals.

J. W. Baker.

Inulin. II. L. Schmid and G. Bilowitzki (Monatsh., 1926, 47, 768—789).—Inulin and water-soluble starch dissolve slightly in cold and readily in warm butylamine or piperidine. Inulin also dissolves in phenol at 100° or 180°. It is recovered from these solvents unchanged in quantity and in specific rotation. Solutions of inulin in dry phenol show practically no cryoscopic depression; this solvent, therefore, unlike liquid ammonia (A., 1925, i, 1386), does not depolymerise inulin.

H. E. F. Notton.

Röntgen diagram of mercerised cellulose. R. O. Herzog (Ber., 1927, 60, [*B*], 600—603).—Characteristic differences are observed between the Röntgen diagrams of fibres in the natural and mercerised condition. Since cotton which has been esterified and de-esterified without destruction of its fibrous nature gives diagrams of the first type, whereas that which has been subjected to a precisely similar chemical treatment during which it has passed into solution gives diagrams of the second type, it is considered that mercerisation involves a purely physical change, as it is improbable that the act of dissolution causes chemical alteration.

H. Wren.

Reducing action of parchment paper used in dialysis. A. Gutbier, B. Ottenstein, and W. Jehring (Biochem. Z., 1926, 179, 426—431).—Parchment yields on extraction with water a reducing substance, apparently of a carbohydrate nature, which may be determined by Bang's method; it reduces gold chloride and ammoniacal silver nitrate solutions. In cases where reducible metallic preparations are being dialysed, a thorough preliminary washing of the parchment paper is recommended.

J. Pryde.

Lignin. II. Formaldehyde as product of the fission of lignin. K. Freudenberg and M. Harder (Ber., 1927, 60, [*B*], 581—585).—Under the conditions prescribed by Tollens for the determination of pentosans, lignin evolves formaldehyde to the extent of 0·6—0·8%, as deduced from its compound with barbituric acid. In like circumstances, piperonylic acid yields formaldehyde in one third the amount expected from its methylenedioxy-content, the remainder undergoing condensation with the liberated protocatechuic acid. Apparently formaldehyde is united to neighbouring hydroxyl groups in lignin as in piperonal, in which case the evolved formaldehyde represents only a portion of that present in the lignin. According to Tollens' method, the presence of pentoses or carbohydrates in "hydrochloric acid lignin" cannot be detected. Degradation of lignin by chlorine dioxide yields chlorinated, water-soluble products, whereas those derived from hexoses are insoluble in water. The presence of formaldehyde must be taken into account in the determination of pentosans in wood; pine wood contains about 1·5% less pentosan than previously assumed, owing to the presence of 0·20—0·25% of formaldehyde.

A modified method of isolating lignin from wood is described.

H. Wren.

Ultra-violet absorption spectrum of lignin. I. R. O. Herzog and A. Hillmer (Ber., 1927, 60, [*B*], 365—366).—The absorption spectra of sulphite waste liquor, technical ligninsulphonic acid, and Klason's α-ligninsulphonic acid resemble closely those of *iso*-eugenol and coniferin and differ widely from that of vanillin.

H. Wren.

Tetra-alkylammonium tetroxides and tetra-alkylammonium hydroxoxides. W. Traube, E. Burmeister, and B. Blaser (Ber., 1927, 60, [*B*], 439—446).—Tetramethylammonium hydroxide resembles potassium hydroxide in that its aqueous solutions when mixed with a large excess of hydrogen peroxide and evaporated to complete dryness at the atmospheric temperature under diminished pressure leave a yellow residue which dissolves in water or acid with evolution of oxygen and production of hydrogen peroxide, and hence contains *tetramethylammonium tetroxide*, $(NMe_4)_2O_4$, since the molecular ratio, $H_2O_2 : O_2$ is 1 : 1. An occasional preponderance of hydrogen peroxide indicates incomplete transformation of the intermediate tetramethylammonium peroxide. The tetramethylammonium radical does not suffer oxidation to an appreciable extent. Tetraethylammonium hydroxide yields a similar *tetroxide*, but if a smaller excess of hydrogen peroxide is used, the product contains the *peroxide*, $(NEt_4)_2O_2,H_2O_2$.

Solid tetramethylammonium hydroxide is very readily converted by ozone into an intensely red *compound*, for which the name *tetramethylammonium hydroxoxide* is proposed. The quantity of oxygen absorbed may attain 7% of the weight of the tetramethylammonium hydroxide; excess of ozone is quantitatively converted into oxygen by contact with the hydroxide. The hydroxoxide is decomposed by

water with evolution of " indifferent " oxygen (unable to liberate iodine from acidified potassium iodide), but without production of hydrogen peroxide. It therefore resembles closely the analogous compounds of potassium, rubidium, and cæsium, from which, however, it is distinguished by considerably greater stability (cf. A., 1916, ii, 613). H. WREN.

Derivative of αα′α″-triaminotrimethylamine. F. B. KIPPING and F. G. MANN (J.C.S., 1927, 528—530).—Bromomethylphthalimide, on treatment with gaseous ammonia in xylene solution, gives *triphthalimidotrimethylamine* (I), $(C_6H_4{:}C_2O_2{:}N{\cdot}CH_2)_3N$, m. p. 235° (+Me·$CO_2$H, m. p. 222—223°), which condenses with hydrazine hydrate to give (II), *triphthalylhydrazidotriaminotrimethylamine* (?), $N(CH_2{\cdot}NH{\cdot}C<^{C_6H_4}_{N{\cdot}NH}>CO)_3$, m. p. above 330°. Hydrolysis of (I) or (II) with hydrochloric acid gives formaldehyde and ammonia. αα′α″-Triaminotrimethylamine is therefore, like methylenediamine, unstable except in the form of its acyl derivatives. Bromomethylphthalimide reacts with pyridine, giving *phthalimidomethylpyridinium bromide*, m. p. 244°, which yields on hydrolysis phthalic acid, formaldehyde, ammonia, and pyridine. Reaction with anhydrous diethylamine gives phthalimide as the main product. M. CLARK.

Constitution and synthesis of spermidine, a base isolated from animal tissues. H. W. DUDLEY, O. ROSENHEIM, and W. W. STARLING (Biochem. J., 1927, 21, 97—103).—*Spermidine phosphate*, $(C_7H_{19}N_3)_2,3H_3PO_4,6H_2O$, m. p. 207—209°, is found in the mother-liquors after isolation of spermine phosphate (A., 1925, i, 294). The *picrate*, $C_7H_{19}N_3,3C_6H_3O_7N_3$, m. p. 210—212°, the *hydrochloride*, $C_7H_{19}N_3,3HCl$, slightly deliquescent, the *chloroaurate*, $C_7H_{19}N_3,3HAuCl_4$, m. p. 220—222°, and the m-*nitrobenzoyl* compound, m. p. 148—150° and 102° (probably hydrate), were prepared. The *chloroplatinate* and *mercurichloride* are very soluble.

Spermidine was proved by synthesis to be α-(γ′-aminopropylamino)-δ-aminobutane, $NH_2{\cdot}[CH_2]_3{\cdot}NH{\cdot}[CH_2]_4{\cdot}NH_2$, in the following way: α-(γ′-*phenoxypropylamino*)-δ-*aminobutane hydrobromide*, isolated as a by-product from the preparation of α-δ-*bis*-(γ′-*phenoxypropylamino*)*butane hydrobromide* used in the synthesis of spermine (A., 1926, 1128), was heated in a sealed tube at 100° with hydrobromic acid, yielding α-(γ-*bromopropylamino*)-δ-*aminobutane hydrobromide*, m. p. 234—235°. Spermidine was obtained from this bromo-compound by heating the latter in a sealed tube with alcoholic ammonia and distilling the resulting solid with potassium hydroxide in steam. The picrate, hydrochloride, chloroaurate, and *m*-nitrobenzoyl derivative prepared from the synthetic compound were found to be identical with the corresponding derivatives from natural spermidine.

The properties of spermidine are very similar to those of spermine. It accompanies the latter base through all the stages of isolation by the three methods described by the authors (A., 1925, i, 294). Like spermine, it gives a pyrrole reaction and is optically inactive. It appears in the lysine fraction on applying the method of Kossel and Kutscher. Its *phosphotungstate* is insoluble in acetone.

S. S. ZILVA.

Action of ammonia on propylene oxide. P. A. LEVENE and A. WALTI (J. Biol. Chem., 1927, 71, 461—463).—The aminopropanol recently prepared by the authors (A., 1926, 937) by the action of ammonia on propylene oxide, has been proved to be α-aminopropan-β-ol by the preparation of the phenylthiocarbamate, m. p. 107—108°. C. R. HARINGTON.

Synthesis of α-amino-β-hydroxy- and γ-amino-β-hydroxy-valeric acids. A. E. OSTERBERG (J. Amer. Chem. Soc., 1927, 49, 538—540).—Treatment of ethyl α-chloropropyl ether with ethyl sodiophthalimidomalonate suspended in cold benzene, followed by hydrolysis of the product with alcoholic sodium hydroxide and subsequent acidification, affords *α-amino-β-ethoxyvaleric acid*, m. p. 227°, together with a little glycine, from the former of which, by treatment with boiling hydrobromic acid, *α-amino-β-hydroxyvaleric acid*, m. p. 220°, is obtained. Reduction of β-hydroxylævulic acid oxime (cf. Wolff, A., 1891, 1185) with sodium amalgam and 50% aqueous alcohol affords *γ-amino-β-hydroxyvaleric acid*, m. p. 188°. Neither of the above aminohydroxyvaleric acids possesses the properties of Wilder's " bios " (cf. Eddy, Kerr, and Williams, A., 1925, i, 342).

F. G. WILLSON.

Action of α-oxides on the esters of amino-acids. II. A. KIPRIANOV (Ukraine Chem. J., 1926, 2, 236—249; cf. A., 1926, 950).—By the action of ethylene oxide on glycine, a syrup is obtained which slowly deposits crystals of *dihydroxydiethylaminoacetic acid*, m. p. 193°. The same product is formed by distilling the residual syrup (b. p. 160—200°/5 mm. with violent decomp.) and evaporating the distillate with water to dryness. The *picrate* (+H_2O), m. p. 95°, and *dibenzoyl* derivative are described. When the acid is distilled, water is eliminated and 1-*hydroxyethyl*-3-*morpholone*, b. p. 175—176°/5 mm., is formed [*chloroplatinate*, m. p. 190° (decomp.)]. Ethylene oxide and the ethyl ester of α-alanine yields *α-dihydroxydiethylaminopropionic acid*, m. p. 136° (*picrate*, m. p. 80—85°; *dibenzoyl* derivative, m. p. 42—43°). On distillation, water is eliminated, with formation of 2-*methyl*-1-*hydroxyethyl*-3-*morpholone*, b. p. 171°/5 mm. [*chloroplatinate*, m. p. 179—180° (decomp.)]. E. ROTHSTEIN.

Constitution of carnitine. I. Synthesis of α-hydroxy-γ-butyrotrimethylbetaine. J. W. C. CRAWFORD and J. KENYON (J.C.S., 1927, 396—402; cf. Engeland, A., 1921, i, 880).—β-Chloropropaldehyde diethylacetal, b. p. 74°/20 mm., $d_4^{18\cdot7}$ 0·9951, $n_D^{18\cdot7}$ 1·4206, prepared by the action of alcoholic hydrogen chloride on acraldehyde, is hydrolysed by water to β-chloropropaldehyde (*sodium hydrogen sulphite* compound). The *potassium hydrogen sulphite* compound, on treatment with potassium cyanide, gives *γ-chloro-α-hydroxy*-n-*butyronitrile*, b. p. 91·5°/3 mm., $d_4^{19\cdot1}$ 1·0795, $n_D^{19\cdot1}$ 1·4399 (*benzoyl* derivative, m. p. 59°, b. p. 147°/3—4 mm.; *acetyl* derivative, b. p. 116—117°/11 mm., 1·4342). The nitrile is converted by addition of trimethylamine into *γ-dimethylamino-α-hydroxy*-n-*butyronitrile methochloride*, m. p. 137°

[*chloroaurate*, m. p. 95°; *chloroplatinate*, m. p. 239—240° (decomp.)], which yields on hydrolysis with hydrochloric acid the hydrochloride of α-hydroxy-γ-butyrotrimethylbetaine. This compound gives a chloroaurate, m. p. 173°, and a chloroplatinate, m. p. 216° [the *chloroplatinate* of the *ethyl* ester of *α-hydroxy-γ-butyrotrimethylbetaine* (?) has m. p. 218° (decomp.)], and is therefore identical with that described by Fischer and Göddertz (A., 1911, i, 19). Their synthesis, questioned by Engeland (*loc. cit.*), is thus confirmed. Contrary to the statement of Engeland, α-hydroxy-γ-butyrotrimethylbetaine is decomposed by sulphuric acid at temperatures up to 130°, with evolution of carbon monoxide, and cannot therefore be identical with carnitine, which loses water, yielding *apo*carnitine.

The d-*camphorsulphonate* of the synthetic betaine could not be resolved. M. CLARK.

Isolation of histidine. H. B. VICKERY (J. Biol. Chem., 1927, 71, 303—307).—Addition of excess of 2 : 4-dinitro-α-naphthol-7-sulphonic acid to a solution containing histidine causes, even in presence of mineral acid, almost complete precipitation of the amino-acid as the *disulphonate*, $C_6H_9N_3O_2,2C_{10}H_6O_8N_2S,0{\cdot}5H_2O$, m. p. 251—254° (decomp.) after darkening at 246°; recrystallisation from water causes partial dissociation, but in presence of excess of the sulphonic acid this does not occur. The *monosulphonate* (+$3H_2O$), prepared from the theoretical amounts of histidine and the sulphonic acid in aqueous-alcoholic solution, sinters at 190° and has m. p. 212—214°. The free amino-acid can be recovered from the disulphonate by decomposition with dilute mineral acid and extraction of the sulphonic acid with butyl alcohol.

C. R. HARINGTON.

Reaction between diazonium salts and malonyldiurethane. M. A. WHITELEY and D. YAPP (J.C.S., 1927, 521—528).—Malonyldiurethane condenses with benzenediazonium salts in presence of acetic acid, giving the *phenylhydrazone* of *mesoxalyldiurethane* (I), m. p. 203° (decomp.), the constitution of which is shown by alternative preparation from monobromomalonyldiurethane and phenylhydrazine. In presence of sodium carbonate, the condensation yields the *urethane* derivative of *formazylcarboxylic acid* (II), m. p. 159° (decomp.). On treatment with potassium hydroxide, (I) and (II) undergo internal condensation, eliminating alcohol and yielding, respectively, the *carbourethane* (III), m. p. 203° (decomp.), and the *benzeneazo*-derivative (IV), m. p. 256° (decomp.), of 3 : 5-*diketo*-2-*phenyltetrahydro*-1 : 2 : 4-*triazine*. Hydrolysis of (II) or (IV) with hot 10% potassium hydroxide solution yields formazylcarboxylic acid.

$(CO{\cdot}NH{\cdot}CO_2Et)_2C{:}N{\cdot}NHPh$ (I.)

$NPh{-}N{:}C(CO{\cdot}NH{\cdot}CO_2Et){\cdot}CO{\cdot}NH{\cdot}CO$ (III.)

$(CO{\cdot}NH{\cdot}CO_2Et)C(N{:}NPh){:}N{\cdot}NHPh$ (II.)

$NPh{-}N{:}C{\cdot}C{\cdot}N{:}NPh$ (IV.)
$CO{\cdot}NH{\cdot}CO$

Similar condensations with the *p*-toluene- and the *o*-nitrobenzene-diazonium salt yield both the hydrazone and the formazyl compound. The *p*-nitrobenzenediazonium salt yields the hydrazono in two isomeric forms, but no formazyl compound, and each of the isomeric hydrazones yields the same triazine compound. The *m*-nitrobenzenediazonium salt yields only the hydrazone, which could not be converted into the corresponding triazine. The following are described: o-*nitrophenylhydrazone*, m. p. 208° (decomp.), m-*nitrophenylhydrazone*, m. p. 215°, p-*nitrophenylhydrazone*, m. p. 218° (decomp.) [*isomeride*, m. p. 208° (decomp.)], and p-*tolylhydrazone*, m. p. 186°, of *mesoxalyldiurethane*; *urethane* derivative, +Me·CO_2H, m. p. 105°, of *di*-o-*nitroformazylcarboxylic acid*; *urethane* derivative, m. p. 153°, of *di*-p-*tolylformazylcarboxylic acid*, m. p. 182°; *urethane* derivative, m. p. 205°, of 3 : 5-*diketo*-2-p-*nitrophenyltetrahydro*-1 : 2 : 4-*triazine*-6-*carboxylic acid*; *urethane* derivative, m. p. 218° (decomp.), of 3 : 5-*diketo*-2-p-*tolyltetrahydro*-1 : 2 : 4-*triazine*-6-*carboxylic acid*; 3 : 5-*diketo*-2-o-*nitrophenyl*-6-o-*nitrobenzeneazotetrahydro*-1 : 2 : 4-*triazine*, m. p. 224° (decomp.); 3 : 5-*diketo*-6-p-*tolueneazo*-2-p-*tolyltetrahydro*-1 : 2 : 4-*triazine*, m. p. 246°.

M. CLARK.

Decarboxylated peptides and their derivatives. I. J. VON BRAUN and W. MUNCH (Ber., 1927, 60, [*B*], 345—358).—Decarboxylated peptides, $NH_2{\cdot}CHR{\cdot}CO{\cdot}NH{\cdot}CH_2R'$, appear to be pharmacologically inactive (cf. Guggenheim, A., 1913, i, 773). Their *N*-monomethyl and monoethyl derivatives behave similarly, whereas the corresponding propyl and more highly alkylated compounds are so highly active that it is not possible to establish an exact relationship between degree of activity and magnitude of the alkyl group. The introduction of a second alkyl group renders the compound as inactive as the parent substance.

The decarboxylated peptides are in general prepared by introducing an α-halogenated fatty acid residue into an organic amine and treatment of the resultant halogenated amide with ammonia or a derivative thereof. Treatment of the chlorides of amino- or alkylamino-acids with organic bases offers no advantage with the simpler compounds. The reaction of primary and secondary amines on the chloroacylamides proceeds exclusively according to the scheme $NH_2R'' + Cl{\cdot}CHR{\cdot}CO{\cdot}NHR' \longrightarrow NHR''{\cdot}CHR{\cdot}CO{\cdot}NHR'$, even when R''=Me or Et. With ammonia, the change is more complex, and mixtures of primary, secondary, and tertiary products result. Increase in the weight of R favours the production of primary compounds, whilst, unexpectedly, a similar effect is produced by increase in R'. The following substances are described: *aminoacetethylamide* (*glycyldecarboxyalanine*), $NH_2{\cdot}CH_2{\cdot}CO{\cdot}NHEt$, b. p. 136—138°/13 mm. (*hydrochloride*, m. p. 134°; *picrate*, decomp. 162—164°); aminoacetmethylamide could not be isolated; *chloroacetisoamylamide*, b. p. 134—135°/13 mm., m. p. 0°, whence *aminoacetisoamylamide*, b. p. 159—160°/11·5 mm., m. p. 26° [very hygroscopic *hydrochloride*; *picrate*, m. p. 152—154° (decomp.)], and *dimethylaminoacetisoamylamide*, b. p. 136—137°/12 mm., m. p. +6—8° (very hygroscopic *hydrochloride*; *picrate*, m. p. 129°); *chloroacet*-β-*phenylethylamide*,

m. p. 67°, b. p. 186—189°/14 mm. (slight decomp.); *aminoacet-β-phenylethylamide, hydrochloride*, m. p. 165° after softening (the free base is non-crystalline and cannot be distilled without decomposition), and the secondary *compound*, $NH(CH_2{\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}CH_2Et)_2$, m. p. 109—110° (*hydrochloride*, m. p. 210°; *nitroso*-derivative, m. p. 185°), and tertiary *compound*, m. p. 111—112° (*hydrochloride*, m. p. 152°); *β-phenylethylaminoacet-β-phenylethylamide*, m. p. 35° (*hydrochloride*, m. p. 33°); *α-bromopropionisoamylamide*, b. p. 138°/12 mm., m. p. 24°; *α-aminopropionisoamylamide*, b. p. 144—145°/11 mm. (hygroscopic *hydrochloride*; *benzoyl* derivative, m. p. 112—113°), and the corresponding secondary *derivative*, m. p. 65° (*hydrochloride*, m. p. 217°); *α-methylaminopropionisoamylamide*, b. p. 145°/14 mm.; *α-ethylaminopropionisoamylamide*, b. p. 149°/13 mm.; α-n-*propylaminopropionisoamylamide*, b. p. 157°/14 mm. (*hydrochloride*, m. p. 135°; *picrate*, m. p. 86—87°); α-n-*butylaminopropionisoamylamide*, b. p. 168°/14 mm. (hygroscopic *hydrochloride*); α-iso*amylaminopropionisoamylamide*, b. p. 167—168°/10 mm. (*hydrochloride*, m. p. 193°); α-iso*hexylaminopropionisoamylamide*, b. p. 182—183°/13·5 mm. (*hydrochloride*, m. p. 183°); *α-bromopropion-β-phenylethylamide*, m. p. 92°; *α-aminopropion-β-phenylethylamide*, b. p. 199—201°/13 mm., m. p. 20—21° (hygroscopic *hydrochloride*); *α-β′-phenylethylamino-β-phenylethylamide hydrochloride*, m. p. 198—199° (non-crystalline base); *α-bromoisohexomethylamide*, b. p. 142—145°/13 mm., m. p. 70—71°; *α-aminoisohexomethylamide*, b. p. 146—147°/12·5 mm. (*picrate*, m. p. 157—159°); *α-bromoisohexoethylamide*, m. p. 93°; *α-aminoisohexoethylamide*, b. p. 145—146°/12 mm. (hygroscopic *hydrochloride*; *chloroplatinate*, decomp. 195—197°), and the corresponding secondary derivative (*hydrochloride*, m. p. 215°). The following α-alkylaminoisohexoethylamides are described: *methyl*, b. p. 139°/13 mm. (hygroscopic *hydrochloride*; *picrate*, m. p. 130°); *ethyl*, b. p. 145°/11 mm. (*hydrochloride*, m. p. 139°); *diethyl*, b. p. 141°/11 mm. (hygroscopic *hydrochloride*); n-*propyl*, b. p. 152°/13 mm. (*hydrochloride*, m. p. 128°; *picrate*, m. p. 150°); n-*butyl*, b. p. 161°/13 mm. (*picrate*, m. p. 83°; *hydrochloride*, m. p. 120°); iso*amyl*, b. p. 167°/13 mm. (*hydrochloride*, m. p. 129°); *di*isoamyl, b. p. 171—174°/12 mm. (very hygroscopic *hydrochloride*); iso*hexyl*, b. p. 179°/13 mm. (*hydrochloride*, m. p. 122°); *heptyl*, b. p. 188°/13 mm. (*hydrochloride*); n-*nonyl*, b. p. 204—206°/11 mm. (*hydrochloride*). *α-Bromo*isohexo-*β′-phenylethylamide*, m. p. 76°, yields with ammonia *α-amino*isohexo-β-*phenylethylamide hydrochloride*, m. p. 203—204° (non-crystalline *base*). *α-β″-Phenylethylamino*isohexo-β-*phenylethylamide* gives a *hydrochloride*, m. p. 214°. The reaction of *α-bromo-β-phenylpropionmethylamide*, m. p. 104°, is complicated by the tendency towards intramolecular loss of hydrogen bromide with formation of cinnammethylamide, but *α-amino-β-phenylpropionmethylamide hydrobromide*, m. p. 198—200°, can be obtained in modest yield. *α-Bromo-β-phenylpropion-β′-phenylethylamide* is rather more smoothly transformed into *α-amino-β-phenylpropion-β-′phenylethylamide*, m. p. 56° (m. p. 177—178°), *cinnam-β-phenylethylamide*, m. p. 127°, being also produced. *α-β″-Phenylethylamino-β-phenylpropion-β′-phenylethylamide hydrochloride*, m. p. 180°, is described. H. WREN.

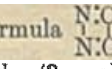
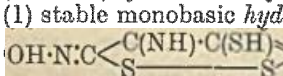
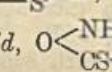
Specific action of peptidases. I. Fission of amides of substituted amino-acids. E. WALDSCHMIDT-LEITZ, W. GRASSMANN, and A. SCHAFFNER (Ber., 1927, **60**, [*B*], 359—364).—The action of peptidases towards aminoacetethylamide, α-aminopropion*iso*amylamide, α-amino*iso*hexomethylamide, α-amino*iso*hexoethylamide, aminoacetamide, α-amino-*iso*hexoamide (cf. von Braun and Munch, preceding abstract), glycylarsanilic, diglycylarsanilic, triglycylarsanilic, *p*-glycyl- and di-*p*-glycyl-aminobenzoic acids (cf. Giemsa and Tropp, A., 1926, 1162) has been investigated. The substances are smoothly and completely hydrolysed by intestinal erepsin, whereas no action is observed with erepsin-free trypsin activated by enterokinase. As with the parent peptides, hydrolysis by erepsin occurs asymmetrically when an amino-acid compound of the substrate has an asymmetric carbon atom. A definite, qualitative difference in the hydrolysis of peptamines by animal and vegetable erepsin is observed, since yeast peptidase has no action. H. WREN.

Mixed aquo-ammonocarbonic acids. L. A. PINCK and J. S. BLAIR (J. Amer. Chem. Soc., 1927, **49**, 509—514; cf. A., 1926, 277).—Guanylcarbamide (dicyanodiamidine) is converted, by the action of anhydrous alcohol in presence of hydrogen chloride at 140°, into carbethoxyguanidine (cf. Nencki, A., 1875, 479). Biuret affords similarly ethyl allophanate, which, when heated with alcohol and hydrogen chloride at 156—157°, is converted into urethane. Carbethoxyguanidine is not produced by heating carbethoxycyanamide with alcohol and ammonium chloride or nitrate, by heating ammonium carbethoxycyanamide, either alone or with alcoholic ammonia, at 110°, or by the action of cyanamide on urethane. Treatment of dicarbethoxycyanamide with ammonium nitrate in absolute alcohol at 100° affords *as-dicarbethoxyguanidine*, m. p. 184°, which indicates that Bassler's dicarbethoxycyanamide is also unsymmetrical (A., 1878, 214). Treatment of sodium dicyanodiamide with ethereal ethyl chloroformate at 90—100° affords *carbethoxydicyanodiamide*. F. G. WILLSON.

So-called "diethyl dicyanoglutaconate" and some derivatives. Y. URUSHIBARA (Bull. Chem. Soc. Japan, 1927, **2**, 26—36).—Pure "diethyl αγ-dicyanoglutaconate" (I), prepared by condensing ethyl cyanoacetate with iodoform and sodium ethoxide, gives a colourless sodio-derivative (cf. Errera, A., 1898, i, 297, 490, 632; Ruhemann and Browning, J.C.S., 1898, **73**, 280), and agrees in composition and mol. wt. with the formula $(C_{11}H_{12}O_4N_2)_2,H_2O$. Since it does not lose water when heated at 150°, it has probably the constitution $(C_{10}H_{12}O_4N){\cdot}CO{\cdot}NH{\cdot}C(NH)(C_{10}H_{12}O_4N)$. With bromine in chloroform solution, it yields a brick-red *perbromide*, $(C_{11}H_{12}O_4N_2)_2,H_2O,HBr,Br_6$, m. p. 146—149°, which is decomposed by moist ether into *αγ-dicarbethoxyglutaconamide hydrobromide*, $C_{11}H_{16}O_6N_2,HBr$, decomp. 180°, and bromine. The corresponding *picrate*, m. p. 196·5°, may be obtained from the hydrobromide or perbromide, or directly

from (I) and picric acid in aqueous alcohol. The hydrobromide, which gives no colour with ferric chloride, is converted by boiling with dilute hydrobromic acid into a diethyl dihydroxynicotinate (Guthzeit, A., 1899, i, 450), identical with that obtained by Ruhemann on boiling an alcoholic solution of (I). H. E. F. NOTTON.

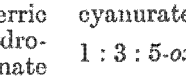
Reaction of organo-magnesium compounds with nitriles. Dimethylcyanamide. L. VUYLSTEKE (Bull. Acad. roy. Belg., 1926, [v], **12**, 535—544).—Magnesium phenyl bromide reacted vigorously with dimethylcyanamide to give, on treatment with sodium hydroxide solution, *dimethylbenzamidine*, b. p. 118°/11 mm., d_4^{20} 1·0160 (*dihydrochloride*, m. p. about 250°). The product of the reaction between dimethylcyanamide and magnesium benzyl chloride yielded, on treatment with water, an analogous compound, $CH_2Ph{\cdot}CH{:}N{\cdot}NMe_2$, converted by 20% sodium hydroxide solution into phenylacetic acid and dimethylamine. Phenylmalononitrile, m. p. 71°, separated on treating the original aqueous mass with hydrochloric acid. Finally, by treating the original reaction product with hydrochloric acid, followed by ammonium chloride and ammonia, a *compound*, $C_{19}H_{20}N_4$, m. p. 120—121° (decomp.), was obtained, formed by the union of the acidic function of the phenylmalononitrile with the basic function of the amidine compound. From the reaction of dimethylcyanamide with magnesium ethyl bromide, no definite product could be isolated except ethane. S. J. GREGG.

Two new acids of the cyanic series. B. MELIS (Annali Chim. Appl., 1927, **17**, 74—80).—The properties of ψ-thiocyanogen or perthiocyanogen, a product of the oxidation of thiocyanates, are best expressed by the formula  . The action of sodium hydroxide (3 mols.) on this compound (2 mols.) yields thiocyanate and two new acids: (1) stable monobasic *hydro-ψ-thiocyanic acid*,  ; (2) the unstable dibasic *oxyperthiocyanic acid*,  , which exists only in solution, but forms a stable *silver* salt.

T. H. POPE.

Colour reactions of nitroprusside. L. CAMBI (Annali Chim. Appl., 1927, **17**, 55—58).—Polemical against Tarugi (this vol., 46). The author's previous views are upheld (A., 1913, i, 606; 1914, i, 967) and the conclusion is reached that nitroprussides give complex salts (ferropentacyanides), often highly coloured, with all compounds containing groupings with mobile hydrogen able to react with free or combined nitrous acid to form *iso*nitroso- or nitroso-derivatives (cf. Küster, A., 1926, 821).

T. H. POPE.

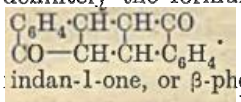
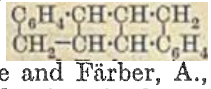
Carbimides. II. Transformations of methylcarbimide under the influence of triethylphosphine. K. H. SLOTTA and R. TSCHESCHE (Ber., 1927, **60**, [*B*], 295—301; cf. A., 1925, i, 1047).—Methylcarbimide, b. p. 37·4—37·8°, conveniently prepared by heating a mixture of potassium cyanate, potassium methyl sulphate, and finely-divided calcium oxide, is converted by triethylphosphine in cold, absolute ethereal solution into a mixture of trimethyl *iso*cyanurate, 2-*methylimino*-4 : 6-*diketo*-3 : 5-*dimethyl*-1 : 3 : 5-*oxdiazine*,  , m. p. 114°, and 2 : 4 : 6-*triketo*-3 : 5-*dimethyl*-1 : 3 : 5-*oxdiazine*, which sublimes at 255—258° (more conveniently prepared by addition of solid carbon dioxide to methylcarbimide dissolved in ether at −80°) and is hydrolysed by water to *s*-dimethylcarbamide. The methylimino-derivative is quantitatively converted by boiling water into αγε-trimethylbiuret, m. p. 126°; prolonged ebullition in solvents of high b. p. causes conversion into trimethyl *iso*cyanurate. It is transformed by hydrogen chloride in moist carbon tetrachloride into 2 : 4 : 6-triketo-3 : 5-dimethyl-1 : 3 : 5-oxdiazine. The latter substance is transformed by methyl alcohol and potassium hydroxide into *methyl dimethylallophanate*, $NHMe{\cdot}CO{\cdot}NMe{\cdot}CO_2Me$, b. p. 104—105°/15 mm., m. p. 47°; the corresponding *ethyl* ester, b. p. 105—106°/10 mm., m. p. 31°, and the *amide*, m. p. 149°, are described. α-*Nitroso*-αγ-*dimethylbiuret*, decomp. 101°, and αγ-*dimethyl*-ε-*ethylbiuret*, m. p. 78°, have been prepared.

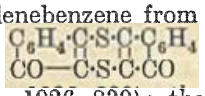
H. WREN.

Carbimides. III. The principle of symmetry in the formation of trimethylcyanuric esters. K. H. SLOTTA and R. TSCHESCHE (Ber., 1927, **60**, [*B*], 301—304; cf. preceding abstract).—Attempts to prepare cyanuric acid derivatives containing methyl groups attached to oxygen and nitrogen within the molecule, lead, in accordance with the principle of symmetry, to compounds having the methyl groups attached exclusively to oxygen or nitrogen or to mixtures of such compounds. Thus cyanuric acid is transformed by diazomethane into the *N*-trimethyl derivative, whereas its *O*-dimethyl compound, m. p. 186°, affords the *O*-trimethyl derivative. Cyanuric chloride and sodium methoxide (1 mol.) give unchanged material and *O*-trimethyl compound. Similarly, *N*-dimethylcyanuric acid, m. p. 222° (obtained by heating methylcarbamide at 230°), is transformed by the action of methyl iodide on its silver salt into the *N*-trimethyl derivative. *N*-Dimethylcyanuric acid could not be caused to react with thionyl chloride or phosphorus pentachloride. A mixture of the *O*- and *N*-trimethylcyanuric acid appears to result from the action of methyl iodide on silver cyanate or cyanurate.

H. WREN.

Phosphinocarboxylic acids. A. E. ARBUZOV and A. A. DUNIN (Ber., 1927, **60**, [*B*], 291—295; cf. A., 1914, i, 653; Nylén, *ibid.*, 1925, i, 1134).—Ethyl phosphinoacetate, b. p. 138·5—138·75°/10 mm., is hydrolysed by dilute hydrochloric acid at 100—120° to phosphinoacetic acid, m. p. 139·5°. β-Phosphinopropionic acid, m. p. 167—168° (Nylén, A., 1926, 826, records m. p. 178—180°), and its *barium* salt are described. α-Phosphinopropionic acid is too hygroscopic to permit analysis. Hydrolysis of ethyl phosphinoformate with concentrated hydrochloric acid yields only phosphorous acid. Ethyl phosphinoacetate resembles ethyl acetoacetate in possessing a reactive methylene group; it is converted by sodium and methyl iodide into ethyl α-phosphinopropionate, b. p. 143—144°/12 mm. H. WREN.

α-Truxillic acid, truxone, truxane, indene, and the so-called truxene. H. Stobbe and F. Zschoch (Ber., 1927, 60, [*B*], 457—473).—Attempts are described to eliminate the uncertainties indicated in the scheme: truxillic acid $(C_9H_8O_2)_2$ [bimolecular] ⟶ truxone (probably bimolecular) ⟶ truxene (bi- or ter-molecular) ⟶ truxenequinone [tribenzoylenebenzene] (termolecular). "Bromotruxone" is converted by zinc dust and acetic acid into the colourless truxone and the colourless, so-called, "dihydrotruxone," m. p. 132°; determinations of mol. wt. in boiling alcohol as well as in benzene and acetone indicate the formula $(C_9H_8O)_2$ for the latter substance. Truxone in boiling cumene and in camphor (cf. Carlsohn, this vol., 300) is also bimolecular. "Bromotruxone" is therefore dibromotruxone, $C_{18}H_{10}O_2Br_2$, dihydrotruxone is truxanediol, and truxone has definitely the formula of a dibenzoylene*cyclo*butane,  . Truxene, prepared from truxone, indan-1-one, or β-phenylpropionic acid, forms colourless crystals, m. p. 369—370° (decomp.); it is termolecular in boiling phenol or cumene, and hence is undoubtedly tribenzylenebenzene (I). The apparently simple reduction of truxone to truxene is therefore accompanied by a change in aggregation. If truxone is heated for a considerable time with amalgamated zinc and hydrochloric acid, truxane (dibenzylene*cyclo*butane),  , m. p. 116°, is obtained (cf. Stobbe and Färber, A., 1925, i, 19). If, however, the reduction is less prolonged, a "truxane oil" is obtained from which truxanediol separates. A similar oil is formed when the diol is converted into the corresponding iodide, which is subsequently treated with zinc and glacial acetic acid. The diol is therefore an intermediate product of the conversion of truxone into truxane. In a high vacuum, truxane can be distilled almost without decomposition, whereas when boiled under atmospheric pressure it becomes depolymerised to indene. It thus behaves similarly to many other *cyclo*butane derivatives and is to be regarded therefore as diindene. The relationship of truxane to indene is confirmed optically by observation of their absorption spectra in comparison with those of α-truxillic and *trans*-cinnamic acids. The possibility which is thus suggested that indene is a precursor of truxene is established by the formation of the latter in considerable amount when indene is heated at its b. p. for a protracted period; the trimerisation of indene is effected by condensation with loss of hydrogen, which causes "autoreduction" to hydrindene. The reaction truxone ⟶ truxene by the action of hydriodic acid and phosphorus at 180° consists of a normal production of bimolecular truxane, which becomes depolymerised at the temperature of the change to indene, from which termolecular truxene and hydrindene are derived. It is therefore proposed to substitute the name tribenzylenebenzene for truxene, reserving the latter for the unknown dibenzylene*cyclo*butadiene. Logically, the name "truxenequinone" must be replaced by tribenzoylenebenzene.

The formation of tribenzoylenebenzene from anhydrobisindanedione is due to the initial fission of the latter compound into two molecules of indanedione, followed by condensation of three unimolecular products or of one such product with a molecule of anhydrobisindanedione to the termolecular compound. A similar explanation is advanced for the formation of tribenzylenebenzene from indanone and for that of tribenzoylenebenzene from 2 : 3-dichloroindone or the dithiin,  as recorded by Brass and Mosl (A., 1926, 839); the di-indonylene of these authors is identical with tribenzoylenebenzene.

H. Wren.

Hydrogenation of xanthone. V. Ipatiev and N. Orlov (Bull. Soc. chim., 1927, [iv], **41**, 208—212).—See this vol., 251.

Acenaphthene. III. Nitro- and amino-derivatives of acenaphthenemonosulphonic acids. K. Dziewoński and T. Orzelski (Bull. Acad. Polonaise, 1926, **A**, 347—359).—In the nitration of acenaphthene-3-sulphonic acid or in the sulphonation of 5-nitroacenaphthene, the unsubstituted ring is attacked, as in the naphthalene series. Thus with chlorosulphonic acid in nitrobenzene, 5-nitroacenaphthene affords 5-*nitroacenaphthene*-7-*sulphonic acid* (*sodium* and *barium* salts; *chloride*; *methyl* ester, m. p. 146°), oxidised by sodium dichromate in acetic acid to 5-*nitro*-3-*sulphonaphthalene*-1 : 8-*dicarboxylic acid*. 5-*Aminoacenaphthene*-7-*sulphonic acid* is obtained on reduction of the nitro-sulphonic acid; the diazonium derivative of this with sodium formate, formic acid, and copper powder affords an acenaphthenemonosulphonic acid isomeric with the known 3- and 5-monosulphonic acids (A., 1924, i, 1178), and hence *acenaphthene*-4-*sulphonic acid* (*sodium* and *barium* salts; *amide*, m. p. 182—183°). Sodium amalgam in aqueous solution converts it into acenaphthene. Sodium acenaphthene-3-sulphonate with nitric acid (*d* 1·38) in acetic acid (cf. Morgan and Yarsley, A., 1926, 280) affords 6-*nitroacenaphthene*-3-*sulphonic acid* (*sodium* and *barium* salts; *chloride*; *methyl* ester, m. p. 143—144°), yielding on oxidation 6-*nitro*-2-*sulphonaphthalene*-1 : 8-*dicarboxylic acid*. 6-*Aminoacenaphthene*-3-*sulphonic acid* with sodium amalgam in aqueous solution affords 5-aminoacenaphthene, m. p. 108°. The above reactions establish the structure of the two isomeric nitroacenaphthenesulphonic acids. 1′-*Hydroxynaphthalene*-4′-*azo*-6-*acenaphthene*-4-*sulphonic acid*, violet-brown, dyeing wool in reddish-brown shades, 1′-*hydroxynaphthalene*-4′-*azo*-6-*acenaphthene*-3-*sulphonic acid*, dark violet, 7-*benzeneazo*-6-*aminoacenaphthene*-4-*sulphonic acid*, cherry-red, dyeing wool in Bordeaux-red shades, and 7-*benzeneazo*-6-*aminoacenaphthene*-3-*sulphonic acid*, dark red, are described.

R. Brightman.

Derivatives of fluorene. A. Korczyński, G. Karlowska, and L. Kierzek (Bull. Soc. chim., 1927, [iv], **41**, 65—74).—Attempts to obtain 2 : 2′-difluorenyl by the decomposition of 2-diazofluorene or by the action of copper on 2-iodofluorene in nitrobenzene or at 300° have been unsuccessful. 2-Iodo-

fluorene affords no Grignard reagent with active magnesium in ether, and attempts to achieve the synthesis by means of the benzidine transformation also failed. *2-Iodofluorene*, m. p. 128°, obtained by the action of iodine on fluorenylhydrazine hydrochloride in aqueous potassium iodide solution, is also formed by the action of iodine on a boiling alcoholic solution of fluorene in the presence of mercuric oxide. Potassium dichromate in acetic acid oxidises it to *2-iodofluorenone*, m. p. 142—143° (*phenylhydrazone*, m. p. 146°). Bromination of 2-nitrofluorene in boiling acetic acid affords *9-bromo-2-nitrofluorene*, m. p. 143°, yielding on oxidation 2-nitrofluorenone, m. p. 222°, and on reduction in acetic acid solution with zinc and hydrochloric acid, 2-aminofluorene. With copper powder in boiling nitrobenzene, 9-bromo-2-nitrofluorene affords *2 : 2′-dinitrobisdiphenylene-ethane*, m. p. 257—258°, which is oxidised by lead oxide at 150—180° or by sodium dichromate and acetic acid to 2-nitrofluorenone; boiling in nitrobenzene converts it into *2 : 2′-dinitrobisdiphenylene-ethylene*, m. p. above 360°.

Addition of an alcoholic solution of 2-aminofluorene and potassium acetate to a concentrated aqueous solution of fluorene-2-diazonium chloride affords *2 : 2′-diazoaminofluorene*, m. p. 193°; *2 : 2′-diazoaminofluorenone*, m. p. 238—239°, is similarly prepared. *2′-Diazofluorene-2′-aminofluorenone* from aminofluorene and fluorenonediazonium chloride has m. p. 212°; prepared from fluorenediazonium chloride and aminofluorenone, it melts at 230°. It is not established whether the difference in m. p. is due to isomerism or to impurities. Fluorene-2-diazonium chloride and dimethylaniline in alcohol afford *4-dimethylaminobenzeneazo-2′-fluorene*, m. p. 227°. *4-Dimethylaminobenzeneazo-2′-fluorenone* is similarly prepared. R. BRIGHTMAN.

Fluorene series. C. COURTOT and C. VIGNATI (Compt. rend., 1927, **184**, 607—609).—The structure of the 2-bromo-7-nitrofluorene recently described (this vol., 234) has now been definitely established by conversion of the bromoaminofluorenone, m. p. 233—234°, obtained from it into 2 : 7-dibromofluorenone, m. p. 197—198° (Schmidt and Bauer, A., 1906, i, 28), by means of the Sandmeyer reaction. *2-Chlorofluorene*, m. p. 97°, is similarly obtained from 2-aminofluorene. R. BRIGHTMAN.

Electrochemical oxidation of benzene homologues. IV. *o*-Xylene. F. FICHTER and M. RINDERSPACHER (Helv. Chim. Acta, 1927, **10**, 40—45; cf. Law and Perkin, J.C.S., 1907, **91**, 258).—Electrochemical oxidation of *o*-xylene emulsified in 2*N*-sulphuric acid with a lead dioxide anode and lead cathode, using a diaphragm, yields *o*-tolualdehyde (17—22%), *o*-toluic acid (by oxidation of the side-chain), 3 : 4-dimethylphenol (0—6%), toluquinone (7—12%), 1 : 6-dimethyl-*p*-benzoquinone (0—1·3%), and resinous matter (33—44%) probably containing a di-*o*-xylenol. The current efficiency is small. 3 : 4-Dimethylphenol dissolved in *o*-xylene is oxidised in a similar way to resinous di-*o*-xylenol (65—76%), toluquinone (16—28%), and 1 : 6-dimethyl-*p*-benzoquinone (0—6%). The formation of the last two compounds is not due to the presence of impurities in the starting materials, but to the intermediate formation of 3 : 4-dimethyl-ψ-cumol (Bamberger, A., 1903, i, 557), which may then isomerise to the *m*-xyloquinone or lose a methyl group, giving toluquinone. The presence of 3 : 4-dimethyl-ψ-quinol is shown by the formation of an azo-compound from it with *p*-nitrophenylhydrazine. H. E. F. NOTTON.

Electrochemical oxidation of benzene homologues. V. Ethylbenzene. K. ONO (Helv. Chim. Acta, 1927, **10**, 45—52).—Electrochemical oxidation of ethylbenzene emulsified in *N*-sulphuric acid (cf preceding abstract) without a diaphragm afforded benzaldehyde (0·99%), acetophenone (0·39%), and traces of *s*-diphenyldimethylethylene glycol and ethylquinol, the greater part of the material being oxidised to carbon dioxide and water. In a mixture of acetone and 2*N*-sulphuric acid, the products are acetophenone (2·42%), *p*-ethylphenol (1·78%), phenylmethylcarbinol (0·04%), *p*-benzoquinone (0·74%), ethyl-*p*-benzoquinone (3·37%), and a *diethyldiphenol* (3·59%), m. p. 131°, together with a large quantity of resin. In neither case was β-phenylethyl alcohol obtained (cf. Law and Perkin, A., 1905, i, 761). In order to elucidate the course of the reaction, *o*- and *p*-ethylphenols were oxidised in a similar way. The latter gave the diethyldiphenol, m. p. 131°, with traces of *p*-benzoquinone and acetic acid, whilst the former gave ethyl-*p*-benzoquinone (10%), identified as *ethylquinol diacetate*, m. p. 71°. The mode of formation of these products is discussed. H. E. F. NOTTON.

Preparation of *p*-dinitrobenzene. G. CHAPAS (Bull. Soc. chim., 1927, [iv], **41**, 193—196).—Addition of the sodium nitrite to the diazonium salt solution before mixing with the molecular copper, and final decomposition of the excess nitrite with nitric acid (63%), afford on steam distillation slightly higher (59·5%) yields of *p*-dinitrobenzene than those obtained by Vesely and Dvorak (A., 1922, i, 690). The author concludes that neither the Sandmeyer nor the Gattermann method for the introduction of groups by the diazonium reaction is quantitative. R. BRIGHTMAN.

Reactivity of halogenated hydrocarbons. I. Transformations with α- and β-bromonaphthalene. J. LOEVENICH and A. LOESER (Ber., 1927, **60**, [*B*], 320—326).—Reactivity of halogen atoms attached to the aromatic nucleus depends, not only on their tenacity, but also to a great extent on the substance with which action occurs. Bromobenzene is generally less active than the bromonaphthalenes, but a general decision cannot be made between the reactivities of the latter compounds. Bromobenzene does not react with potassium cyanide in boiling ethylene glycol, whereas α- and β-bromonaphthalenes are converted into the corresponding naphthoic acids in about 15% yield. β-Bromonaphthalene, ethyl chloroformate, and sodium amalgam give a 12·5% yield of β-naphthoic acid (after hydrolysis of the primary ester). α-Bromonaphthalene and benzamide afford benz-α-naphthalide in 51·4% yield, but reaction does not occur with salicylamide; with β-bromonaphthalene, the yields of the naphthalides are 42·3% and 18·4%, respectively, whereas with

bromobenzene the yield is about 50% of the anilide in each case. Sodium acetate converts the α- and β-bromonaphthalenes into the corresponding naphthols in 42·7% and 12% yield. Magnesium and carbon dioxide transform β-bromonaphthalene mainly into ββ′-dinaphthyl, whereas α-bromonaphthalene gives α-naphthoic acid in almost quantitative yield. In the formation of ethers from aryl halides and alkali aryl oxides, bromobenzene and α-bromonaphthalene are more reactive than β-bromonaphthalene. Benzophenone, β-bromonaphthalene, and sodium afford naphthalene (31·2%) and diphenyl-β-naphthylcarbinol (66·2%), the reaction thus resembling that of bromobenzene. H. WREN.

Synthesis of *meso*-alkyl and *meso*-aryl anthracene derivatives. I. E. DE B. BARNETT, J. W. COOK, and I. G. NIXON (J.C.S., 1927, 504—512).—*o*-Benzoylbenzoic acid is reduced with zinc dust and ammonia to *o*-benzylbenzoic acid (*methyl* ester, b. p. 320°; *ethyl* ester, b. p. 325°; *phenyl* ester), contrary to the statement of Ullmann (A., 1896, i, 563), and the reduced acid is converted quantitatively by concentrated sulphuric acid into anthrone (cf. Gresley, A., 1886, 1028). Magnesium phenyl bromide converts the esters of benzylbenzoic acid into a mixture of 9 : 9-diphenyl-9 : 10-dihydroanthracene and s-oo′-*dibenzylpinacol*, $[CH_2Ph{\cdot}C_6H_4{\cdot}CPh(OH){\cdot}]_2$, m. p. 175°; the pinacol is oxidised by chromic acid to *o*-dibenzoylbenzene. *Hydroxyphenyldimethylphthalan*, m. p. 118°, obtained from dimethylphthalide and magnesium phenyl bromide, on distillation yields o-iso*propenylbenzophenone*, b. p. 208—209°/45 mm., m. p. 44°, this substance being oxidised by chromic acid to *o*-benzoylbenzoic acid. *Hydroxyphenyldiethylphthalan* has m. p. 94—95°. From *o*-dibenzoylbenzene and magnesium phenyl bromide, hydroxytriphenylphthalan is probably obtained, since heating the product at 300° yields diphenylanthrone. This last substance on reduction with zinc dust and acetic–hydrochloric acids yields *tetraphenyltetrahydrodianthryl*, $\left(\begin{matrix}CPh_2{\cdot}C_6H_4\\ |\\ C_6H_4{\cdot}CH-\end{matrix}\right)_2$, m. p. above 340°, the same substance being produced when diphenyldihydroanthracene is heated in a current of oxygen. 9 : 9-*Diphenyl*-10 : 10-*diphenylmethylene*-9 : 10-*dihydroanthracene*, $\begin{matrix}CPh_2{\cdot}C_6H_4\\ |\\ C_6H_4{\cdot}C{:}CPh_2\end{matrix}$, m. p. 286°, is obtained by heating 9 : 9-diphenyl-9 : 10-dihydroanthracene with benzophenone chloride, and 10-*chloro*-9 : 9 : 10-*triphenyl*-9 : 10-*dihydroanthracene*, m. p. 193—194°, is prepared by the action of hydrogen chloride on triphenyldihydroanthranol. 9 : 9 : 10-Triphenyl-9 : 10-dihydroanthracene is best obtained by reducing the anthranol with sodium and amyl alcohol. Aluminium chloride converts 9 : 9-diphenyl-9 : 10-dihydroanthracene, in carbon disulphide solution, into 9-phenylanthracene, and 9 : 10-diphenyldihydroanthracene mainly into 9 : 10-diphenylanthracene. Methyl and *ethyl triphenylmethane*-o-*carboxylates*, m. p. 69°, react with magnesium phenyl bromide, giving *diphenyl*-ωω-*diphenyl*-o-*tolylcarbinol*, m. p. 218° (cf. Haller and Guyot, A., 1904, i, 660). H. BURTON.

Synthesis of triphenyl. R. KUHN and A. WINTERSTEIN (Ber., 1927, 60, [*B*], 432—434; cf. Pummerer and Bittner, A., 1924, i, 381).—Reduction of cinnamaldehyde by zinc–copper couple affords triphenyl (*p*-diphenylbenzene), m. p. 209—210°, in addition to hydrocinnamoin. The identity of the hydrocarbon is established by its conversion successively into *p*-phenylbenzoic acid and diphenyl. H. WREN.

Coloured hydrocarbons. IV. Dehydrogenation of the difluorenyls. V. Difulvenes and their hydrogen derivatives. VI. Absorption spectra of the difulvenes. A. A. VANSCHEIDT (J. Russ. Phys. Chem. Soc., 1926, 58, 249—269, 269—288, 289—306).—IV. The mobile hydrogen atoms of the >CH·CH< groups of the difluorenyls can be removed by atmospheric oxidation and by the action of silver oxide and other silver salts. Difluorenyl forms an alkali derivative by the action of alcoholic potassium hydroxide. Agitation with air in cold pyridine gives the coloured bisdiphenylene-ethene and the alkali peroxide, $>CK{\cdot}CK< + O_2 = >C{:}C< + K_2O_2$. This method has been applied with success to other difluorenyl derivatives. Prolonged agitation in air gives further oxidation products. s-*Diphenylene-di*-α-*naphthylene-ethylene*. $\begin{matrix}C_6H_4\\ C_{10}H_6\end{matrix}>C{:}C<\begin{matrix}C_6H_4\\ C_{10}H_6\end{matrix}$, m. p. 317—318°, as-*diphenylenedi*-α-*naphthylene-ethylene*, m. p. 315°, *phenylenetri*-α-*naphthylene-ethylene*, m. p. about 300°, and tetra-α-naphthylene-ethylene, are described. All the above compounds can be easily reduced or oxidised to colourless substances. The hydrocarbons can also be prepared by the action of sodium on a boiling xylene solution of the difluorenyls. Prolonged action gives a brownish-red, insoluble metallic derivative, but the hydrocarbon is regenerated by vigorous agitation in air.

Silver oxide in a mixture of ammonia and pyridine or silver acetate in pyridine readily oxidises the difluorenyls. Metallic silver is precipitated. The absence of alkali hydroxides renders the resulting hydrocarbons much more stable to air. *Tetra*-α-*naphthylene-ethane*, m. p. 357°, can be prepared pure by this method from tetranaphthofluorenyl and silver acetate in boiling pyridine. The other difluorenyls give by this method compounds identical with those obtained by atmospheric oxidation, except bischrysofluorenyl and bisdiphenylene-ethane, which give amorphous, orange precipitates, probably further oxidation products.

Oxy-salts of copper and mercury oxidise only the highly reactive bisdinaphthofluorenyl. The action is very slow, as also when quinoline is used as a solvent.

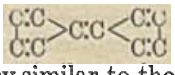
V. The colour of the naphthodifulvenes changes from orange-red to dark green with increase in number of naphthalene nuclei. The hydrodifulvenes have a high temperature coefficient of solubility, whereas the difulvenes are readily soluble in the cold. Naphthalene nuclei depress the solubility in both classes of compounds. The difulvenes have a higher m. p. than the hydrodifulvenes, except in the case of tetraphenylene-ethene; they also differ in crystalline structure. They react readily with warm, concentrated sulphuric acid, showing the phenomena of halochromism, but are almost unaffected by alcoholic potassium hydroxide (except tetranaphthylmethene),

whereas the hydrodifulvenes give no colour with sulphuric acid, but react with the alkali to give brown, metallic derivatives.

In pyridine, both oxidation of the hydrodifulvenes by silver salts, air, etc., and the reduction of the fulvenes by hydrogen, platinum-black, hydrogen sulphide, stibine, and ammonium sulphide are easy, especially if there are several naphthalene nuclei in the molecule. Thus the polynaphthalene derivatives lose their hydrogen when heated with the oxy-salts of copper and mercury, *p*-benzoquinone, or iodine.

Tetraphenylenemethene adds two atoms of bromine to the central double linking, but its naphtho-derivatives substitute bromine in the nucleus, preserving the chromophore grouping.

VI. Phenyldibenzofulvene, $CHPh{:}C(C_6H_4)_2$, and diphenyldibenzofulvene, $CPh_2{:}C(C_6H_4)_2$, were found to lack the characteristic bands in the ultra-violet of the fluorenes, but did not show a peculiar spectrum of their own, whereas the difulvenes all showed a spectrum type differing markedly from that of the fluorenes, both in the ultra-violet and also in the visible portion. The absorption bands persist even when the solution layers are reduced to 1/30 of the initial thickness, thus showing much greater absorbing power than the quinones.

The introduction of naphthalene nuclei shifts the bands towards the red, but does not alter their nature. These results show that a "difulvene" chromophore of the structure  exists. The absorption curves are very similar to those of indigotin and thioindigotin. Further analogies between the difulvene and indigotin groups are traced, which lend support to the Claaz formulation. M. Zvegintzov.

Perylene and its derivatives. XII. A. Zinke, K. Funke, and N. Lorber (Ber., 1927, 60, [*B*], 577—581; cf. A., 1925, i, 383, 384).—The action of tribromophenol and aluminium chloride on perylene in nitrobenzene solution (cf. Kohn, A., 1912, i, 760) leads unexpectedly to the production of 4 : 10-dichloroperylene, identified by conversion into 4 : 10-dichlorodinitroperylene. Under certain conditions, aluminium chloride appears able to chlorinate perylene, although reaction between the compounds does not occur at 100—150°. In the presence of nitrobenzene as oxidising agent, perylene is transformed by aluminium chloride or bromide into 4 : 10-dichloroperylene or 4 : 10-dibromoperylene, m. p. 290°; if manganese dioxide is also present, 3 : 4 : 9 : 10-tetrachloroperylene is produced. Perylene and phosphorus pentachloride in nitrobenzene afford 4 : 10-dichloroperylene, whereas hexachloroperylene results from di- or tetra-nitroperylene. Dinitroperylene is obtained by the action of nitric acid (*d* 1·2) on perylene in carbon tetrachloride. Conversion of perylene into 4 : 10-dichloroperylene by nascent chlorine is effected by the addition of sodium dichromate in acetic acid to a solution of perylene and acetic acid in nitrobenzene, through which hydrogen chloride is continuously passed. 4 : 10-Dibromoperylene is analogously prepared by addition of aqueous sodium bromide and acetic acid and hydrogen peroxide and acetic acid to perylene dissolved in nitrobenzene. H. Wren.

Action of sulphuric acid on perylene. C. Marschalk (Bull. Soc. chim., 1927, [iv], 41, 74—81).—Sulphonation of perylene with sulphuric and acetic acids at 75—80° affords a mixture of *perylene*-3 : 9-*disulphonic acid* and *perylene*-3 : 10-*disulphonic acid*, the former being the less soluble. Bromine in acetic acid converts both acids into the corresponding dibromoperylene, a reaction which establishes their constitution. On fusion with potassium hydroxide at 180°, the 3 : 9-disulphonic acid affords a yellow product, probably a hydroxyperylenesulphonic acid; at 250°, the mass gives an orange solution in water, with green fluorescence, from which air oxidation precipitates a brown substance differing from the violet quinone obtained by the action of sulphuric acid on 3 : 9-dibromoperylene. Perylene-3 : 10-disulphonic acid when fused with alkali at 270—280° affords a similar product, accompanied by sublimation of perylene. Aqueous sodium hydroxide (*d* 1·38) is without action on these disulphonic acids even at 200°. The *sodium* salts (greenish-yellow) of these acids are described. Perylene-3 : 10-quinone is readily obtained by the action of nitrosylsulphuric acid on perylene at 70—100°. R. Brightman.

Thermal decomposition of benzylideneaniline. G. Pyl (Ber., 1927, 60, [*B*], 287—291).—Benzylideneaniline is decomposed by heat into benzonitrile and benzene and into phenanthridine and hydrogen. At 600°, in a porcelain tube, the formation of phenanthridine is not appreciable; maximum yields (2·3%) of the base are obtained at 800°, whereas at 900° it appears to suffer decomposition. Substitution of iron for porcelain or addition of iron turnings, iron oxide, nickel or its oxide, aluminium oxide, or ignited bauxite does not improve the yield of base, whereas iron appears to favour the production of benzonitrile. The phenanthridine does not owe its origin to benzonitrile and aniline (always produced in small amount during the change) or to benzylaniline. Nascent benzylideneaniline does not give better results than the pre-formed compound. H. Wren.

Decomposition of *O*-benzoyldibenzylhydroxylamine. S. Gambarjan and O. Cialtician (Ber., 1927, 60, [*B*], 390—391; cf. A., 1925, i, 1260).—*O*-Benzoyldibenzylhydroxylamine, m. p. 95·5—96·5°, prepared by the action of a slight excess of dibenzylamine on benzoyl peroxide in boiling ethereal solution, is very readily hydrolysed to dibenzylhydroxylamine and is converted in boiling xylene into benzoic acid and benzylbenzylideneamine. H. Wren.

Inhibitory effect of substituents in chemical reactions. I. Reactivity of the amino-group in substituted arylamines. G. M. Dyson, H. J. George, and R. F. Hunter (J.C.S., 1927, 436—445).—Primary aromatic amines react with thiocarbonyl chloride, yielding thiocarbamyl chlorides, which in presence of water usually eliminate hydrogen chloride, giving thiocarbimides. If an inhibitory group (*e.g.*, bromine, see this vol., 141) is present in the benzene nucleus, elimination of hydrogen chloride is difficult and *s*-diarylthiocarbamides are produced instead of thiocarbimides. The results obtained show that combinations of nuclear methyl groups, hydroxy-

or alkyloxy-substituents do not affect thiocarbimide formation, whereas halogeno-, nitro-, or cyano-groups show inhibitory action, two *o*-chlorine atoms stopping the action completely. Sulpho- and carboxyl groups are markedly inhibitory. The results are not explicable by the steric hindrance hypothesis. The following thiocarbimides were prepared: m-*xylyl*-2-, b. p. 247°/760 mm.; o-*xylyl*-3-, b. p. 262—263°/760 mm.; o-*anisyl*-, b. p. 266—267°/760 mm.; m-*anisyl*-, b. p. 267°/760 mm.; 2 : 5-*dimethoxyphenyl*-, m. p. 32°; 3 : 4-*dimethoxyphenyl*-; o-*ethoxyphenyl*-, b. p. 273—275°/760 mm.; m-*ethoxyphenyl*-, b. p. 278°/758 mm.; o-*carbethoxyphenyl*-, b. p. 150—151°/1 mm.; m-*carbethoxyphenyl*-, b. p. 152°/10 mm.; p-*carbethoxyphenyl*-, m. p. 58°; p-*dimethylaminophenyl*-, m. p. 67°; p-*acetylphenyl*-, m. p. 76°; m-*cyanophenyl*-, an oil, decomp. at 250°; p-*cyanophenyl*-, m. p. 45°; 2 : 5-*dicyanophenyl*-, decomp. without melting; o-*bromophenyl*-, b. p. 257°/770 mm.; 2 : 5-*dibromophenyl*-, b. p. 240°; m. p. 17—18°; o-*iodophenyl*-, m. p. 39°; m-*iodophenyl*-, m. p. 46°; 3 : 5-*dibromo*-o-*tolyl*-, m. p. about 25°, b. p. 280°; 3-*nitro*-o-*tolyl*-, m. p. 69°; 2-*nitro*-4-*ethoxyphenyl*-, m. p. 78°. 2 : 6-Dichloro-, -dibromo-, -di-iodo-*p*-nitroanilines, 4 : 6-dibromo-*o*-nitroaniline, 2 : 4 : 6-tribromo-*m*-nitroaniline, and sulphanilic acid do not react with thiocarbonyl chloride. The thiocarbimides, on treatment with warm alcoholic ammonia, yield the following thiocarbamides: m-*xylyl*-2-, m. p. 190°; o-*xylyl*-3-, m. p. 182°; o-*anisyl*-, m. p. 148—149°; m-*anisyl*-, m. p. 160°; 2 : 5-*dimethoxyphenyl*-, m. p. 161°; 3 : 4-*dimethoxyphenyl*-, m. p. 234°; o-*ethoxyphenyl*-, m. p. 126°; m-*ethoxyphenyl*-, m. p. 167°; m-*carbethoxyphenyl*-, m. p. 294—295°; p-*carbethoxyphenyl*-, m. p. 159°; p-*dimethylaminophenyl*-, m. p. 190°; p-*acetylphenyl*-, m. p. 215° (decomp.); m-*cyanophenyl*-, m. p. 137°; p-*cyanophenyl*-, m. p. 169°; 2 : 5-*dicyanophenyl*-, m. p. 228°; o-*bromophenyl*-, m. p. 125°; 2 : 5-*dibromophenyl*-, m. p. 130°; o-*iodophenyl*-, m. p. 157°; m-*iodophenyl*-, m. p. 160°; and 2-*nitro*-4-*ethoxyphenyl*-, m. p. 177°. Condensation of the thiocarbimides with the corresponding arylamines yields the *s*-diarylthiocarbamides: s-*di*-m-*xylyl*-2-, m. p. 208°; s-*di*-o-*anisyl*-, m. p. 134°; s-*di*-m-*anisyl*-, m. p. 126°; s-*bis*-2 : 5-*dimethoxyphenyl*-, m. p. 127°; s-*bis*-3 : 4-*dimethoxyphenyl*-, m. p. 140°; s-*di*-o-*ethoxyphenyl*-, m. p. 125°; s-*di*-m-*ethoxyphenyl*-, m. p. 115°; s-*di*-m-*carbethoxyphenyl*-, decomp. without melting; s-*di*-p-*carbethoxyphenyl*-, m. p. 165°; s-*di*-p-*acetylphenyl*-, m. p. 198°; s-*di*-m-*cyanophenyl*-, m. p. 144°; s-*di*-p-*cyanophenyl*, m. p. 171°; s-*di*-o-*bromophenyl*-, m. p. 157°; s-*bis*-2 : 5-*dibromophenyl*-, m. p. 154°; and s-*di*-o-*iodophenyl*, m. p. 164° (decomp.). s-*Bis*-3 : 5-*dinitrophenyl*-, m. p. 160°; s-*di*-o-*carboxyphenyl*-, m. p. 300° (decomp.), and s-*di*-p-*acetamidophenyl*-*thiocarbamides*, m. p. 220° (decomp.), are formed directly from the substituted aniline and thiocarbonyl chloride. The *o*-substituted thiocarbimides have an unpleasant. pungent odour, whilst the *p*-substituted have the odour of aniseed. H. BURTON.

p-Cymene. VI. 6-Nitro-2-amino-p-cymene and new azo-dyes. A. S. WHEELER and C. R. HARRIS (J. Amer. Chem. Soc., 1927, 49, 494—499).—Addition of *p*-cymene to concentrated nitric and sulphuric acids (1 : 2) at below 0° affords chiefly 2 : 6-dinitro-*p*-cymene, m. p. 54° (cf. Alfthan, A., 1920, i, 253), together with mono- and di-nitrotoluenes. Reduction of the dinitrocymene with ammonium sulphide yields 6-*nitro*-2-*amino*-p-*cymene*, yellow, m. p. 53° (*hydrochloride*, m. p. 207—208°, slight decomp. at 175°; *hydrobromide*, m. p. 233° after darkening at 210—230°; *sulphate*, m. p. 115—140°; *nitrate*, m. p. 165° after darkening at 155°; *acetyl* derivative, m. p. 115°; *benzoyl* derivative, m. p. 179°). Boiling nitric acid (*d* 1·5) converts the dinitrocymene into 2 : 6-dinitro-*p*-toluic acid, whilst fuming nitric acid at 130° affords 2 : 6-dinitroterephthalic acid. The following *dyes* were prepared from the diazotised nitroamine and the components mentioned: phenol, claret-brown, m. p. 240°; resorcinol, red, m. p. 253°; thymol, chocolate, m. p. 242°; carvacrol, bluish-black, m. p. 216°; β-naphthol, carmine, m. p. 251°; α-naphthol-2-sulphonic acid, grenadine-red, m. p. 243°; α-naphthol-4-sulphonic acid, carmine, m. p. 256°; and 1 : 8-dihydroxynaphthalene-3 : 6-disulphonic acid, purple, m. p. not below 325°. The shades given by these dyes on textiles are listed, as well as their colour reactions with concentrated sulphuric acid.

F. G. WILLSON.

Ammonium character of tri- and di-arylamines. II. E. WEITZ and H. W. SCHWECHTEN (Ber., 1927, 60, [*B*], 545—551).—The salt-like nature of triarylaminium compounds (this vol., 49) is established further by the observation that tri-*p*-tolylaminium perchlorate and 1 : 1′-dibenzyl-4 : 4′-dipyridinium dichloride in concentrated alcoholic solution give an immediate precipitate of 1 : 1′-dibenzyl-4 : 4′-dipyridinium perchlorate (cf. A., 1922, i, 366), whilst the solution retains its intensely blue colour. When a solution of tri-*p*-tolylaminium perchlorate in methyl alcohol is diluted with the same solvent, the intensity of the colour rapidly diminishes and decomposition ensues. When, however, the solvent is methyl alcohol containing 2% of perchloric acid (70%), the solution closely obeys Beer's law. The repression of dissociation by addition of the acid is considered to exclude the possibility that the perchlorate is a quinhydrone, $2N(C_7H_7)_3,(ClO_4)_2$. Evidence is adduced in favour of the view that the compound $N(C_7H_7)_3,SbCl_5$ isolated by Wieland and the *product* $N(C_7H_7)_3,SbBr_5$, obtained from tri-*p*-tolylamine, phosphorus tribromide, and bromine, are salt-like in nature and contain quadrivalent antimony. A similar view is scarcely tenable for the compound $N(C_7H_7)_3,PCl_5$, but it is probable that this compound contains a greater proportion of chlorine. This hypothesis is strengthened by the production from ferric chloride of ferrous chloride and a complex aminium salt. Further, halides which readily form complex compounds but have no oxidising action ($HgCl_2$, $AlCl_3$, $BiCl_3$) do not give a blue coloration with tri-*p*-tolylamine except after addition of halogen. Treatment of di-*p*-tolylamine with iodine and silver perchlorate in ether or glacial acetic acid gives unstable blue solutions which doubtless contain the aminium perchlorate; the compound from di-*p*-tolylmethylamine is somewhat more stable. Under similar conditions, the *para* hydrogen atom of diphenylamine suffers replacement. H. WREN.

Preparation of 4- and 5-nitro- and -amino-hydrindene. J. LINDNER and J. BRUHIN (Ber., 1927, 60, [*B*], 435.—439).—Hydrindene is converted by a mixture of nitric and sulphuric acids at −10° into a mixture of 4- and 5-nitrohydrindene, which is separated into its components by alternate fractional distillation under reduced pressure and freezing of the individual fractions. 5-Nitrohydrindene has m. p. 40—40·5°, b. p. 152°/14 mm.; 5-aminohydrindene, m. p. 37—38°, b. p. 131°/15 mm., and its acetyl derivative, m. p. 106°, are described. 4-*Nitrohydrindene*, m. p. 44—44·5°, b. p. 139°/10 mm., is reduced to 4-*aminohydrindene*, m. p. −2° to 0°, b. p. 128°/about 15 mm. (*acetyl* derivative, m. p. 126—127°). The structure of the nitro-compounds is established by their oxidation to the corresponding nitrophthalic acids. The 4-derivatives do not appear identical with those described by Borsche and John (A., 1924, i, 723). H. WREN.

New transformation of naphthylamine-sulphonic acids. A. WAHL and G. VERMEYLEN (Compt. rend., 1927, 184, 334—336).—When α-naphthylamine-8-sulphonic acid is agitated with excess of concentrated sulphuric acid at 75—80° for some hrs., it is converted into the 4-sulphonic acid, identified by conversion into 1 : 4-dichloronaphthalene. The transformation may be explained by hydrolysis of the 8-acid, followed by normal sulphonation in the 4-position. The 8-acid hydrolyses more readily than the 4-acid. E. W. WIGNALL.

Additive compounds between quadri- and bivalent metals and organic bases. Probable nature of secondary valencies. G. SCAGLIARINI (Atti R. Accad. Lincei, 1926, [vi], 4, 574—576).—Debye and Hückel's theory of solutions is discussed in relation to the compositions of the complex compounds formed by treatment of halides of tin, titanium, cobalt, or nickel with organic bases in various solvents. A rational explanation of the formation of such compounds may be reached on the assumption that the secondary valencies are identical with the residual affinities due to their electric moments. T. H. POPE.

Manufacture of nitro-derivatives of aromatic amines. J. W. LEITCH AND CO., LTD., and A. E. EVEREST.—See B., 1927, 101.

***p*-Cymene. VII. Bromination of 2 : 6-diamino-*p*-cymene.** A. S. WHEELER and E. DE W. JENNINGS (J. Amer. Chem. Soc., 1927, 49, 572—575).—The bromination of 2 : 6-diacetamido-*p*-cymene (cf. Alfthan, A., 1920, i, 253) in cold carbon tetrachloride yields 3-*bromo*-2 : 6-*diacetamido*-p-*cymene*, m. p. 261°, from which 3-*bromo*-2 : 6-*diamino*-p-*cymene*, m. p. 99—100°, is obtained by hydrolysis with boiling aqueous hydrochloric acid [*monohydrochloride*, m. p. 162—168° (decomp.); *dibenzoyl* derivative, m. p. 257°]. Bromination of free 2 : 6-diamino-*p*-cymene in cold carbon tetrachloride yields 3 : *o*-*dibromo*-2 : 6-*diamino*-p-*cymene dihydrobromide*, m. p. 136° (decomp.) after darkening at 125°. The *diacetyl* derivative, m. p. 232°, and *dibenzoyl* derivative, m. p. 215°, of the dibromo-*p*-cymylenediamine are described. F. G. WILLSON.

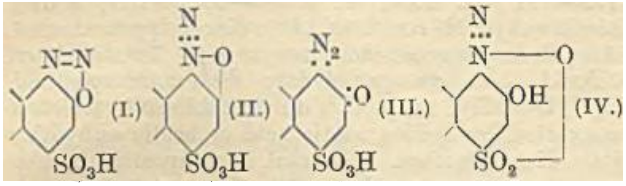
Action of nitrobenzene on aromatic diamines. G. B. CRIPPA [with P. CASTELLI] (Gazzetta, 1927, 57, 15—19).—When a nitrobenzene solution of a phenylenediamine containing sodium carbonate is subjected to prolonged boiling, the amine reacts with the solvent, giving an aminoazo-derivative. In this way, *p*-phenylenediamine yields *p*-aminoazobenzene, a small proportion of azoaniline, and a black, vitreous mass. For the formation of *p*-aminoazobenzene, two mechanisms are possible: (1) $NH_2{\cdot}C_6H_4{\cdot}NH_2 + Ph{\cdot}NO_2 = H_2O + NH_2{\cdot}C_6H_4{\cdot}N{:}NPh{:}O \longrightarrow NH_2{\cdot}C_6H_4{\cdot}N{:}NPh$; (2) $Ph{\cdot}NO_2 \xrightarrow{O} Ph{\cdot}NO$ and $NH_2{\cdot}C_6H_4{\cdot}NH_2 + Ph{\cdot}NO = H_2O + NH_2{\cdot}C_6H_4{\cdot}N{:}NPh$. The azoaniline formed is doubtless a bimolecular oxidation product of the *p*-phenylenediamine. The black compound resembles aniline-black and may consist of polynuclear oxidation products derived from tetra-aminodiphenylbenzoquinonedi-imine formed initially. T. H. POPE.

Nickel and cobalt arylazo-β-naphthylamine compounds. G. B. CRIPPA (Gazzetta, 1927, 57, 20—25).—Unlike copper and iron (A., 1926, 307), powdered nickel and cobalt yield compounds of the type $Ni(or\ Co)(R{\cdot}N_2{\cdot}C_{10}H_6{\cdot}NH_2)_2$ when boiled with arylazo-β-naphthylamines in aniline or nitrobenzene solution. If the boiling is prolonged for several hrs., the catalytic action of the metal comes into play and the corresponding triazoles are gradually formed. The nickel arylazo-β-naphthylamines crystallise in green needles, are highly stable towards alkalis, and are readily decomposed by dilute acid with liberation of the arylazo-β-naphthylamines. The cobalt compounds have similar properties and are violet-brown. When the amino-group of the azo-derivative is not in the *ortho*-position, the linking with the metal is unstable and the compound cannot be isolated.

[With E. VIGEVANI.]—Nickel (cobalt) *compounds* of the following azo-derivatives were prepared: benzeneazo-β-naphthylamine, m. p. 260° (265°); *o*-tolueneazo-β-naphthylamine, m. p. 245° (215—217°); *m*-tolueneazo-β-naphthylamine, m. p. 267° (220°); *p*-tolueneazo-β-naphthylamine, m. p. 281° (281°); ψ-cumeneazo-β-naphthylamine, m. p. 264—266° (268°); *p*-chlorobenzeneazo-β-naphthylamine, m. p. 271—272° (215—217°); *p*-bromobenzeneazo-β-naphthylamine, m. p. 262—263° (235—237°); *p*-acetophenone-1-azo-β-naphthylamine, m. p. 285° (270°); α-naphthalene-1-azo-β-naphthylamine, m. p. 271°. Cobalt α'-naphthalene-1-azo-β-naphthylamine has m. p. 250°. T. H. POPE.

Constitution of the diazonium derivative of 1-amino-2-naphthol-4-sulphonic acid. M. BATTEGAY and J. SCHMIDT (Bull. Soc. chim., 1927, [iv], 41, 205—208).—Of the alternative formulæ for the diazonium derivative of 1-amino-2-naphthol-4-sulphonic acid, (II) is dismissed as improbable, since the presence of the strongly basic diazonium hydroxide group with the sulphonic group in the same molecule would probably lead to internal salt formation. The resultant betaine structure (IV) is not consistent with the formation of definite sodium, magnesium, or zinc salts by precipitation from the neutral diazonium

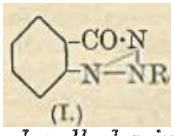
solution. The quinonoid structure (III) is rejected on account of the stability of the diazonium compound towards potassium iodide solutions, no oxidising



power being observed. The adopted formula (I) is further supported by the isolation of an acidic *copper* compound, $(C_{10}H_7O_5N_2S)_2Cu,6H_2O$, brown crystals with a metallic lustre, which gives no precipitate with sodium hydroxide and yields a yellow solution with ammonia. R. BRIGHTMAN.

Cold oxidation (decolorisation) of colouring matters in acid media by sodium hypochlorite. A. SEYEWETZ and E. CHAISE (Bull. Soc. chim., 1927, [iv], **41**, 196—205).—The action of cold sodium hypochlorite on suspensions of nitrophenols and nitroamines in dilute hydrochloric acid at 15—20° has been examined. Nitro-phenols and -naphthols undergo chlorination in the first stage of the reaction and are subsequently oxidised, the final products being carbon dioxide, chloropicrin, and nitric acid. Chlorination takes place first in all cases when the phenol contains a free *meta* position with respect to the nitro-group. In the case of picric acid, in which the *meta* positions are occupied, reaction is very slow, and affords mainly chloropicrin and carbon dioxide, with formation of picryl chloride as a side reaction. The latter compound is not attacked under the conditions described. The presence of a *p*-nitro-group appears to favour the formation of chloro-quinones. Thus *p*-nitrophenol affords more chloranil and nitric acid, although the main oxidation products are chloropicrin and carbon dioxide; 2-chloro- and 2 : 6-dichloro-4-nitrophenol are formed initially. 2 : 4-Dinitrophenol behaves similarly, affording 6-chloro-2 : 4-dinitrophenol initially, and chloranil as an oxidation by-product. With 2 : 4-dinitro-α-naphthol, 2-chloro-α-naphthaquinone is first formed and subsequently oxidised to phthalic and oxalic acids. 2 : 4-Dinitro-1-naphthol-7-sulphonic acid (naphthol-yellow *S*) is rapidly oxidised to 4-sulphophthalic acid and chloropicrin. With nitroamines, chlorination takes place unaccompanied by oxidation. Thus *p*-nitroaniline affords 2-chloro- and 2 : 6-dichloro-4-nitroaniline, *o*-nitroaniline gives 4 : 6-dichloro-2-nitroaniline, *m*-nitroaniline affords a mixture, and dinitroaniline a *chloronitroaniline*, m. p. 145—146°. 2 : 4 : 6-Trinitroaniline, picramic acid, and di-, tetra-, and hexa-nitrodiphenylamines are unattacked. *o*-Nitrophenol is attacked much more slowly than the *p*-isomeride; 4 : 6-dichloro-2-nitrophenol is formed initially and subsequently oxidised to carbon dioxide, chloropicrin, and nitric acid.
R. BRIGHTMAN.

Reduction of *o*-nitrophenyl*iso*diazomethanes. F. D. CHATTAWAY and A. J. WALKER (J.C.S., 1927, 323—333; cf. A., 1925, i, 1193; 1926, 169).—1-2′ : 4′-Dibromophenyl-3-*o*-nitrophenyl*iso*diazomethane is reduced by boiling alcohol or stannous chloride



(I.)

to cycloazi-2 : 4-*dibromophenylbenztriazone* (I, R=$C_6H_3Br_2$), m. p. 178°, which on further reduction with tin and hydrochloric acid in the cold gives o-*aminobenzoyl*-2 : 4-*dibromophenylhydrazine*, m. p. 184° (o-*acetyl* derivative, m. p. 210°; o-α-*diacetyl* derivative, m. p. 184°), identical with the reduction product of β-o-*nitrobenzoyl*-2 : 4-*dibromophenylhydrazine*, m. p. 180°. Alcoholic potassium hydroxide converts (I) into *potassium* 2 : 4-*dibromodiazoaminobenzene*-2′-*carboxylate*, m. p. 230—240° (decomp.) [*acid*, m. p. 151° (decomp.)], and an isomeric compound isolated as an *acid*, $C_{13}H_9O_2N_3Br_2$, m. p. 275°. By similar methods, cycloazi-p-*bromophenylbenztriazone*, m. p. 197°; cycloazi-2 : 4-*dichlorophenylbenztriazone*, m. p. 167° (labile), 157° (stable); and cycloazi-2 : 4 : 6-*trichlorophenylbenztriazone*, m. p. 258°, were obtained. Hydrolysis of the *cycloazi*-2 : 4-dichloro-compound gives 2 : 4-*dichlorodiazoaminobenzene*-2′-*carboxylic acid*, m. p. 163—167° (decomp.), and an *acid*, $C_{13}H_9O_2N_3Cl_2$, m. p. 275°.

To show that the *cycloazi*-benztriazones had constitution (I) and not (II), there were prepared p-*bromophenylbenztriazone* (II, R=C_6H_4Br),



m. p. 196°, from methyl *p*-bromodiazoaminobenzene-*o*′-carboxylate by oxidation with alcohol; and 2 : 4-*dibromophenylbenztriazone*, m. p. 136°. Hydrolysis of the last substance with alcoholic potassium hydroxide gave 2 : 4-dibromodiazoaminobenzene-2′-carboxylic acid as the sole product. H. BURTON.

[Nuclear condensation of phenols with nitriles.] K. HOESCH (Ber., 1927, **60**, [*B*], 389; cf. Houben, this vol., 143).—A question of priority.
H. WREN.

Terpenes and related compounds. III. Isomerisation of safrole under reduced pressure. N. HIRAO (J. Soc. Chem. Ind. Japan, 1927, **30**, 81—82).—A mixture of 3 parts of powdered potassium hydroxide and 100 parts of safrole is heated to boiling for 3·5 hrs. under 13—18 mm. pressure, and 94% isomerisation is obtained without resinification. When the amount of alkali is reduced to 2 parts, the mixture has to be heated for 5 hrs. to complete the reaction. The reaction is retarded by the presence of a small amount of water, but it can be completed by protracting the time of heating. The isomerisation is unsatisfactory when sodium hydroxide is used. K. KASHIMA.

3-Nitro-*p*-phenetidine. F. REVERDIN (Helv. Chim. Acta, 1927, **10**, 3—4).—D.R.-P. 101778/1898 states that the nitration of *p*-ethoxyacetanilide dissolved in sulphuric acid with nitric and sulphuric acids at 5° yields a yellow product which is hydrolysed by 25% sulphuric acid to 2-nitro-4-aminophenetole, m. p. 170°. It is now shown that pure 2-nitro-4-acetamidophenetole, m. p. 123°, prepared by this method, is almost colourless, and is hydrolysed to 2-nitro-4-aminophenetole (3-nitro-*p*-phenetidine), m.p. 40°. H. E. F. NOTTON.

Electrochemical oxidation of phenols. *m*-Xylenol, thymol, and potassium *iso*eugenyl sulphate. F. FICHTER and M. RINDERSPACHER

(Helv. Chim. Acta, 1927, **10**, 102—106).—Electrochemical oxidation of an emulsion of *s*-*m*-xylenol in 2*N*-sulphuric acid affords *m*-xyloquinone and a dixylenol resin. The same products were obtained, in 30% and 11% yield, respectively, in sulphuric acid–acetone solution. The resin is obtained in larger quantities when the xylenol is dissolved in *o*-xylene; it gives, on distillation in a high vacuum, a fraction, b. p. 185—190°, which has the composition of a dixylenol. Further experiments on the electrochemical oxidation of thymol (cf. A., 1914, i, 946) have resulted in the isolation of pure dithymol as its hydrate, m. p. 140° (cf. A., 1908, i, 84), in addition to thymoquinone and much resinous matter. A solution of potassium *iso*eugenyl sulphate in aqueous sodium carbonate is oxidised in a similar way to vanillin (50%), vanillic acid (4%) (A., 1925, i, 813), and a brown, amorphous *substance* (20%), probably a divanillic acid. H. E. F. Notton.

Action of nitrous acid on *ar*-tetrahydro-α-naphthol and on 5 : 8- and 5 : 6(or 7 : 8)-dihydro-α-naphthols. F. M. Rowe and E. Levin (J.C.S., 1927, 530—531).—Schroeter's statement (A., 1922, i, 130) that nitrous acid converts *ar*-tetrahydro-α-naphthol into 4-nitroso-*ar*-tetrahydro-α-naphthol (cf. J.C.S., 1918, **113**, 965) is confirmed, since the product is identical with that obtained by interaction of *ar*-tetrahydro-α-naphthaquinone and hydroxylamine. Oxidation of the nitroso-compound with dilute nitric acid yields 4-*nitro*-ar-*tetrahydro-α-naphthol*, m. p. 123°. The products of interaction of phenylhydrazine and *ar*-tetrahydro-α-naphthaquinone, of aniline and 4-nitroso-*ar*-tetrahydro-α-naphthol, and of diazobenzene chloride and *ar*-tetrahydro-α-naphthol are also identical. The compounds previously described as 4-nitro-5 : 8-dihydro-α-naphthol and 4-nitro-5 : 6-(or 7 : 8)-dihydro-α-naphthol (*ibid.*, 1921, **119**, 2024) are shown by analysis to be 4-nitroso-5 : 8- and 5 : 6-(or 7 : 8)-dihydro-α-naphthols. M. Clark.

Acetylbenzoyl derivatives of 7-amino-β-naphthol. L. C. Raiford and W. F. Talbot (J. Amer. Chem. Soc., 1927, **49**, 559—561).—Treatment of 7-amino-β-naphthol with acetic anhydride in pyridine solution affords the *diacetyl* derivative, m. p. 156°, which, on hydrolysis with alcoholic sodium hydroxide, yields the corresponding acetamidonaphthol, m. p. 232° (cf. Kehrmann and Wolff, A., 1900, i, 449), from which 7-*acetamido*-β-*naphthyl benzoate*, m. p. 177°, is obtained by benzoylation in alkaline solution. On hydrolysis, the latter loses the benzoyl group. 7-Benzamido-β-naphthyl benzoate, m. p. 181° (cf. Sachs, *ibid.*, 1906, i, 829), affords 7-*benzamido*-β-*naphthol*, m. p. 243—246°, on hydrolysis, and this, on acetylation, yields 7-*benzamido*-β-*naphthyl acetate*, m. p. 177°. No rearrangement characteristic of acetylbenzoyl derivatives of *o*-aminophenols (cf. Raiford and Coutare, A., 1924, i, 1304) was observed. F. G. Willson.

Aromatic thionyl and chlorothionyl derivatives. I. Thionylpyrocatechol and dichlorothionylquinol. A. Green (J.C.S., 1927, 500—504).—Thionylpyrocatechol, $C_6H_4<^{O}_{O}>SO$, b. p. 137—138°/105 mm., is best obtained by treating pyrocatechol with thionyl chloride in carbon disulphide–pyridine solution. Boiling acetic acid with a trace of pyridine converts it into *monoacetylpyrocatechol*, b. p. 189—191°/102 mm., m. p. 57—58°, whilst boiling acetic anhydride converts it into diacetylpyrocatechol. *Acetylbenzoylpyrocatechol* has m. p. 78°. Thionyl chloride converts quinol into *dichlorothionylquinol*, $C_6H_4(O{\cdot}SOCl)_2$, m. p. 75°, an unstable solid which is converted by boiling acetic acid or acetic anhydride into diacetylquinol. Thermal decomposition yields *p*-benzoquinone together with other products. H. Burton.

Action of chlorosulphonic acid on phenols. IV. J. Pollak and E. Gebauer-Fulnegg (Monatsh., 1926, **47**, 537—558).—Phloroglucinol reacts with ten times its weight of chlorosulphonic acid at the ordinary temperature to yield the trisulphonic acid, which, however, could not be freed from inorganic acids, and was isolated as its *ammonium* salt, $+1{\cdot}5H_2O$, decomp. 272—275° (depending on manner of heating). The crude acid treated with potassium hydroxide and methyl sulphate is not methylated, but yields only its *potassium* salt, $+1{\cdot}5H_2O$, and the action of bromine followed by potassium acetate yields only 2 : 4 : 6-tribromophloroglucinol. Either the free acid or its ammonium salt when heated with phosphorus pentachloride for 4 hrs. at 130° yields Δ^2-octachloro*cyclo*hexenone. The acid when heated in ether solution with aniline yields only aniline sulphate, but when heated with the free base it yields *s*-trianilinobenzene. When the acid is heated with *p*-aminophenol for 0·5 hr. at 105—110°, only the sulphate of the base is obtained, but in boiling nitrobenzene the product is 2 : 4 : 6-*tri*-p-*hydroxyanilinophloroglucinol*, decomp. above 350°. These reactions show the ease with which the sulphonic acid groups are removed, and short heating with hydrochloric acid (1 : 1) effects their removal quantitatively, a little phloroglucide also being formed. At higher temperatures (110°) or with 20—50 times the quantity of chlorosulphonic acid, phloroglucinol yields *phloroglucinol*-2 : 6-*disulphonyl chloride*, m. p. 184°, which when treated with aniline in ether solution yields the *anilide*, decomp. 275°, but when heated with aniline without a solvent it yields trianilinobenzene. The chlorosulphonyl groups are quantitatively eliminated by heating with hydrochloric acid, but the anilide is relatively stable towards acids. The potassium salt of the disulphonic acid, treated with 6 mols. of chlorosulphonic acid, is converted into the trisulphonic acid. Conversely, long treatment of the latter with a large excess of chlorosulphonic acid converts it into the disulphonyl chloride. At 150—160°, the reaction between phloroglucinol and chlorosulphonic acid yields pentachlorophenol and hexachlorobenzene.

[With O. Litvay.]—The action of chlorosulphonic acid on pyrogallol for 0·75 hr. at 100° yields the *disulphonyl chloride*, m. p. 178° (decomp.), identical with that obtained by the action of chlorosulphonic acid on the disulphonic acid obtained by Delage (A., 1901, i, 274). By the action of phosphorus pentachloride at 140° or of thionyl chloride at 100° on pyrogalloldisulphonyl chloride, 1-*chloro*-2 : 6-*dihydroxybenzene*-3 : 5-*disulphonyl chloride*, decomp. 187—189°, is obtained, whilst at a higher temperature penta-

chlorophenol and hexachlorobenzene are the sole products. The last two products are also obtained by the action of chlorosulphonic acid on pyrogallol at higher temperatures.

[Correction.]—The compound to which the constitution *p*-dichlorobenzodiquinone was previously assigned (Pollak and Gebauer-Fülnegg, A., 1926, 1244) is now shown to be chloranilic acid. J. W. BAKER.

Benzyl δ-chlorobutyl ether: a new unsymmetrical derivative of tetramethylene glycol. G. M. BENNETT and A. L. HOCK (J.C.S., 1927, 472—476).—Benzyl chloride reacts with the sodium derivative of trimethylene glycol, yielding *benzyl γ-hydroxypropyl ether*, b. p. 155°/23 mm., 172°/43 mm., d_4^{20} (vac.) 1·0474, $n^{i\cdot0}$ 1·5128, which on treatment with thionyl chloride furnishes *benzyl γ-chloropropyl ether*, b. p. 129°/16 mm., d_4^{20} (vac.) 1·0706, n_a^{20} 1·5102. This chloro-ether is converted by aqueous-alcoholic sodium cyanide into *γ-benzyloxybutyronitrile*, b. p. 157°/12 mm., 166°/16 mm., d_4^{20} (vac.) 1·026, n_a^{20} 1·5005, which on hydrolysis and esterification gives *ethyl γ-benzyloxybutyrate*, b. p. 160°/14 mm., d_4^{20} (vac.) 1·036, n^{20} 1·4930. *Ethyl* β*-benzyloxyethylmalonate*, b. p. 213°/22 mm., d_4^{20} (vac.) 1·0795, n_a^{20} 1·4908, obtained by condensing benzyl β-chloroethyl ether with ethyl sodiomalonate, on hydrolysis and thermal decomposition gives *γ-benzyloxybutyric acid*, which on esterification yields the above ethyl ester. This ester on reduction in toluene solution with sodium and ethyl alcohol yields *benzyl δ-hydroxybutyl ether*, b. p. 157°/12 mm., d_4^{20} (vac.) 1·029, n_a^{20} 1·5107, which is converted by thionyl chloride into *benzyl δ-chlorobutyl ether*, b. p. 135°/12 mm., d_4^{20} (vac.) 1·0572, n_a^{20} 1·5083. *Benzyl* β*-iodoethyl ether* has b. p. 148—149°/14 mm.; it reacts with magnesium, giving a Grignard reagent. H. BURTON.

Diphenylphenylacetylenylcarbinol [triphenylpropargyl alcohol]. III. Esters. IV. Attempts to obtain the free radical, triphenylpropargyl, $CPh_2{:}C{\cdot}CPh_2$. C. MOUREU, C. DUFRAISSE, and A. S. HOUGHTON (Bull. Soc. chim., 1927, [iv], **41**, 53—56, 56—58).—III. The following esters of triphenylpropargyl alcohol have been obtained by treating the chloride (cf. A., 1923, i, 921; 1925, i, 136) with the appropriate silver salt in benzene: *acetate*, m. p. 93—94°; *propionate*, m. p. 83—84°; *butyrate*, m. p. 73—74°; *benzoate*, m. p. 95—100°. The esters are stable in a vacuum, especially over sulphuric acid, and are hydrolysed by alcoholic but not by aqueous potassium hydroxide. With methyl or ethyl alcohol, they afford the corresponding triphenylpropargyl ether.

IV. Treatment of triphenylpropargyl chloride with iron in glacial acetic acid in a current of carbon dioxide at 40° affords *αγγδδ′-hexaphenyl-*$\Delta^{\alpha\epsilon}$*-hexadiinene*, $(CPh_2{:}C{\cdot}CPh_2{\cdot})_2$, m. p. 179°, together with a yellow substance, m. p. 245°. The corresponding bromide with magnesium in ether affords the same products. R. BRIGHTMAN.

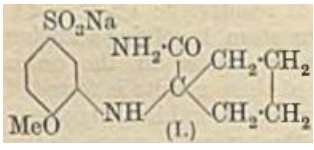
Influence of the sulphur atom on the reactivity of adjacent atoms or groups. I. Qualitative comparison of reactivities of chlorine and hydroxyl in α-, β-, γ-, and δ-positions to a sulphur atom. G. M. BENNETT and A. L. HOCK (J.C.S., 1927, 477—483).—*γγ′-Dibenzyloxydipropyl sulphide* and *δδ′-dibenzyloxydibutyl sulphide*, obtained by the action of aqueous-alcoholic sodium sulphide on the corresponding chloro-ethers, are converted by cold, fuming hydrobromic acid into *γγ′*-dihydroxydipropyl sulphide (*di*-p-*nitrobenzoyl* derivative, m. p. 104—105°) and *tetrahydrothiophen-δ-hydroxybutylsulphonium bromide*, $(C_4H_8S{\cdot}[CH_2]_4{\cdot}OH)Br$ (I) [*picrate*, m. p. 189—190°; *bromoplatinate*, decomp. without melting at 165—170°; *bromoaurate*, m. p. 65—70° (decomp.)]. Decomposition of (I) by heat furnishes tetrahydrothiophen [methiodide, m. p. 195—197° (decomp.) (von Braun and Trümpler, A., 1910, i, 275, give m. p. 185—190°); mercurichloride, m. p. 127—133° (decomp.) (Grischkevitsch-Trochimovski, A., 1917, i, 153, gives m. p. 124·5—125·5°); *bromoplatinate*, decomp. 236—238°]. *Tetrahydrothiophen-δ-bromobutylsulphonium bromide* (*picrate*, m. p. 92—96°) was produced from (I) by keeping it in a vacuum for several weeks.

A study of the reactivities of the hydroxyl groups or chlorine atoms in the α-, β-, γ-, and δ-positions to the sulphur atom (cf. A., 1926, 146; 1923, i, 734) gives the following order of reactivity: $\alpha>\beta>\gamma<\delta$. The reactivity of the sulphur atom, involving addition of methyl iodide or oxygen, varies in the order $\alpha<\beta<\gamma$. An explanation of these results is founded on the electronic theory of valency, and it is suggested that the high reactivity of the hydroxyl group in the δ-position is due to transmission of the polar effect of the sulphur atom through space, not along the carbon chain. H. BURTON.

Constitution and colour. XIII. Constitution of triphenylmethane dyes. F. KEHRMANN, H. GOLDSTEIN, and A. VON SALIS (Helv. Chim. Acta, 1927, **10**, 33—39).—A close parallelism exists between the absorption spectra of corresponding mono-, di-, and tri-acid salts of malachite-green, $NMe_2{\cdot}C_6H_4{\cdot}CPh{:}C_6H_4{:}NMe_2Cl$, and Bindschedler's green, $NMe_2{\cdot}C_6H_4{\cdot}N{:}C_6H_4{:}NMe_2Cl$, between those of corresponding mono- and di-acid salts of fuchsonimine and *N*-phenylbenzoquinonedi-imine; and between those of dimethylfuchsonimonium salts, $CPh_2{:}C_6H_4{:}NMe_2X$, and phenylbenzoquinoneiminedimethylimonium, $NPh{:}C_6H_4{:}NMe_2X$, salts. Corresponding compounds differ only in the replacement of the $\cdot CPh{:}$ group by $\cdot N{:}$ and, since the quinoneimine derivatives undoubtedly possess a *p*-quinonoid structure, the triphenylmethanes must be similarly constituted. H. E. F. NOTTON.

Condensation of substituted anilines with *cyclo*pentanonecyanohydrin. Derivatives of 1-anilino*cyclo*pentane-1-carboxylic acid. S. H. OAKESHOTT and S. G. P. PLANT (J.C.S., 1927, 484—493).—A mixture of *o*-toluidine and *cyclo*pentanone in acetic acid, when treated with potassium cyanide, yields 1-o-*toluidino*-1-*cyano*cyclo*pentane*, m. p. 68°, which is hydrolysed by cold, concentrated sulphuric acid to 1-o-*toluidino*cyclo*pentane*-1-*carboxylamide*, m. p. 122° (*hydrochloride*). Further hydrolysis of the amide gives 1-o-*toluidino*cyclo*pentane*-1-*carboxylic acid*, m. p. 128°. By a similar reaction there were prepared the following derivatives of 1-cyano*cyclo*pentane: 1-o-*anisidino*-; 1-m-*anisidino*-, m. p. 132°; 1-p-

anisidino-; 1-*veratrylamino-*, m. p. 98°; 1-mm′-*dimethoxyanilino-*, m. p. 150°; 1-o-*chloroanilino-*; 1-m-*chloroanilino*, m. p. 47°; 1-p-*chloroanilino-*, m. p. 73°; 1-o-*bromoanilino-*; 1-m-*bromoanilino-*; 1-p-*bromoanilino-*, m. p. 69°; 1-m-*nitroanilino-*, m. p. 95°; 1-p-*nitroanilino-*, m. p. 165°; 1-o-*carboxyanilino-*, m. p. 122°; 1-m-*carboxyanilino-*, m. p. 153°; and 1-p-*carboxyanilino-*, m. p. 189—190°. *o*-Nitroaniline does not furnish a cyano*cyclo*pentane, and it is found that the rate of formation of these nitriles is dependent on the position of the substituent in the benzene nucleus. The corresponding nitriles on hydrolysis yield the following derivatives of *cyclo*pentane-1-carboxylic acid: 1-p-*anisidino-*, m. p. 160° (*amide*, m. p. 81—82°); 1-o-*chloroanilino-*, m. p. 145° (*amide*, m. p. 113°); 1-m-*chloroanilino-*, m. p. 112° (*amide*, m. p. 118°); 1-p-*chloroanilino-*, m. p. 144° (*amide*, m. p. 132°); 1-o-*bromoanilino-*, m. p. 140° (*amide*, m. p. 128°); 1-m-*bromoanilino-*, m. p. 130° (*amide*, m. p. 126°); 1-p-*bromoanilino-*, m. p. 130° (*amide*, m. p. 145°); 1-m-*nitroanilino-*, m. p. 137° (*amide*, m. p. 144°); 1-p-*nitroanilino-*, m. p. 187° (*amide*, m. p. 231°); and 1-p-*carboxyanilino-*, m. p. 225° (decomp.) (*amide*, m. p. 272°). 1-*o*-Anisidino-1-cyano*cyclo*pentane on treatment with sulphuric acid is hydrolysed and sulphonated, *sodium* 1-o-*anisidino*cyclo*pentane*-1-*carboxylamide*-5′-*sulphonate* (I), being isolated. 1-o-*Carboxy*- and 1-m-*carboxy-anilino*cyclo*pentane*-1-*carboxylamides* have m. p. 225° and 153°, respectively.



1-*o*-Toluidino*cyclo*pentane-1-carboxylic acid on heating at 270—320° with potassium hydroxide and sodium ethoxide yields 1-methylcarbazole, which is further evidence for the view that the carbazoles are formed by the enlargement of the *cyclo*pentane ring (see A., 1925, i, 1271; 1926, 843). 3 : 5-*Dimethoxyaniline*, b. p. 178°/20 mm. (*acetyl* derivative, m. p. 157°), is obtained by reducing 3 : 5-dimethoxynitrobenzene, the preparation of which from *s*-trinitrobenzene is given. H. BURTON.

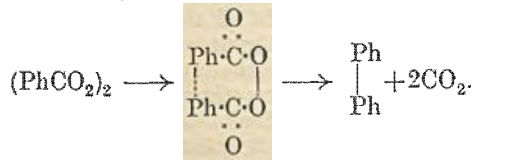
Three-carbon system. XI. Mechanism of isomeric change in unsaturated acids. R. P. LINSTEAD (J.C.S., 1927, 362—371).—In an endeavour to show that the mechanism of tautomeric change in unsaturated acids in the presence of alkali is explained by the system $>CH\cdot C(OH)\cdot CH\cdot CO_2H \rightleftharpoons >CH\cdot C{:}C\cdot CO_2H \quad >C{:}C\cdot CH\cdot CO_2H$, a quantitative study of the action of potassium hydroxide solutions of varying concentration at different temperatures, on *cyclo*hexylacetic acid, *cyclo*hexylideneacetic acid, and Δ^1-*cyclo*hexenylacetic acid was made. The results show that the rate of isomeric change depends on the concentration of alkali, although the position of equilibrium of the unsaturated acids does not. The equilibration of the three acids is shown by the author's bromine addition method (cf. *ibid.*, 355) to be a unimolecular reversible reaction. It is concluded that the isomeric change of unsaturated acids is tautomeric and does not depend on the addition and removal of water. *Sodium* cyclo*hexylideneacetate* has m. p. 276° (decomp.). H. BURTON.

Action of benzoyl peroxide on benzene at low temperatures and in the presence of iron and aluminium chlorides. A. F. A. REYNHART (Rec. trav. chim., 1927, **46**, 54—61).—The action of benzoyl peroxide on benzene in the presence of aluminium and ferric chlorides at various temperatures from —30° to +50° has been investigated. With either catalyst, the main primary products formed are benzoic acid and phenyl benzoate, small quantities of carbon dioxide and diphenyl also being produced, the quantities of these increasing with rise in temperature. Since, however, aluminium chloride forms a stable molecular complex with phenyl benzoate, an equimolecular quantity of the catalyst must be employed for the complete decomposition of the peroxide. With ferric chloride the reaction is slower, but 0·2 mol. is sufficient to complete the decomposition, since the molecular complex with phenyl benzoate is unstable. With an excess of ferric chloride, the phenyl benzoate further reacts with benzene and ferric chloride to yield benzoic acid, and a brown, complex product containing iron. The same products are obtained when benzene is added to the complex formed by the addition of ferric chloride to phenyl benzoate in carbon disulphide solution, the peroxide not being attacked by ferric chloride under the same conditions. Even at 50°, the reaction, $(Ph\cdot CO_2)_2+C_6H_6 \longrightarrow Ph\cdot Ph+CO_2+Ph\cdot CO_2H$, observed by Gelissen and Hermans (A., 1925, i, 545) is only a subsidiary one. J. W. BAKER.

Action of benzoyl peroxide on chlorides and oxychlorides of phosphorus and antimony. A. F. A. REYNHART (Rec. trav. chim., 1927, **46**, 62—67).—Antimony pentachloride accelerates the decomposition of benzoyl peroxide in petroleum (b. p. 40—60°) at 10°, the products being phenyl benzoate and carbon dioxide. The only definite products which can be isolated when the peroxide is decomposed with an equimolecular quantity of phosphorus pentachloride in petroleum (b. p. 80—100°) at 100° are carbon dioxide and benzoyl chloride, but when the two substances are cautiously heated together at 96—98° without solvent (the reaction tends to become explosive), the products are benzoyl chloride, chlorobenzene, carbon dioxide, and phosphoryl chloride, the quantities of each obtained being approximately those required by the equation $(Ph\cdot CO_2)_2+PCl_5 \longrightarrow Ph\cdot COCl+PhCl+CO_2+POCl_3$. Phosphoryl chloride at its b. p. (107°) has no effect on the thermal decomposition of the peroxide, which proceeds normally, yielding mainly phenyl benzoate and carbon dioxide, but with a large excess of phosphoryl bromide at its b. p. (194°), 1 mol. of carbon dioxide is liberated, and benzoic acid and bromobenzene could be isolated, after treatment with ice, from the products of the reaction, which probably proceeds in accordance with the equations $(Ph\cdot CO_2)_2+POBr_3 \longrightarrow Ph\cdot CO_2POBr_2+CO_2+PhBr$: $Ph\cdot CO_2POBr_2+3H_2O \longrightarrow Ph\cdot CO_2H+H_3PO_4+2HBr$. J. W. BAKER.

Decomposition of benzoyl and succinyl peroxides at a high temperature and without solvents. A. F. A. REYNHART (Rec. trav. chim., 1927, **46**, 68—71).—Thermal decomposition (at

about 300°) of benzoyl peroxide in an apparatus specially designed so that the diphenyl formed is rapidly removed before it has much opportunity of itself reacting with the peroxide, gives a 68% yield of this compound. Since no trace of bromobenzene is obtained when the decomposition is carried out in the presence of bromine vapour, it follows that free phenyl radicals are not produced at any period of the reaction, the 2 mols. of carbon dioxide being liberated at the moment of formation of diphenyl in accordance with the scheme,



Thermal decomposition of succinyl peroxide under the same conditions yields adipic acid and carbon dioxide. J. W. BAKER.

Action of chlorinated hydrocarbons on benzoyl peroxide with or without the presence of aluminium chloride. A. F. A. REYNHART (Rec. trav. chim., 1927, **46**, 72—76).—Carbon tetrachloride has no action on benzoyl peroxide in the presence of aluminium chloride at 0°, but in chloroform solution at the same temperature the main products formed are benzoyl chloride, benzoic acid, and carbonyl chloride, no trace of *p*-trichloromethylbenzoic acid being detected. The reaction is represented by the equation $(Ph\cdot CO_2)_2+CHCl_3 \longrightarrow Ph\cdot CO_2H+Ph\cdot COCl+COCl_2$. At the same time, a secondary reaction, $(Ph\cdot CO_2)_2+CHCl_3 \longrightarrow C_6H_6+CO_2+Ph\cdot CO_2CCl_3$ $(=Ph\cdot COCl+COCl_2)$, yields a small quantity of benzene. This secondary reaction is favoured at 50°, but the benzene reacts under the catalytic influence of the aluminium chloride with the benzoyl chloride and carbonyl chloride to yield, respectively, benzophenone and a further quantity of benzoyl chloride. The action of an excess of tetrachloroethylene at its b. p. on benzoyl peroxide yields chlorobenzene, αββ-trichlorostyrene (40% yield), and carbon dioxide, but when the tetrachloroethylene is not in excess, hexachloroethane and some high-boiling, chlorinated products are also obtained. Aluminium chloride has no catalytic effect on this reaction. J. W. BAKER.

Metallic derivatives of the enolic forms of monocarbonyl compounds. V. Interaction of phenylacetylene with ethyl potassiophenylacetates. VI. Action of alkali metals on ethyl phenylacetate. H. SCHEIBLER and A. Z. MAHBOUB (Ber., 1927, **60**, [*B*], 558—564; 564—568).—V. Ethyl potassiophenylacetate is converted by phenylacetylene at 125—130° into 2:5-*diphenyl*-3:6-*dibenzyl*-p-*benzoquinone*, m. p. 156° (corr.); if the potassium derivative formed during the condensation is decomposed by dry carbon dioxide instead of by water, a colourless compound separates which passes gradually into the yellow quinone. The latter is unusually stable towards reducing agents, but is converted by zinc dust and glacial acetic acid into the corresponding *quinol*, m. p. 111·5° (corr.). The quinone is transformed by sodium ethoxide or by alcoholic potassium hydroxide into a *substance*, $C_{66}H_{54}O_5$, m. p. 256° (corr.). In addition to the quinone, a *compound*, $C_{32}H_{24}O_2$, m. p. 208° (corr.) (2:4-*diphenyl*-1-*benzyl*-Δ^1-cyclo*pentene*-3:5-*dione*), is occasionally obtained during the action of phenylacetylene on ethyl potassiophenylacetate; it is derived from ethyl αγ-diphenylacetoacetate.

VI. During the action of potassium on an ethereal solution of ethyl phenylacetate, the changes (1) $CH_2Ph\cdot CO_2Et+K=CHPh{:}C(OEt)\cdot OK+H$ and (2) $CHPh{:}C(OEt)\cdot OK+CH_2Ph\cdot CO_2Et+K=$ $CH_2Ph\cdot C(OK){:}CPh\cdot CO_2Et+EtOK+H$ occur simultaneously. Since the velocity of (1) greatly exceeds that of (2), the main product is ethyl potassiophenylacetate, provided that an excess of ester is not present during or after dissolution of the metal. In the preparation of ethyl potassiophenylacetate, it is advisable to work as rapidly as possible with a slight deficiency of the metal, and to finish the preparation without delay. If ethyl potassiophenylacetate covered by ether is treated with a small quantity of ethyl phenylacetate, solution follows with formation of ethyl potassio-αγ-diphenylacetoacetate. This is due to decomposition of ethyl potassiophenylacetate by liberated ethyl alcohol (cf. equation 2), whereby ethyl phenylacetate is regenerated, thereby allowing the change to continue until formation of ethyl potassio-αγ-diphenylacetoacetate is almost quantitative. The corresponding sodium derivatives do not differ so widely in their solubilities as the potassium compounds, so that the initial precipitate does not become completely dissolved when an excess of ethyl phenylacetate is present. Ethyl αγ-diphenylacetoacetate, m. p. 78—79°, and the *potassium* derivatives of ethyl phenylacetate and αγ-diphenylacetoacetate are described. H. WREN.

Xanthophanic acids. II. Production of naphthalene compounds from derivatives of acetoacetic esters. F. FEIST, H. JANSSEN, and C. A. CHEN (Ber., 1927, **60**, [*B*], 199—208; cf. this vol., 151).—The by-product, $C_{20}H_{22}O_5$, isolated by Liebermann during the preparation of diethylxanthophanic acid according to Claisen is formed by fission of the latter acid by ozone or, with great readiness, by means of boiling alcohol or the protracted action of alcohol at the ordinary temperature. It is identified as ethyl acetyl-1:6-dimethylnaphthalenedicarboxylate, since it is hydrolysed to a dibasic acid, m. p. 273°, which is converted by distillation with lime into 1:6-dimethylnaphthalene and passes at 350° into *acetyl*-1:6-*dimethylnaphthalenemonocarboxylic acid*, m. p. 184°. The formation of the "by-product" from ethyl acetoacetate and ethyl ethoxymethyleneacetoacetate depends on the primary formation of ethyl methenyldiacetoacetate (cf. *loc. cit.*), which, under the influence of alkali (derived from ethyl sodioacetoacetate), becomes decarboxylated to ethyl diacetylcrotonate; the latter substance is readily converted by loss of water into the naphthalene derivative. Acetyl-1:6-dimethylnaphthalenedicarboxylic acid is oxidised by permanganate in alkaline solution to 1:6-*dimethylnaphthalene*-2:4:7-*tricarboxylic acid*, m. p. 360° (also *hemihydrate*); the *silver* salt and the *triethyl* ester, m. p. 75—76°, are described.

The *diethyl* ester, m. p. 231—232°, of the tricarboxylic acid is obtained by treatment of the " by-product " with boiling nitric acid (31%), together with two neutral nitrogenous *compounds*, $C_{20}H_{21}O_6N$, m. p. 131—132°, and (?) $C_{20}H_{19}O_5N$, m. p. 75—85°; all three substances are converted by alkali hydroxide into 1 : 6-dimethylnaphthalene-2 : 4 : 7-tricarboxylic acid. H. WREN.

Reaction of lactones and of furan derivatives with aromatic hydrocarbons and aluminium chloride. E. J. KING (J. Amer. Chem. Soc., 1927, 49, 562—566).—When treated with phthalide and aluminium chloride, benzene and naphthalene yield, respectively, *o*-benzylbenzoic acid, m. p. 114°, and *o*-β-naphthylmethylbenzoic acid, m. p. 136—137°. In benzene solution, phenylphthalide, naphthalene, and aluminium chloride yield only triphenylmethane-2-carboxylic acid, but in carbon disulphide solution 2-phenyl-4-β-naphthylmethylbenzoic acid is obtained. No reaction was observed between diphenylphthalide, benzene, and aluminium chloride. Coumarin, benzene, and aluminium chloride yield α-phenyl-αβ-dihydrocoumarin, whilst coumarilic acid and benzene yield similarly *α-phenyl-αβ-dihydrocoumarilic acid*, m. p. 147—147·5° (*silver* salt; *methyl* ester, m. p. 68—69°). Bromination of the latter in carbon disulphide affords a *monobromo*-derivative, m. p. 241°, whilst bromination in chloroform yields an *isomeride*, m. p. 127°, which is converted into the isomeride of higher m. p. when its sodium salt is boiled in aqueous or alcoholic solution. Coumarilic acid and toluene yield analogously α-p-*tolyl-αβ-dihydrocoumarilic acid*, m. p. 165—165·5° (*methyl* ester, m. p. 87—88°; β-*bromo*-derivative, m. p. 260°). Pyromucic acid, benzene, and aluminium chloride yield what is presumably β-*phenyl-αβ-dihydropyromucic acid*, m. p. 159° (*silver* salt), which, on bromination in chloroform, affords the δ-*bromo*-derivative, m. p. 251°.

F. G. WILLSON.

Compounds of sexavalent uranium with aromatic hydroxy-acids. R. WEINLAND and K. HAGER (Z. anorg. Chem., 1927, **160**, 193—208).—The following compounds are described: *uranyl methyl salicylate* ($+C_5H_5N$), *aniline* and *piperidine disalicylatouranates*, *ammonium tribenzoatouranate*, *ammonium* ($+3H_2O$), *aniline* ($+4H_2O$), o-*toluidine* ($+3H_2O$), *pyridine* ($+4H_2O$), and *piperidine* ($+3H_2O$) *tri*-p-*hydroxybenzoatouranates*, *pyridine* ($+7H_2O$) and *aniline tri*-m-*hydroxybenzoatouranates*, *pyridine* ($+H_2O$), *triethylamine*, o-*toluidine*, m-*nitroaniline*, *toluylenediamine*, *methylamine* ($+5H_2O$), *guanidine* ($+6H_2O$), *potassium* (+9 and $13H_2O$), *ammonium* (+9 and $13H_2O$), and *barium* (+10 and $14H_2O$) *tri-salicylatouranates*. The variety of complexes which may be formed is due to the amphoteric nature of uranyl hydroxide, which is thus able to react with both the carboxyl and phenolic groups. The structure of the compounds is discussed from the point of view of residual valency. H. F. GILLBE.

Purification of o-methoxybenzoic acid. E. CATTELAIN (Bull. Soc. chim., 1927, [iv], 41, 114—115).—The crude *o*-methoxybenzoic acid is dissolved in water with a slight excess of sodium hydroxide, the solution neutralised with acetic acid, and after addition of a little sodium acetate acidified with acetic acid. The *o*-methoxybenzoic acid is precipitated, salicylic acid remaining in solution, and is filtered cold and washed with a little water.

R. BRIGHTMAN.

Thyroxin. III. Constitution and synthesis of thyroxin. C. R. HARINGTON and G. BARGER (Biochem. J., 1927, **21**, 169—183; cf. A., 1926, 644, 724).—The orientation of the iodine atoms in the tetraiodo-derivative of the *p*-hydroxyphenyl ether of tyrosine (thyroxin) has been established by degradation and by synthesis of thyroxin. Thyroxin on fusion with potassium hydroxide at a high temperature in the absence of oxygen yielded products exhibiting pyrogallol reactions, thus suggesting the probable conversion of one or both of the benzene rings of thyroxin into 3:4:5-trihydroxy-derivatives. It was also found that the colour reaction of thyroxin with nitrous acid and ammonia (Kendall and Osterberg, A., 1920, i, 180) was also given in general by benzene derivatives containing two iodine atoms in the *ortho*-positions to a hydroxyl or an amino-group, which suggested that thyroxin contained a similar grouping. By exhaustive methylation of thyroxin with methyl iodide after boiling the product with alcoholic potassium hydroxide, an unsaturated *acid*, $C_{16}H_{10}O_4I_4$, melting indefinitely above 290°, was obtained. On oxidising this acid with potassium permanganate, an *aldehyde*, $C_{14}H_8O_3I_4$, m. p. 198°, was obtained, which by further oxidation gave an acid, $C_{14}H_8O_4I_4$, m. p. 283°, *methyl* ester, m. p. 233°, *ethyl* ester, m. p. 171·5°. The acid was shown to be 3 : 5-*di-iodo*-4-(3′:5′-*di-iodo*-4′-*methoxyphenoxy*)*benzoic acid* by synthesis in the following way:

3 : 5-*Di-iodo*-4-(4′-*methoxyphenoxy*)*nitrobenzene*, yellow, m. p. 144°, was prepared by boiling a solution of quinol monomethyl ether and 3 : 4 : 5-tri-iodonitrobenzene in methyl ethyl ketone with dry potassium carbonate. The *aniline*, m. p. 121—122°, was then obtained by reducing the above nitro-compound in glacial acetic acid with stannous chloride and hydrogen chloride (*hydrochloride*, m. p. 216°; *sulphate*, m. p. 201°). The base was converted by Sandmeyer's reaction into 3 : 5-*di-iodo*-4-(4′-*methoxyphenoxy*)*benzonitrile*, m. p. 167—169°. The nitrile when boiled with a mixture of hydriodic and acetic acids underwent simultaneous hydrolysis and demethylation, yielding 3 : 5-*di-iodo*-4-(4′-*hydroxyphenoxy*)*benzoic acid*, m. p. 252—254°. The latter compound on treatment in concentrated ammonia with iodine in potassium iodide yielded 3 : 5-*di-iodo*-4-(3′ : 5′-*di-iodo*-4′-*hydroxyphenoxy*)*benzoic acid*, m. p. 255°. Finally, by methylating the last compound it was converted into the methoxy-derivative, which was found to be identical with the above acid product, $C_{14}H_8O_4I_4$, obtained by degradation of thyroxin.

The starting point in the actual synthesis of thyroxin was 3 : 5-*di-iodo*-4-(4′-*methoxyphenoxy*)*benzaldehyde*, m. p. 121°, obtained from the nitrile by a modification of Stephen's method (A., 1925, i, 1131). From this compound the *azlactone*, yellow, m. p. 211°, was prepared by heating a mixture of the aldehyde and sodium acetate with hippuric acid and acetic anhydride. The *azlactone* was converted into *ethyl* 3 : 5-*di-iodo*-α-*benzamido*-4-(4′-*methoxyphenoxy*)-

cinnamate, m. p. 203°, by warming with absolute alcohol containing 10% of sulphuric acid. The cinnamic ester when boiled with hydriodic acid and red phosphorus yielded *α-amino-β-3 : 5-di-iodo-4-(4'-hydroxyphenoxy)phenylpropionic acid*, which on iodination in ammoniacal solution gave *α-amino-β-3 : 5-di-iodo-4-(3' : 5'-di-iodo-4'-hydroxyphenoxy)phenylpropionic acid*, identical chemically and physiologically with thyroxin isolated from the thyroid gland.

S. S. Zilva.

Constitution in the acenaphthene and naphthalene series. K. Dziewonski, (Mlle.) H. Galitzerówna, and A. Kocwa (Bull. Acad. Polonaise, 1926, *A*, 209—242).—The monosulphonic acid (I) obtained from acenaphthene and sulphuric acid at 100° (cf. A., 1924, i, 1178) is oxidised to a sulphonaphthalic acid (II), from which, on alkaline fusion at 250°, a compound, m. p. 257°, previously supposed to be identical with 4-hydroxynaphthalic anhydride (Graebe, A., 1903, i, 408), is obtained. Since, however, it has the formula $C_{12}H_6O_3$, gives β-naphthol when distilled with calcium hydroxide, and forms 1 : 8-phenylpyridazone-2-naphthaquinone, m. p. 238—240° (A., 1924, i, 1199) without loss of carbon dioxide, it must be *7-hydroxy-1-naphthoic acid* (*benzoyl* derivative, m. p. 194°; *methyl ether*, m. p. 167·5°, and its *silver* salt). Accordingly, (II) is 2-sulphonaphthalic acid (2-sulphonaphthalene-1 : 8-dicarboxylic acid) and (I) is acenaphthene-3-sulphonic acid. The second acenaphthenesulphonic acid (amide, m. p. 222—223°) is therefore the 5-derivative. Acenaphthene behaves on sulphonation in the same way as naphthalene, substitution taking place in the α-(5)-position at lower, and in the β-(3)-position at higher temperatures. *2-Hydroxynaphthalic anhydride*, m. p. 242°, is obtained by fusing (II) with potassium hydroxide at 150°. Acenaphthene-5-sulphonic acid is oxidised to 4-sulphonaphthalic acid, from which *4-chlorosulphonylnaphthalic anhydride*, m. p. 191—193° (corresponding *sulphonamide*, m. p. 316°, and *methyl sulphonate*, m. p. 210°), is prepared. Further evidence for the constitution of 4-hydroxynaphthalic anhydride (III), m. p. 350—351°, obtained by fusing the sulphonic acid with potassium hydroxide at 240°, is furnished by its conversion into α-naphthol when distilled with calcium hydroxide and by the preparation of yellowish-brown *3-nitroso-4-hydroxynaphthalic anhydride*, m. p. 230° (red *zinc* salt, dark green *iron* lake). The following derivatives of (III) are described : the *methyl ether*, m. p. 257°; *acetyl* derivative, m. p. 188—189°; *benzoyl* derivative, m. p. 235—236°; colourless *potassium* salt; *phenylhydrazone*, m. p. 335—336°; *oxime*, m. p. above 350° (red *sodium* salt); *mononitro*-derivative, m. p. 222°; also *4-hydroxynaphthalimide*, m. p. above 300°; *ammonium 4-aminonaphthalate*, m. p. 222° (decomp.), and *4-aminonaphthalic anhydride*, m. p. above 350°, which may also be prepared by reducing Graebe's 4-nitronaphthalic anhydride.

1 : 8-Phenylpyridazone-4-naphthaquinone, m. p. 201—202° (*loc. cit.*); 1 : 8-(*p-nitrophenylpyridazone*)-*4-naphthaquinone*, m. p. 305—307°, and 1 : 8-*α-naphthylpyridazone-4-naphthaquinone* are formed from (III) and the appropriate diazonium salt. 4-Hydroxynaphthalic anhydride condenses with resorcinol in presence of zinc chloride to *4-hydroxynaphthafluorescein*, orange-red, which dyes dark reddish-brown on a chromium mordant.

H. E. F. Notton.

Application of the Perkin reaction to phenolic aldehydes. S. Ogawa (Bull. Chem. Soc. Japan, 1927, 2, 20—26).—The uncertain m. p. of the products previously obtained by means of the Perkin reaction from phenolic aldehydes (Tiemann, A., 1877, 893; 1878, 579; Vorlander, *ibid.*, 1906, i, 317) were due to the presence of by-products. Vanillin gives, in addition to 4-acetoxy-3-methoxycinnamic acid, *4-(4'-acetoxy-3'-methoxycinnamoxy)-3-methoxycinnamic acid* (*acetylferuloylferulic acid*), m. p. 250° (decomp.) (*methyl* ester, m. p. 204—205·5°), which may also be prepared from *4-acetoxy-3-methoxycinnamoyl chloride*, m. p. 133—134°, and 4-hydroxy-3-methoxycinnamic acid, in presence of pyridine. Similarly, the product from *p*-hydroxybenzaldehyde contains *4-p-acetoxycinnamoxycinnamic acid*, m. p. 222—223° (*methyl* ester, m. p. 166—167°), and a *substance*, $C_{29}H_{22}O_8$, m. p. 231° (decomp.) (*methyl* ester, m. p. about 200°), probably p-(4-p'-*acetoxycinnamoxycinnamoxy*)*cinnamic acid*, as well as pure *p*-acetoxycinnamic acid, m. p. 205—205·5°. Experiments with veratraldehyde and acetylvanillin show that only aldehydes with a free hydroxyl group give these complex products. *4-p*-Acetoxycinnamoxycinnamic acid is also obtained from p-*acetoxycinnamoyl chloride*, m. p. 118—119°, and *p*-hydroxycinnamic acid in pyridine solution.

H. E. F. Notton.

Compounds similar to chaulmoogric acid. I. G. A. Perkins and A. O. Cruz (J. Amer. Chem. Soc., 1927, **49**, 517—522).—Treatment of ethyl Δ^2-*cyclo*pentenylmalonate (cf. Noller and Adams, A., 1926, 1137) with powdered sodium in toluene, followed by addition of an alkyl halide, affords the corresponding ethyl Δ^2-*cyclo*pentenylalkylmalonates, from which the corresponding disubstituted malonic acids are obtained on hydrolysis. The following were prepared : Δ^2-cyclo*pentenylethylmalonic acid*, m. p. 156° (decomp.); Δ^2-cyclo*pentenyl*-n-*propylmalonic acid*, m. p. 153° (decomp.); Δ^2-cyclo*pentenyl*iso*propylmalonic acid*, m. p. 178° (decomp.); Δ^2-cyclo*pentenylallylmalonic acid*, m. p. 146° (decomp.); Δ^2-cyclo*pentenyl*-n-*butylmalonic acid*, m. p. 134° (decomp.); and *di*-Δ^2-cyclo*pentenylmalonic acid*, m. p. 184° (decomp.). When heated at the m. p., the above acids lose carbon dioxide, with formation of the following respective acids : *α*-Δ^2-cyclo*pentenyl-butyric*, b. p. 145—150°/20 mm.; -n-*valeric*, b. p. 150—160°/20 mm.; -iso*valeric*, b. p. 158—161°/20 mm.; -α-allylacetic, b. p. 158—160°/20 mm.; -*hexoic*, b. p. 167—169°/20 mm.; and *di*-Δ^2-cyclo*pentenylacetic acid*, b. p. 185—187°/20 mm. All the above substituted acetic acids decomposed when kept.

F. G. Willson.

New method of preparation of methyl phenylethylmalonate. M. M. Rising and T.-W. Zee (J. Amer. Chem. Soc., 1927, **49**, 541—545).—α-Phenylbutyronitrile (cf. Bodroux and Taboury, A., 1910, i, 557) is converted, by treatment with sodium in dry ether, into the sodio-derivative, which is condensed with ethereal methyl chloroformate, giving *methyl α-cyano-α-phenylbutyrate*, b. p. 180—192°/17 mm. Treatment of the latter with hydrogen chloride

in absolute methyl alcohol and ether affords the corresponding *iminohydrochloride*, m. p. 102°, which, on hydrolysis, yields methyl phenylethylmalonate, m. p. 39·5° (cf. Rising and Stieglitz, A., 1918, i, 271). The reactions of the above sodio-compound suggest the existence of the *tautomeride*, CEtPh:C:NNa.

F. G. Willson.

Bromine derivatives of some δ-ketonic esters. G. A. Hill (J. Amer. Chem. Soc., 1927, **49**, 566—571).—Treatment of benzylidenepinacolone with ethyl malonate and sodium ethoxide in alcohol affords *ethyl β-pivalyl-α-phenylethylmalonate*, $CH_2(CO{\cdot}CMe_3){\cdot}CHPh{\cdot}CH(CO_2Et)_2$, m. p. 44·5°. On bromination in carbon tetrachloride, this yields a *monobromo*-derivative, m. p. 80—81°, which is unchanged after an hour at 200°. *Methyl β-pivalyl-α-phenylethylmalonate*, m. p. 82·5°, is obtained analogously, together with the *monomethyl* ester, m. p. 103°. Bromination of the former in carbon tetrachloride affords a *monobromo*-derivative, m. p. 83·5°, together with an *isomeride*, m. p. 85°, the ratio of the former to the latter being 2 : 1. In methyl alcohol, the isomeric bromo-derivatives are produced in equal quantities. Further bromination of the isomeride of lower m. p. could not be satisfactorily effected. Treatment of this isomeride in benzene with methyl-alcoholic sodium methoxide affords *methyl 3-pivalyl-2-phenylcyclopropanedicarboxylate*, m. p. 86°, this compound being obtained from the isomeride of m. p. 85° by the action of sodium methoxide, *p*-toluidine, or ammonia. The isomeride of m. p. 83·5° is unaffected by methyl-alcoholic potassium iodide and by methyl-alcoholic hydrogen bromide, whilst the latter reagent converts the isomeride of m. p. 85° into the derivative of lower m. p. The latter yields, when heated for an hour at 250°/35 mm., *γ-pivalyl-α-carbomethoxy-β-phenylbutyrolactone*, m. p. 128°. The last is obtained from *β-pivalyl-α-phenylethylmalonic acid*, m. p. 137°, by bromination in chloroform, followed by treatment with sodium carbonate and esterification of the product with methyl alcohol and hydrogen chloride. When boiled with water, β-pivalyl-α-phenylethylmalonic acid is converted into γ-pivalyl-β-phenylbutyric acid, m. p. 122°. The above bromo-derivative, m. p. 85°, yields, when heated for an hour at 150°/25 mm., an isomeric *γ-pivalyl-α-carbomethoxy-β-phenylbutyrolactone*, m. p. 103·5°, which, on hydrolysis with sodium methoxide, yields a *γ-pivalyl-α-carboxy-β-phenylbutyrolactone*, m. p. 135°, the latter being reconverted, on esterification, into the original ester, m. p. 103·5° (cf. Kohler, A., 1922, i, 552).

F. G. Willson.

Opianyl chloride. A. Kirpal (Ber., 1927, **60**, [*B*], 382—383; cf. Rodionov and Fedorova, this vol., 151).—Opianyl *ψ*-chloride, m. p. 94°, prepared by the action of phosphorus pentachloride on opianic acid at 80°, is converted by methyl alcohol at the atmospheric temperature into the corresponding *ψ*-ester, m. p. 105°, which is transformed by prolonged contact with methyl-alcoholic hydrogen chloride into the normal ester, m. p. 83°.

H. Wren.

Complex compounds from pyromellitic anhydride. R. Seka and H. Sedlatschek (Monatsh., 1926, **47**, 511—517).—Pyromellitic anhydride combines with various phenol ethers to form coloured additive compounds, containing 1 mol. of each component. These are produced by simple crystallisation of the anhydride from excess of the ether, or by mixed fusion, and readily decompose into the original constituents in a vacuum at 100°. The following *compounds* are obtained: from anisole, yellow laminæ, m. p. 250—260°; from veratrole, orange-red, m. p. 195—200°; from quinol dimethyl ether, crimson, m. p. 180—185°; from tetralin, yellow, m. p. 215—220°. Pyromellitic anhydride may either be regarded as a combination of two furanquinones (if the benzene nucleus is given its centric formula) or as a combination of maleic anhydride and a fulgide system (if the Kekulé phase is used) (cf. Pfeiffer, A., 1922, i, 341; Stobbe and Dietzel, *ibid.*, 1923, i, 39), the formation of complex compounds with only 1 mol. of the phenol ether supporting the latter view.

J. W. Baker.

Condensation products of pyromellitic anhydride. R. Seka, O. Schmidt, and K. Sekora (Monatsh., 1926, **47**, 637—641).—Pyromellitic anhydride condenses with commercial xylene in the presence of aluminium chloride to yield a mixture of the isomeric *dixyloylbenzenedicarboxylic acids* in 65·9% yield. Fractional crystallisation from acetic acid yields a sparingly soluble portion, m. p. 312°, and a readily soluble one, m. p. 283°. Reduction of the mixture gives a mixture of the isomeric *lactones*, $C_{26}H_{22}O_4$, m. p. 105—110°, in 90% yield. Similar condensation with *p*-cymene yields a mixture of isomeric *p-cymoylbenzenedicarboxylic acids*, m. p. 295° after crystallisation, in 52·5% yield. 5 : 7 : 12 : 14-Dinaphthanthradiquinone-1 : 4 : 8 : 11-tetracarboxylic acid (Philippi and Seka, A., 1923, i, 576), on treatment with phosphoryl chloride and phosphorus pentachloride, yields the *chloride*, decomp. 320° (in a sealed tube), which, heated for 12 hrs. with methyl or ethyl alcohol, yields the *tetramethyl* and *tetraethyl* esters, respectively, the former decomp. 370°.

J. W. Baker.

Compound derived from *o*-nitrobenzaldehyde and diazomethane and its transformation products. F. Arndt and W. Partale (Ber., 1927, **60**, [*B*], 446—456).—*o*-Nitrobenzaldehyde is readily converted by an ethereal solution of diazomethane at −10° into the *compound*, $C_6H_4\langle\begin{matrix}N{-}O\\ \\ CH{-}O\end{matrix}\rangle CH_2$, m. p. 65°, b. p. 144°/10 mm., 150°/15 mm., for which the non-committal name "*nitraldin*" is proposed; *o*-nitroacetophenone is not formed to a considerable extent, if at all. Nitraldin does not react with acetic anhydride, phenylcarbimide, semicarbazide, or *o*-nitrophenylhydrazine. It explodes by contact with sulphuric acid, and decomposes violently at 200° with evolution of formaldehyde. It is transformed by very cautious treatment with formic acid into the *nitroso*-derivative, $NO{\cdot}C_6H_4{\cdot}CH\langle\begin{matrix}O\\ \\ O\end{matrix}\rangle CH_2$, m. p. 103—104° (decomp.), which is converted by warm 2*N*-hydrochloric acid into formaldehyde and *methylenedibenziso*oxazolone, $CO\langle\begin{matrix}C_6H_4\\ \\ O\end{matrix}\rangle N{\cdot}CH_2{\cdot}N\langle\begin{matrix}C_6H_4\\ \\ O\end{matrix}\rangle CO$, which

is also derived by the action of mineral acids on nitraldin. The constitution of the latter substance is established by its production from benz*iso*oxazolone and formaldehyde in presence of 2*N*-hydrochloric acid and from hydroxymethylbenz*iso*xazolone and acid with evolution of formaldehyde. Benz*iso*oxazolone is converted by boiling aqueous formaldehyde into *hydroxymethylbenz*isooxazolone, m. p. 116—117°, which, in solution, appears to be in equilibrium with the compounds from which it is derived. In neutral media, the equilibrium is greatly in favour of the hydroxymethyl compound, so that it may be crystallised from water or acetic anhydride. In alkaline solution, equilibrium is in favour of the components, so that benzoyl chloride and alkali hydroxide convert it into *N*-benzoylbenz*iso*oxazolone and ammonia (which combines with the formaldehyde) transforms it into benz*iso*oxazolone. For a similar reason, its conversion into methylenedibenz*iso*oxazolone (*v. s.*) by hydrochloric acid is prevented by the addition of a large excess of formaldehyde.

H. WREN.

Condensation products from *o*-aminobenzaldehyde. Preparation of the aldehyde. E. BAMBERGER (Ber., 1927, 60, [*B*], 314—319; cf. Seidel, A., 1926, 1140; Weitnauer, Diss., Zurich, 1904).—Anhydrotris-*o*-aminobenzaldehyde, (?) $CH\langle^{C_6H_4\cdot NH}_{N=C_6H_4}\rangle CH\cdot NR\cdot C_6H_4\cdot CHO$, (R=H), m. p. 230—251°, according to the mode of heating, is obtained when *o*-aminobenzaldehyde is preserved in aqueous or ethyl-alcoholic solution or, more slowly, when the solid aldehyde is kept in a closed vessel. It is converted by *p*-nitrophenylhydrazine in feebly acid solution into the *p*-nitrophenylhydrazone of *o*-aminobenzaldehyde. The action of methyl-alcoholic hydrogen chloride on *o*-aminobenzaldehyde gives *methylanhydrotris-o-aminobenzaldehyde* (R=Me), m. p. 240° (decomp.); the corresponding *ethyl* and *n-propyl* derivatives, m. p. 200° and 216—217°, respectively, are analogously prepared. *o*-Aminobenzaldehyde and β-phenylhydroxylamine give the *compound*, $C_{27}H_{22}ON_4$, m. p. 215—229° (decomp.), according to the manner of heating.

Improved directions are given for the preparation of *o*-amino- from *o*-nitro-benzaldehyde. H. WREN.

Chlorovanillin and some of its derivatives. R. M. HANN and G. C. SPENCER (J. Amer. Chem. Soc., 1927, 49, 535—537).—A chlorovanillin, presumably 5-chloro-4-hydroxy-3-methoxybenzaldehyde, m. p. 165°, is obtained by the action of chlorine on vanillin in glacial acetic acid at the ordinary temperature (cf. Menke and Bentley, A., 1898, i, 661). The *oxime*, m. p. 172—173° [*hydrochloride*, m. p. 168—169° (decomp.); *hydrobromide*, m. p. 153—154° (decomp.)], *hydrazone*, m. p. 248—249° (decomp.), *phenylhydrazone*, m. p. 106—107°, *diphenylhydrazone*, m. p. 155—156°, *semicarbazone*, m. p. 198—199° (decomp.), and *thiosemicarbazone*, m. p. 216—217°, are described. Condensation of chlorovanillin with ethyl cyanoacetate in presence of piperidine affords the *ethyl* ester, m. p. 201°, of *o-chloro-4-hydroxy-o-methoxy-α-cyanocinnamic acid*, yellow, m. p. 233—234° (decomp.), whilst treatment with aniline and β-naphthylamine in alcohol yields, respectively, *chlorovanillylideneaniline*, m. p. 160° [*picrate*, m. p. 226—227° (decomp.)], and chlorovanillylidene-β-naphthylamine, m. p. 130—131° [*dibromide*, m. p. 150—155° (decomp.); *picrate*, brick-red, m. p. 214° (decomp.)]. F. G. WILLSON.

Synthesis of *p*-hydroxybenzophenone. W. T. MINAEV (J. Russ. Phys. Chem. Soc., 1926, 58, 307—313).—The various methods for the preparation of the aromatic polyhydroxy-ketones are discussed from the point of view of their value in dye chemistry. Dobner's method of condensing the phenol with benzoyl chloride in presence of zinc chloride was adopted. On gently warming the mixture of phenol and benzoyl chloride, hydrogen chloride is evolved quantitatively, and the phenolic ester, $Ph\cdot CO_2Ph$, is formed. Further action of benzoyl chloride at 180° in presence of zinc chloride gives a 93% yield of the *para*-benzoylated ester, $Ph\cdot CO\cdot C_6H_4\cdot CO_2Ph$, which, on prolonged hydrolysis with alkali, gives an extremely small yield (7%) of the impure *p*-hydroxy-ketone.

It was found that the action of alkali, zinc chloride, or hydrochloric acid on the pure *p*-hydroxy-ketone gave tars. On completion of the second stage of the synthesis, therefore, the *p*-benzoylated ester was separated from the zinc chloride, and repeatedly hydrolysed with small quantities of alkali, the crystals of the *p*-hydroxy-ketone which separated being removed in each case. A 51·5% yield of pure ketone m. p. 133·8—133·9°, was obtained.

The possibility of a migration to the nucleus of the benzoyl group, $Ph\cdot CO\cdot O\cdot Ph \longrightarrow Ph\cdot CO\cdot C_6H_4\cdot OH$ is discussed. M. ZVEGINTZOV.

Reactions of hydrazines with hydroxymethylene-ketones and their derivatives. I. K. VON AUWERS and H. MAUSS (Annalen, 1927, 452, 182—210).—The intermediate products in the production of 1 : 3- and 1 : 5-diphenylpyrazoles from hydroxymethyleneacetophenone and phenylhydrazine (Auwers and Schmidt, A., 1925, i, 585) are now shown not to be hydrazones, but hydrazides of the composition $CHBz{:}CH\cdot NPh\cdot NH_2$ (I) (25%) and $CHBz{:}CH\cdot NH\cdot NHPh$ (II) (75%), which on distillation yield 1 : 3- and 1 : 5-diphenylpyrazoles in the proportions stated. The latter intermediate, *1-phenyl-2-β-benzoylvinylhydrazine*, m. p. 126°, when shaken with air in alcoholic sodium hydroxide solution, is oxidised to *β-benzoylvinylazobenzene* (III), m. p. 50—60°. The sodium salt of the ketone reacts with phenylhydrazine to yield *s*-formylphenylhydrazine, small quantities of (II) and (III), and acetophenone. Hydroxymethyleneacetophenone benzoate (the ketonic structure of which is proved by its oxidation to phenylglyoxylic acid with potassium permanganate in aqueous acetone solution), on treatment with phenylhydrazine yields two initial products, m. p. 120° and 164°, respectively, which are found to be isomorphous forms of *1-phenyl-1-β-benzoylvinylhydrazine* (I), the ring structure previously ascribed (*loc. cit.*) to the one m. p. 164° being incorrect. On oxidation with potassium permanganate, either form yields the anilide of hydroxymethyleneacetophenone, identical with a synthetic specimen, which with phenylhydrazine yields 1 : 5-diphenylpyrazole. Both forms

when treated with *p*-nitrobenzaldehyde yield the p-*nitrobenzylidene* derivative, $CHBz{:}CH{\cdot}NPh{\cdot}N{:}CH{\cdot}C_6H_4{\cdot}NO_2$, m. p. 173—174°, identical with a synthetic specimen prepared from hydroxymethyleneacetophenone and *p*-nitrobenzylidenephenylhydrazine; and with *p*-nitrobenzoyl chloride both yield an *N*-p-*nitrobenzoyl* derivative, $CHBz{:}CH{\cdot}NPh{\cdot}NH{\cdot}CO{\cdot}C_6H_4{\cdot}NO_2$, m. p. 205°, identical with a specimen obtained from the sodium salt of hydroxymethyleneacetophenone and *p*-nitrobenzoylphenylhydrazine. Hence it is the substituted amino-group of phenylhydrazine which reacts with esters and ethers of the hydroxymethylene-ketone. With *s*-formylphenylhydrazine, the ketone yields the *α-phenyl-β-formylhydrazide*, m. p. 148—149°, which when heated with 2*N*-hydrochloric acid for 15 min. yields 1 : 3-diphenylpyrazole. The sodium salt of the ketone reacts with *p*-nitrophenylhydrazine hydrochloride to yield the p-*nitrophenylhydrazide*, m. p. 156—157°, which when heated for 15 min. with acetic acid yields 1-p-*nitrophenyl*-5-*phenylpyrazole*, m. p. 117—118°, b. p. 240—242°/14 mm. (also obtained directly when the benzoate of the ketone is used). This compound, on reduction with stannous chloride and hydrochloric acid, yields 1-p-*aminophenyl*-5-*phenylpyrazole*, m. p. 148·5—149·5°, which yields 1 : 5-diphenylpyrazole when the amino-group is removed. The benzoate of the ketone reacts with *p*-nitrophenylhydrazine in propyl alcohol at the ordinary temperature to yield the nitrodiphenylpyrazole directly, together with a *compound*, m. p. 208—209°. In boiling propyl alcohol a *bis*-p-*nitrophenylhydrazine* derivative, $NO_2{\cdot}C_6H_4{\cdot}NH{\cdot}N{:}CPh{\cdot}CH{:}CH{\cdot}NH{\cdot}NH{\cdot}C_6H_4{\cdot}NO_2$, was obtained, red, m. p. 170—172° (+1 mol. of acetone), yellow, m. p. 195—200° (changing into the red form on heating), which after long heating on a water-bath yields 1-p-*nitrophenyl*-3-*phenylpyrazole*, m. p. 169—169·5°, giving on nitration with nitric acid for 0·5 hr. on a water-bath 1 : 3-*dinitrodiphenylpyrazole*, m. p. 226—228°, identical with the product obtained by direct nitration of 1 : 3-diphenylpyrazole. The constitution $CHBz{:}CH{\cdot}NH{\cdot}NMe{\cdot}CH{:}CHBz$ is now assigned to the compound, m. p. 138°, obtained from hydroxymethyleneacetophenone and methylhydrazine. On methylation with methyl sulphate, it yields *s-dimethyldi-β-benzoylvinylhydrazine*, m. p. 175—176°, identical with the compound obtained from *s*-dimethylhydrazine and the sodium salt of hydroxymethyleneacetophenone. When heated with hydrochloric acid, it yields *s*-tribenzoylbenzene. Treated with methylhydrazine and *p*-nitrobenzaldehyde, the benzoate of the ketone yields 1-p-*nitrobenzylidene*-2-*methyl*-2-*β-benzoylvinylhydrazine*, m. p. 207°.

J. W. BAKER.

Theory of colour lakes. Optically active, internally complex salt of pæonol. P. PFEIFFER, S. GOLTHER, and O. ANGERN (Ber., 1927, 60, [*B*], 305—313; cf. A., 1911, i, 819; 1913, i, 879).—The internally complex structure of lakes is established by the resolution of such substances containing a metallic atom of constant co-ordination number into their optical antipodes; the cobalt derivatives of pæonol (2-hydroxy-4-methoxyacetophenone) being selected. Pæonol is converted by chloropentamminecobaltic chloride in boiling aqueous solution into the *compound* $Co(C_9H_9O_3)_3$ (also $+CHCl_3$), which is not suitable for purposes of resolution. The ketone is transformed by hydroxoaquodiethylenediaminecobalt bromide (cf. Werner and Matissen, A., 1918, i, 379) or by chloroaquodiethylenediaminecobalt sulphate into the *bromide*, $[Co\,en_2(C_9H_9O_3)]Br,H_2O$, from which the corresponding *iodide* (monohydrate and anhydrous), *chlorate*, *perchlorate*, and *dithionate* are derived. Resolution of the bromide is effected by treatment with silver *d*-tartrate and evaporation of the filtrate to a syrup from which the d-*tartrate* of the *l*-base separates, $[\alpha]^{19}_{red}$ −139·4° in water. Treatment of the tartrate with sodium bromide affords the corresponding active *bromide*, $[\alpha]^{19}_{red}$ −175·7° in water.

Pæonol is converted by treatment with copper or nickel sulphate and ammonia into the *compounds* $Cu(C_9H_9O_3)_2$ and $Ni(C_9H_9O_3)_2$, which give additive *derivatives* with pyridine (2 mols.) or aniline (1 mol.).

Amended directions are given for the preparation of carbonatodiethylenediaminecobalt nitrate and the corresponding bromide. H. WREN.

Preparation of alizarin from phthalic anhydride and *o*-dichlorobenzene. M. PHILLIPS (J. Amer. Chem. Soc., 1927, 49, 473—478).—When phthalic anhydride (0·2 mol.) is heated with *o*-dichlorobenzene (1 mol.) and aluminium chloride (0·3 mol.) at 100° for about 14 hrs., o-3 : 4-*dichlorobenzoylbenzoic acid*, m. p. 191·2°, is obtained in 70% yield. When heated with 4 parts of concentrated sulphuric acid at 150° for 4 hrs., the latter affords a practically quantitative yield of 2 : 3-dichloroanthraquinone, and this, when heated with an equal weight of water and 4 parts of potassium hydroxide at 225°, is converted into alizarin (yield, 31·2%). The formation of β-chloroanthraquinone from phthalic anhydride and *o*-dichlorobenzene (Sprent and Dodd, E.P. 204,528) could not be confirmed. F. G. WILLSON.

Polyhydroxyanthraquinones. VII. Structure and synthesis of hydroxyanthrarufin and of rufiopin. S. V. PUNTAMBEKER and R. ADAMS (J. Amer. Chem. Soc., 1927, 49, 486—491; cf. A., 1925, i, 1076).—Treatment of 2′-hydroxy-3 : 4-dimethoxydiphenylmethane-2-carboxylic acid (cf. A., 1925, i, 272) with concentrated sulphuric acid and boric acid at the ordinary temperature, followed by addition of phosphorus pentoxide, affords 5-*hydroxy*-1 : 2-*dimethoxy*-9-*anthrone*, which, on oxidation with chromic acid in glacial acetic acid, yields 5-*hydroxy*-1 : 2-*dimethoxyanthraquinone*, orange, m. p. 230·5—231·5°, and this, on demethylation with hydrobromic acid in acetic acid, is converted into 1 : 2 : 5-*trihydroxyanthraquinone*, brownish-red, m. p. 273—274° (*triacetate*, m. p. 238—239°), identical with hydroxyanthrarufin. Condensation of *p*-bromoguaiacol with opianic acid in presence of concentrated sulphuric acid yields 5 : 6-*dimethoxy*-2-(5′-*bromo*-2′-*hydroxy*-3′-*methoxyphenyl*)*phthalide*, m. p. 163—164°, which, on reduction with zinc and sodium hydroxide, affords 2′-*hydroxy*-3 : 4 : 3′-*trimethoxydiphenylmethane*-2-*carboxylic acid*, m. p. 155—156°. Bromination of the latter in glacial acetic acid yields 5′-*bromo*-2′-*hydroxy*-3 : 4 : 3′-*trimethoxydiphenylmethane*-2-*carboxylic acid*, m. p. 168—169°, whilst treatment with concentrated

sulphuric acid in presence of boric acid affords *5-hydroxy*-1 : 2 : 6-*trimethoxy*-9-*anthrone*. On oxidation, the latter is converted into *5-hydroxy*-1 : 2 : 6-*trimethoxyanthraquinone*, orange, m. p. 245—246°, and this, on demethylation, yields 1 : 2 : 5 : 6-*tetrahydroxyanthraquinone*, red, m. p. 316—318° (*tetra-acetate*, m. p. 237—238°), identical with rufiopin. F. G. WILLSON.

Reduction products of dinaphthanthradiquinone. R. SEKA and K. SEKORA (Monatsh., 1926, **47**, 519—528).—Reduction of dinaphthanthradiquinone with alkaline hyposulphite and benzoylation of the product yields the *dibenzoyl* derivative of the monoquinol, $C_6H_4<^{CO}_{CO}>C_6H_2<^{C(OBz)}_{C(OBz)}>C_6H_4$, decomp. 350° (cf. Philippi, A., 1913, i, 627), which, on further reduction and acetylation with zinc dust, acetic anhydride, and sodium acetate, yields the *monobenzoyltriacetyl* derivative of dinaphthanthradiquinol, decomp. 283—285°. The corresponding *tetra-acetyl* derivative, decomp. 295°, is obtained by similar treatment of the original diquinone. The diquinone, treated in acetic acid suspension with granulated tin and fuming hydrochloric acid, yields *dinaphthanthradiquinol*, decomp. 340—343°, which on acetylation yields the tetra-acetyl derivative already described. On oxidation, either with nitrobenzene or chromic acid, it is reconverted into the diquinone. A preliminary account of the reduction with zinc dust in ammoniacal solution is given. J. W. BAKER.

Nitro-derivatives of dinaphthanthradiquinone and their reactions. R. SEKA and O. SCHMIDT (Monatsh., 1926, **47**, 619—626).—Nitration of dinaphthanthradiquinone with potassium nitrate and sulphuric acid yields two isomeric *mononitro*-derivatives, one soluble with difficulty in nitrobenzene, decomp. above 400° (39·7%), and the other easily soluble in the same solvent, decomp. 310° (36·9%). Nitration with nitric acid (*d* 1·52) at the temperature of the water-bath yields two *dinitro*-derivatives (cf. Phillipi and Seka, A., 1923, i, 577), which are separated by the same method, the one sparingly soluble, decomp. above 400° (40·9%), and the other, decomp. 340° (45·6%). Long heating of the sparingly soluble dinitro-compound with aniline or *p*-toluidine causes replacement of both nitro-groups with the formation of *dianilino*- and *di*-p-*toluidino*-derivatives, decomp. above 400° and decomp. 420°, respectively. The readily soluble dinitro-compound similarly yields an isomeric *dianilino*-compound, decomp. 320°. The sparingly soluble nitro-compound heated with aniline for 3 hrs. yields, not a mono-, but a *di-anilino*-derivative, decomp. 330°. These compounds all give intensely coloured bluish-grey to black dyes when heated with fuming sulphuric acid. J. W. BAKER.

Amino-derivatives of dinaphthanthradiquinone. R. SEKA and O. SCHMIDT (Monatsh., 1926, **47**, 627—634).—Treatment of 2-benzoylanthraquinone-3-carboxylic acid (Phillipi, A., 1913, i, 627) with concentrated sulphuric acid yields dinaphthanthradiquinone in 52·8% yield (calculated on the original dibenzoylbenzenedicarboxylic acids). On nitration with nitric acid (*d* 1·52), 2-*dinitrobenzoylanthraquinone*-3-*carboxylic acid*, m. p. 170°, is obtained, which on reduction with ferrous sulphate yields the corresponding *diamino*-compound, m. p. 170°. These compounds on heating with sulphuric acid (*d* 1·83) yield, respectively, *dinitro*- and *diamino-dinaphthanthradiquinone*, both decomp. 400°. The dinitro-compound exhibits the same colour reactions as the compound obtained by the direct nitration of the diquinone (preceding abstract), but reduction of the latter (decomp. above 400°) with stannous chloride in alkaline solution yields a *diamino*-compound, decomp. 450°, which contains two atoms of hydrogen more than the diaminodiquinone. J. W. BAKER.

Nitriles of the benzanthrone series. KALLE & Co., A.-G.—See B., 1927, 101.

Manufacture of *iso*dibenzanthrones. BADISCHE ANILIN- & SODA-FABRIK.—See B., 1927, 101.

Vat dyes of the *iso*dibenzanthrone series. BADISCHE ANILIN- & SODA-FABRIK.—See B., 1927, 101.

Manufacture of 1 : 4-diarylamino-5 : 8-dihydroxyanthraquinones. I. G. FARBENIND. A.-G.—See B., 1927, 136.

Menthol studies. I. Menthyl esters of the nitro- and amino-cinnamic acids. K. L. MCCLUSKEY and B. C. SHER (J. Amer. Chem. Soc., 1927, **49**, 452—457).—The following menthyl esters were prepared by treating the appropriate acids with thionyl chloride and heating the resulting crude acid chlorides with menthol at 130° : p-*nitrocinnamate*, m. p. 92·5°, $[M]_D^{30}$ —224·00°; m-*nitrocinnamate*, m. p. 85°, $[M]_D^{30}$ —233·61°; o-*nitrocinnamate*, m. p. 49·5°, $[M]_D$ —209·75°; cinnamate, b. p. 174°/3 mm., $[M]^{30}$ —218·46°; benzoate, b. p. 173°/12 mm., $[M]_D^{30}$ —238·17°; and *p*-nitrobenzoate, m. p. 62°, $[M]_D^{30}$ —271·13°. Treatment of menthyl *p*-nitrocinnamate with pyridine dibromide–hydrobromide in glacial acetic acid affords *menthyl* αβ-*dibromo*-β-p-*nitrophenylpropionate*, m. p. 48° (cf. Rosenmund and Kuhnhenn, A., 1923, i, 782). Addition of bromine to menthyl *o*-nitrocinnamate in chloroform solution yields *menthyl* αβ-*dibromo*-β-o-*nitrophenylpropionate*, m. p. 93—93·5°, $[M]^{30}$ —76·03°; *menthyl* αβ-*dibromo*-β-*phenylpropionate*, m. p. 83·5°, $[M]_D^{30}$ —202·11, was prepared analogously. Reduction of the nitro-derivatives with iron powder affords the corresponding amino-compounds : *menthyl* p-*aminocinnamate*, m. p. 122°, $[M]_D^{30}$ —219·30°; m-*aminocinnamate*, b. p. 230°/2 mm., $[M]_D$ —209·14°; o-*aminocinnamate*, m. p. 85°, —182·32°; and p-*aminobenzoate*, m. p. 88°, $[M]^{30}$ —250·53 [*nitrate*, decomp. 150—156; *hydrochloride*, m. p. 196° (decomp.)]. *Menthyl* p-*dimethylaminocinnamate*, m. p. 99°, $[M]_D$ —220·67° (*methiodide*, decomp. above 140°, $[M]_D^F$ —177·68°), was prepared by condensation of *p*-dimethylaminobenzaldehyde with menthyl acetate in presence of sodium. All the above specific rotations were determined in 5% benzene solution. The following *dyes*, obtained by coupling the components mentioned, are described : menthyl *p*-aminocinnamate and β-naphthol, red; menthyl *p*-aminocinnamate and R-salt, maroon; menthyl *m*-aminocinnamate and β-naphthol, orange; menthyl *p*-aminobenzoate and β-naphthol, orange-red; and menthyl *p*-aminobenzoate and F-salt, orange, m. p. 287—288°. F. G. WILLSON.

Decomposition products of menthyl esters of sulphonic acids. T. S. PATTERSON and (MISS) I. M. MCALPINE (J.C.S., 1927, 349—353; cf. *ibid.*, 1906, **89**, 332).—Menthyl benzenesulphonate, naphthalene-β-sulphonate, and naphthalene-α-sulphonate (m. p. 116·5°, $[\alpha]^{17\cdot5}_{5461}$ −114·8°) decompose when distilled at 4 mm. into menthene and benzene sulphonic acid or naphthalene-β- or -α-sulphonic acids. When, however, the decomposition is carried out at about 120° in sealed tubes (no pressure), secondary reactions take place with the formation of hexahydrocymene, dimenthene, an unrecognised gelatinous substance (cf. Tolloczko, A., 1899, i, 440; Kanonnikov, *ibid.*, 1900, ii, 134), and the corresponding sulphonic acid. Decomposition of the esters in nitrobenzene or xylene at about 120° yields only dimenthene and the corresponding sulphonic acid.

J. M. GULLAND.

γ-Terpinene. F. RICHTER and W. WOLFF (Ber., 1927, **60**, [*B*], 477—479).—In striking contrast to the oil from the cultivated plant, that from wild *Crithmum maritimum* (Linn.) contains little dill-apiol; on distillation, it readily yields a terpene hydrocarbon, b. p. 69—73°/20 mm., d 0·8515, n^{18}_D 1·4785, α_D +2·5° (in 1 dm. tube), which is identified as $\Delta^{1:4}$-*p*-menthadiene. The identity of the substance with crithmene (Francesconi and Sernagiotto, A., 1913, i, 636) and moslene (Murayama, *ibid.*, 1921, i, 875) is established.

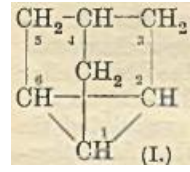
H. WREN.

Production of camphene from pinene hydrochloride. H. GAMDIAY.—See B., 1927, 156.

Camphor and terpenes. V. Addition of hydrocyanic acid to camphorimine, fenchimine, menthimine; cyanohydrins of camphor and menthone. J. HOUBEN and E. PFANKUCH (Ber., 1927, **60**, [*B*], 586—600; cf. A., 1926, 1251).—The action of potassium or silver acetate on 2-*endo*chlorocamphane-2-carboxylamide or of silver acetate on the corresponding nitrile leads to loss of hydrogen chloride and production of camphene-1-carboxylamide and camphene-1-nitrile, respectively, thus excluding the possibility of preparing camphorcyanohydrin from these initial materials. Camphorimine readily adds hydrogen cyanide, giving *2-aminocamphane-2-nitrile*, m. p. 170—171° (decomp.) [*hydrochloride*, m. p. about 270° (decomp.)], which is converted by concentrated hydrochloric acid into camphor. It is transformed by sodium nitrite into *camphor*exo*cyano*endo*hydrin*, m. p. 159°, $[\alpha]^{19}_D$ −32·2° in alcohol, which with hydrochloric acid yields optically inactive 2-endo*chlorocamphane-2-nitrile*, m. p. 181—182°, identified by conversion into 2-chlorocamphane-2-carboxylamide. The action of potassium cyanide on camphornitroimine gives the isomeric camphor*endo*cyano*exo*hydrin, m. p. 209—210°, $[\alpha]^{19}_D$ +32° in glacial acetic acid (cf. Passerini, A., 1925, i, 1290), thus affording a remarkable instance of the isolation of two optically different compounds from the same initial material. The constitution of Passerini's compound is established by converting it by means of phosphorus pentachloride and phosphoryl chloride into the chloronitrile, which is transformed with difficulty into camphene-1-carboxylic acid in addition to (?) *bornylenecarboxylamide*, m. p. 218—219°. Fenchimine is converted by aqueous hydrocyanic acid into *cyanofenchylamine*, m. p. 111° (*hydrochloride*; *acetyl* derivative, m. p. 200—201°), which appears to be converted by nitrous acid into a fenchenenitrile. *Menthimine*, b. p. 94°/12 mm., prepared by the action of ammonia on menthonenitroimine, adds anhydrous hydrocyanic acid with formation of cyanomenthylamine [*hydrochloride*, m. p. about 150° (decomp.), $[\alpha]^{19}_D$ +24·2° in water], which could not be transformed into menthonecyanohydrin. The latter *compound*, m. p. 144—145°, $[\alpha]^{19}_D$ +82·7° in alcohol, is obtained by the action of potassium cyanide on menthonenitroimine. It is hydrolysed by potassium hydroxide apparently to a menthenecarboxylic acid (*amide*, m. p. 122°).

H. WREN.

***apo*Cyclene.** I. S. S. NAMETKIN and Z. P. ALEXANDROVAVA (J. Russ. Phys. Chem. Soc., 1926, **57**, 395—398).—*apo*Cyclene (I) first



(I.)

obtained by Komppa and Roschier (A., 1922, i, 1167) as one of the products of the dehydration of camphenol by the xanthate method, yields, on hydration, various products of doubtful constitution.

The hydration could be 1 : 6 (yielding alcohols derived from camphenilone and α-*iso*camphenilone; cf. A., 1925, i, 1079), 1 : 2 (yielding products derived from *apo*camphor), or 2 : 6 (yielding products derived from camphenilol and *apo*camphor). Actually, an alcohol derived from *apo*camphor was obtained by the authors, and the addition cannot be 1 : 6 [cf. below]. Komppa and Roschier (*loc. cit.*) found as one of the products α-*iso*camphenilol. The authors prepared *apo*cyclene by the oxidation of the hydrazone of camphenilone, m. p. 39—40°, b. p. 136·5—137°/748 mm. (compare Komppa and Roschier, *loc. cit.*). Hydration with glacial acetic acid and sulphuric acid yielded an *ester*, b. p. 104—105°/21 mm. Hydrolysis gave an *alcohol*, m. p. 51—60°, b. p. 100·5—101°/19 mm.; this on oxidation yielded a mixture of ketones, $C_9H_{14}O$, which on further oxidation were converted into *apo*camphoric acid, m. p. 204—205°.

E. ROTHSTEIN.

Constituents of oil of Supa. New natural source of copaene. G. G. HENDERSON, W. MCNAB, and J. M. ROBERTSON.—See B., 1927, 172.

Vat dyes of the 2-thionaphthen-2-indoleindigo series. R. HERZ and J. MÜLLER.—See B., 1927, 136.

Reduction of quinoline-2 : 4-dicarboxylic acid. T. NOZOE (Proc. Imp. Acad. Tokyo, 1926, **2**, 541—543).—Reduction of quinoline-2 : 4-dicarboxylic acid with sodium amalgam gives the di- or tetra-hydro-acid, isolated as *copper* salt (*benzoylated acid*, $C_{18}H_{13\text{ or }15}O_7N,2H_2O$, decomp. 170°), whilst by reduction with hydrogen and platinum-black in acetic acid a quantitative yield of *decahydroquinoline-2 : 4-dicarboxylic acid*, which decomposes at 286—286·5° or, with 1·5AcOH, has m. p. 137° (decomp.). The *sodium* (+$4H_2O$), *barium* (+$6H_2O$), *copper* (+$5H_2O$), and *silver* salts and the low-melting *ethyl* ester (*chloroplatinate*, decomp. 225°) are described. Methylation of the decahydro-acid with methyl-alcoholic potassium hydroxide and methyl iodide

gives the *methylbetaine*, $CO_2H\cdot C_9H_{14}NMe_2<\begin{matrix}CO\\|\\O\end{matrix}$ (*chloroaurate*, decomp. 195—196°). If 10% aqueous potassium hydroxide is used in the methylation, the product is a *betaine* with probably a dipeptide structure, $CO_2H\cdot C_9H_{14}N\cdot CO\cdot C_9H_{14}(CO_2H)NMe_2<\begin{matrix}CO\\|\\O\end{matrix}$ (*chloroaurate*, decomp. 178—179°). C. Hollins.

Syntheses of hæmopyrrolecarboxylic acid. H. Fischer and A. Treibs (Ber., 1927, **60**, [*B*], 377—381).—4-Methylpyrrole-3-propionic acid is converted by treatment with hydrogen cyanide and hydrogen chloride in ether–chloroform followed by hydrolysis of the imine hydrochloride into *5-aldehydo-4-methylpyrrole-3-propionic acid*, m. p. 152° (corr.), which decomposes above its m. p. with formation of porphyrin and is converted by boiling concentrated hydrochloric acid into a *methene* derivative, decomp. 170° after darkening at 140°. It is transformed by treatment with hydrazine hydrate and sodium alkoxide into 4 : 5-dimethylpyrrole-3-propionic acid (hæmopyrrolecarboxylic acid), m. p. 130°. 2 : 4 : 5-Trimethylpyrrole-3-propionic acid (cf. Fischer and Nenitzescu, A., 1924, i, 1233) is converted by phthalic anhydride in glacial acetic acid at 185—195° into the phthalide of 4 : 5-dimethylpyrrole-3-propionic acid, which is hydrolysed to the *phthalidic acid*, m. p. 205° (corr.), converted by glacial acetic and hydriodic acids into 4 : 5-dimethylpyrrole-3-propionic acid. H. Wren.

Transformation products of tetrabromopyrocatechol. F. Zetzsche and S. Sukiennik (Helv. Chim. Acta, 1927, **10**, 91—102).—The yellowish-brown *monopyridine* salt of 2 : 5 : 6-*tribromo*-3 : 4-*dihydroxyphenylpyridinium bromide*, $C_{11}H_7O_2NBr_4,C_5H_5N$, decomp. 155—157°, separates slowly when tetrabromopyrocatechol is treated with dry pyridine at 40°. If the pyridine is slightly moist, the red *dipyridine* salt, m. p. above 260°, is also obtained. When either of these is treated with hydrobromic acid (*d* 1·15), 2 : 5 : 6-*tribromo*-3 : 4-*dihydroxyphenylpyridinium bromide*, m. p. 242—243° (decomp.), is formed. The pyridine ring in this compound is not opened by aniline or by phenylhydrazine as in the case of dinitrophenylpyridinium chloride (A., 1906, i, 454), but aqueous solutions of bases convert it, through an unstable violet intermediate compound, into 2 : 5 : 6-*tribromo*-3 : 4-*dihydroxyphenylpyridinium betaine*, $C_5H_5N\cdot C_6(OH)Br_3\cdot O$ m p 208—209°. This is analogous to the 2 : 4-dinitro-5-hydroxyphenylpyridinium betaine described by Zincke and Weispfenning (A., 1910, i, 585). It is reconverted by pyridine and hydrogen bromide into the red dipyridine salt, and by acids into 2 : 5 : 6-tribromo-3 : 4-dihydroxyphenylpyridinium salts (*sulphate*, m. p. 255°; *chloride*, m. p. 220—222°; *glycerol-β-phosphate*). All the above compounds are oxidised by nitric acid to the corresponding quinone, red 2 : 5 : 6-*tribromo*-3 : 4-*diketo*-3 : 4-*dihydrophenylpyridinium nitrate*, decomp. indefinitely, when heated. This and the corresponding *bromide* give a green colour with alcoholic ferric chloride and are decomposed by alkali with liberation of pyridine. Attempts to prepare compounds of a similar type from tetrabromopyrocatechol with other bases were unsuccessful. Pure tetrabromoveratrole, m. p. 151—152° (Bruggemann, A., 1896, i, 356, gives 118°), does not combine with pyridine. When tetrabromopyrocatechol, in 10% sodium hydroxide solution, is oxidised by the air, a red substance is precipitated which contains sodium bromoanilate and gives 2 : 5-dibromo-3 : 6-dihydroxy-*p*-benzoquinone on acidification. H. E. F. Notton.

Synthesis of 5 : 6-dimethoxyindole and its 2-carboxylic acid. A. E. Oxford and H. S. Raper (J.C.S., 1927, 417—422).—The first stage in the oxidation of tyrosine to 5 : 6-dihydroxyindole and its 2-carboxylic acid by tyrosinase (cf. Raper, this vol., 278) is the production of 3 : 4-dihydroxyphenylalanine, and this is suggested as a possible method by which certain pyrocatechol derivatives may arise in nature.

Condensation of 6-nitrohomoveratrole with ethyl oxalate (cf. Blaikie and Perkin, A., 1924, i, 547) yields *2-nitro-4 : 5-dimethoxyphenylpyruvic acid*, m. p. 193—194° [*phenylhydrazone*, m. p. 170° (decomp.)], which is oxidised by alkaline hydrogen peroxide to *2-nitro-4 : 5-dimethoxyphenylacetic acid*, m. p. 202—204°. The latter when reduced with ferrous sulphate and ammonia yields 5 : 6-dimethoxyindole-2-carboxylic acid, which at its m. p. (202—203°) passes into 5 : 6-dimethoxyindole, m. p. 154—155°, b. p. 198°/8 mm. (*1-acetyl* derivative, m. p. 150—152°). Colour reactions of these compounds are described, but neither the indole nor its acetyl derivative gives the brucine reaction (cf. Lions, Perkin, and Robinson, A., 1925, i, 831; Perkin and Rubenstein, *ibid.*, 1926, 394). J. M. Gulland.

Quinolines. M. Wyler (Ber., 1927, **60**, [*B*], 398; cf. Maschmann, this vol., 158).—Quinolines are readily purified by means of their double salts with zinc chloride $(Base,HCl)_2,ZnCl_2$, from which they are regenerated by treatment with alkali and steam or (as hydrochlorides) by dry distillation. 2 : 8-Dimethylquinoline has m. p. 27°. Distillation of the double salt from 2-methylquinoline under greatly diminished pressure affords occasionally a *chloro-2-methylquinoline*, m. p. 94·5° (*hydrochloride*, m. p. 165°; *picrate*, m. p. 213—214°). H. Wren.

Oxidation of 5-aminouracil. O. Baudisch and D. Davidson (J. Biol. Chem., 1927, **71**, 497—499).—Treatment of 5-aminouracil, in alkaline solution, with potassium ferricyanide gave *diuracilpyridazine*, m. p. above 300°. On the analogy of the previously observed oxidation of *iso*barbituric acid (A., 1925, i, 1188) it is thought that the reaction proceeds through the stage of 5 : 5′-diaminouracil. C. R. Harington.

Action of methylglyoxal on carbamide. L. Seekles (Rec. trav. chim., 1927, **46**, 77—84).—Carbamide reacts with methylglyoxal to yield *methylacetylenediureine*, m. p. 274° (decomp.), as a final product. An intermediate *product*, (I) or (II), m. p. 193° (decomp.) can be isolated. On treatment with fuming nitric acid, both the diureine and its inter-

(I.) $HO\cdot CMe\cdot NH>CO$ / $NH_2\cdot CO\cdot NH\cdot CH—NH$

$NH_2\cdot CO\cdot NH\cdot CMe——NH>CO$ / (II.) $CH(OH)\cdot NH$

mediate product yield nitropyruvic ureide. On hydrolysis in presence of phenylhydrazine, the intermediate product yields methylglyoxalosazone, and with hydrogen peroxide it is converted into a *peroxide*, $CO<^{NH\cdot CMe\cdot OH}_{NH\cdot CH\cdot OOH}$ or $CO<^{NH\cdot CMe\cdot OOH}_{NH\cdot CH\cdot OH}$ m. p. 146° (decomp.). This peroxide is unstable both in the dry state and in solution. Treated with fuming nitric acid, it yields nitropyruvic ureide, with potassium permanganate followed by phenylhydrazine it yields methylglyoxalosazone, and with hydrogen peroxide, acetylcarbamide is obtained. On treatment with hot water, intramolecular oxidation occurs, yielding a *substance*, m. p. 167°, probably pyruvic acid monoureide, $Ac\cdot CO\cdot NH\cdot CO\cdot NH_2$. This yields a *phenylhydrazone*, m. p. 160—162° (resinifying on exposure to air), which is also obtained by the action of phenylhydrazine on the peroxide. J. W. Baker.

Relative stability of cyclic bases. XIII. J. von Braun and O. Goll (Ber., 1927, **60**, [*B*], 339—345; cf. A., 1926, 739).—The systems derived by the insertion of one or two methylene groups in the piperazine ring resemble piperazine itself in stability and thus find their place among the least stable cyclic systems.

Tetrahydro*iso*quinoline is converted by trimethylene bromide into *αγ-ditetrahydroisoquinolyl-n-propane*, b. p. 265—270°/14 mm. (slight decomp.), 230°/1 mm., m. p. 55—56° (hygroscopic *hydrochloride*, decomp. 230—232°; *picrate*, m. p. 190°). The new base is transformed by trimethylene bromide into *ditetrahydroisoquinoliniumditrimethyleninimium bromide*, $C_9H_7N<^{CH_2\cdot CH_2\cdot CH_2}_{CH_2\cdot CH_2\cdot CH_2}>NC_9H_7$, $_{Br}$ $_{Br}$ m p 225° (corresponding *chloride*, decomp. 219—220°; *chloroaurate*, decomp. 158°, after darkening at 140°; *chloroplatinate*, decomp. 220—222°). The diquaternary bromide is converted by tetrahydro*iso*quinoline and a little water at 200° into αγ-ditetrahydro*iso*quinolylpropane in 80% yield, whereas with piperidine under similar conditions it affords αγ-ditetrahydro*iso*quinolyl-*n*-propane, αγ-dipiperidino-*n*-propane, and *α-piperidino-γ-tetrahydroisoquinolyl-n-propane*, b. p. 230—240°/14 mm. (very hygroscopic *hydrochloride*; *picrate*, m. p. 190°).

The action of trimethylene bromide on αβ-dipiperidinoethane or of ethylene bromide on αγ-dipiperidino-*n*-propane affords dipiperidiniumhomopiperazinium bromide, which does not melt below 300° (corresponding *chloride*, m. p. 290—300°, after darkening at 280°, according to the rate of heating; *chloroaurate*, m. p. 212°; *chloroplatinate*, decomp. 285°, after darkening at 250°). The bromide is converted by piperidine at 200° into αβ-dipiperidinoethane and αγ-dipiperidino-*n*-propane; with tetrahydro*iso*quinoline, the products are αβ-ditetrahydro*iso*quinolylethane, αγ-ditetrahydro*iso*quinolyl-*n*-propane, αβ-dipiperidinoethane, αγ-dipiperidino-*n*-propane, and an inseparable mixture of γ-piperidinopropyl- and β-piperidinoethyl-tetrahydro*iso*quinoline. *Ditetrahydroisoquinoliniumhomopiperazinium bromide*, m. p. 279—280° (decomp.) (corresponding *chloride*, m. p. 272°), is transformed by tetrahydro*iso*quinoline into an equimolecular mixture of αβ-ditetrahydro*iso*quinolylethane and αγ-ditetrahydro*iso*quinolyl-*n*-propane. With piperidine, it affords a little dipiperidinoethane and -propane containing tetrahydro*iso*quinoline, mainly β-piperidinoethyl- and γ-piperidinopropyltetrahydro*iso*quinoline, and small amounts of ditetrahydro*iso*quinolyl-ethane and -propane. H. Wren.

Isomerism of reduced derivatives of quinoxaline. II. Stereoisomeric 2 : 3-dimethyl-1 : 2 : 3 : 4-tetrahydroquinoxalines. C. S. Gibson (J.C.S., 1927, 342—349; cf. *ibid.*, 1923, **123**, 1570).—2 : 3-Dimethylquinoxaline, m. p. 104·5—105·5° (cf. Gabriel and Sonn, A., 1908, i, 60), crystallises $+3H_2O$. When reduced with sodium and alcohol, it yields a mixture of meso-2 : 3-*dimethyl*-1 : 2 : 3 : 4-*tetrahydroquinoxaline* (75%), m. p. 111—112° (crystallographic data given), and dl-2 : 3-*dimethyl*-1 : 2 : 3 : 4-*tetrahydroquinoxaline*, m. p. 101—102°, which is probably a pseudo-racemic mixture. The following derivatives of the *meso*-base are described: 1 : 4-*diacetyl*, m. p. 145—146°; 1 : 4-*dibenzoyl*, m. p. 218·5—219·5°; 1-*benzoyl*, m. p. 137—138° (*nitroso*-compound, decomp. 140°, and *hydrochloride* described); 1 : 4-*di*-m-*nitrobenzoyl*, m. p. 243—244°; 1-p-*nitrobenzoyl*, m. p. 167°; 1-p-*toluenesulphonyl*, m. p. 183—184°; 1 : 4-*diphenylcarbamyl*, m. p. 190—191°; 1-*carbamyl*, m. p. 162—163° (crystallographic data given). Resolution of the *dl*-base by *d*- and *l*-tartaric acids yields d-2 : 3-*dimethyl*-1 : 2 : 3 : 4-*tetrahydroquinoxaline*, m. p. 94·5°, $[\alpha]_{5461}$ +112·3° (crystallographic data given; l-*tartrate*, $[\alpha]_{5161}$ +49·9°; 1-*benzoyl* derivative, m. p. 233—234°, $[\alpha]_{5461}$ −369·1°), and l-2 : 3-*dimethyl*-1 : 2 : 3 : 4-*tetrahydroquinoxaline*, m. p. 94·5°, −112·0° [d-*tartrate*, decomp. 149°, $[\alpha]_{5461}$ −50·2°; 1-*benzoyl* derivative, m. p. 233—234° (decomp.), $[\alpha]_{5461}$ +369·7°; 1-p-*toluenesulphonyl* derivative, m. p. 172°, $[\alpha]_{5461}$ +66·9°]. J. M. Gulland.

Preparation of a respiration model with a complex iron compound of indigotin. K. Kunz and A. J. Kress (Ber., 1927, **60**, [*B*], 367—376).—Iron pentacarbonyl slowly evolves carbon monoxide when warmed in anhydrous pyridine at 70—80°, apparently forming the compound, $Fe_2(CO)_7$. In the same solvent, indigotin is transformed by iron pentacarbonyl into the additive *compound*, $(C_{16}H_{10}O_2N_2)_2,Fe(CO)_5,2C_5H_5N$, which is readily decomposed by water and acids with re-formation of indigotin, but is not sensitive towards oxygen, since the iron atom is shielded by carbon monoxide. If, however, the green solution of the compound is warmed with an excess of iron pentacarbonyl, exactly 5 mols. of carbon monoxide are evolved and the red *substance*, $(C_{16}H_{10}O_2N_2)_2Fe$, is produced. The role of the nitrogen atoms in this compound is established by the observation that thioindigotin gives an analogous additive compound with iron pentacarbonyl, but cannot react with iron or other heavy metal alone. The carbonyl group of indigotin is not mainly responsible for the formation of the compound, since di-indolidenemethane gives analogous complex derivatives. It must therefore be assumed that the iron atom is united by four subsidiary valencies to the nitrogen atoms of the four pyrrole nuclei, although participation of the carbonyl oxygen is not absolutely excluded. A parallel is therefore drawn between

the indigotin derivative, hæmoglobin, and chlorophyll. The red compound regenerates indigotin when treated with acids. It is very sensitive towards oxygen and, like hæmoglobin, absorbs exactly 1 mol. of oxygen for each atom of iron. If anhydrous hydrogen cyanide is added to the red solution, the power of absorbing oxygen is lost, and only becomes restored gradually as the hydrogen cyanide is removed in a stream of oxygen. Union of the compound with oxygen is initially feeble; the absorbed oxygen is evolved in a vacuum and the red colour returns to the solution. After a short time at the atmospheric temperature, or more rapidly when warmed, the red colour reappears, the liberated oxygen being used in the oxidation of part of the indigotin. Renewed addition of oxygen renders the solution again green, and the process may be repeated until the indigotin is completely oxidised, whereby considerable heat is evolved. If, however, the green solution is preserved at 0°, the oxygen becomes more firmly united, with production of a *compound*, $(C_{16}H_{10}O_2N_2)_2FeO_2$, which does not evolve oxygen when warmed in a vacuum, but decomposes into indigotin, isatin, and a colourless by-product when warmed in anhydrous media in an atmosphere of nitrogen. In analogy with hæmoglobin, the indigotin derivative might be expected to absorb carbon monoxide, but the result has not been realised experimentally, probably owing to the inhibitive action of pyridine, the only available solvent. Nitric oxide reacts readily, probably forming initially a bluish-green additive compound containing 1 mol. of nitric oxide for each atom of iron. With excess of gas, 5 mols. of nitric oxide are absorbed and indigotin separates. Carbon dioxide does not affect the indigotin compound.

H. WREN.

Synthesis of derivatives of 1 : 8-naphthyridine. G. KOLLER (Ber., 1927, **60**, [*B*], 407—410; cf. Seide, this vol., 62).—Methyl 2-aminopyridine-3-carboxylate, m. p. 84—85°, is converted by ethyl malonate and ethyl-alcoholic sodium ethoxide at 145—150° into *methyl* 2 : 4-*dihydroxy*-1 : 8-*naphthyridine*-3-*carboxylate*, which softens at 236° (*sodium* salt); the basicity of the nitrogen atoms appears so depressed by their proximity and the presence of the hydroxy-groups that the substance is incapable of forming a stable salt. The ester is converted by dilute potassium hydroxide into 2 : 4-*dihydroxy*-1 : 8-*naphthyridine*, which, with phosphorus pentachloride and phosphoryl chloride, affords 2 : 4-*dichloro*-1 : 8-*naphthyridine*, m. p. 125—126° [*gold* salt, $(C_8H_4N_2Cl_2)_2,HAuCl_4$, m. p. 210—212° (decomp.) after softening at 200°].

H. WREN.

Producing amines, their substitution products, nitriles, and tetrazoles. KNOLL & Co., and K. F. SCHMIDT.—See B., 1927, 172.

Structure of furazan oxides. C. R. KINNEY and H. J. HARWOOD (J. Amer. Chem. Soc., 1927, **49**, 514—516).—Oxidation of the four dioximes of camphorquinone yields but one and the same furazan oxide, which has thus probably the symmetrical structure suggested by Green and Rowe (J.C.S., 1913, **103**, 897) and Forster and Fierz (*ibid.*, 1918). Further evidence for the symmetrical structure is afforded by the ozonisation of diphenylfurazan oxide, the chief product of which is benzoic acid, indicating an ethylenic linking between the carbon atoms of the furazan oxide ring.

F. G. WILLSON.

New transformation of tertiary heterocyclic bases into secondary dealkylated bases. M. POLONOVSKI and M. POLONOVSKI (Compt. rend., 1927, **184**, 331—333).—Previous methods of removing an *N*-alkyl group from a heterocyclic base to give the "nor" base have been unsatisfactory. A new method giving good yields from alkaloid bases which are not readily oxidised consists in treating the *N*-alkyl amine oxide with excess of acetic (or benzoic) anhydride; this gives the *N*-acetyl derivative of the nor-base, which is also acetylated at any hydroxyl group present. Saponification removes first *O*-acetyl, then combined acids (*e.g.*, tropic acid), and finally *N*-acetyl. The following compounds are obtained by this method: tropidine *N*-oxide gives *N*-acetylnortropidine, $C_7H_{10}NAc$, a neutral oil soluble in water, and thence nortropidine; tropine oxide gives *ON*-diacetyltropigenine, $C_7H_{11}ONAc_2$, by saponifying *N*-acetyltropigenine, m. p. 124° (hydrochloride, m. p. 162°), and tropigenine, or, with benzoic anhydride, *N*-benzoyltropigenine; *apo*atropine oxide gives *N*-acetylnor*apo*atropine, $C_7H_{11}(CO_2C_8H_7)NAc$, m. p. 114° (hydrochloride, m. p. 140°), saponified to *N*-acetyltropigenine and tropigenine; hyoscyamine oxide gives *ON*-diacetylnorhyoscyamine, $C_7H_{11}(CO_2C_8H_8)ONAc_2$, $[\alpha]_D$ −30°, and thence *N*-acetylnorhyoscyamine, m. p. 158°, $[\alpha]_D$ −15°, *N*-acetyltropigenine, and tropigenine; atropine oxide gives the same derivatives; hyoscine oxide gives *ON*-diacetylnorhyoscine, and thence *N*-acetylnorhyoscine, m. p. 130°, $[\alpha]_D$ −27° (hydrochloride, m. p. 205°), *N*-acetyloscine, and noroscine; *N*-*methylgranatoline oxide*, m. p. 218°, gives *ON*-diacetylgranatoline, m. p. 80°, and thence *N*-acetylgranatoline, m. p. 120°, and granatoline.

Work on ψ-pelletierine, tropinone, alkylpiperidines, and alkaloids of the morphine, eserine, and nicotine groups is announced.

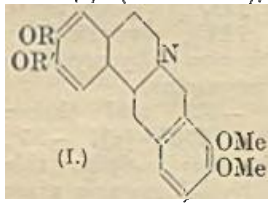
E. W. WIGNALL.

***iso*Quinoline series and synthesis of papaverine.** K. W. ROSENMUND, M. NOTHNAGEL, and H. RIESENFELDT (Ber., 1927, **60**, [*B*], 392—398).—ω-Bromostyrene is converted by potassium phthalimide in presence of cuprous bromide or copper bronze at 195° into ω-*phthalimidostyrene*, m. p. 188—189°, which adds hydrogen bromide in glacial acetic acid solution, yielding the *compound* $C_{16}H_{12}O_2NBr$, m. p. 107—108° (decomp.), and is hydrolysed by alcoholic potassium hydroxide to the corresponding *phthalamic acid*, m. p. 169°; attempts to isolate the unsaturated amine were unsuccessful. Benzamide, ω-bromostyrene, potassium carbonate, and copper acetate in boiling *p*-cymene afford *benzoylphenylvinylamine*, CHPh:CH·NHBz, m. p. 161°; *benzoyl*-3 : 4-*methylenedioxyphenylvinylamine*, m. p. 159°, and *benzoyl*-p-*anisylvinylamine*, m. p. 169°, are similarly prepared. Benzoylphenylvinylamine is converted by aluminium oxide in boiling decahydronaphthalene into 1-*phenylisoquinoline*, m. p. 94° (*picrate*, m. p. 164°), but the success of the operation depends greatly on the quality of the oxide, for the

preparation of which a trustworthy method has not been found.

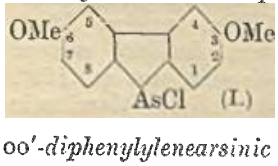
β-Nitrodimethoxystyrene (cf. Rosenmund, A., 1911, i, 34) is converted by a solution of sodium in methyl alcohol into *methyl β-nitro-α-3 : 4-dimethoxyphenylethyl ether*, m. p. 106°; *methyl β-nitro-α-3 : 4-methylenedioxyphenylethyl ether*, m. p. 62°, is described. β-Methoxy-β-3 : 4-dimethoxyphenylethylamine, b. p. 170°/13 mm. (*hydrochloride*, m. p. 185°), yields a *benzoyl* derivative, m. p. 124°, which is converted by phosphoric oxide in boiling toluene into 6 : 7-dimethoxy-1-phenyl*iso*quinoline, identified as the *picrate*, m. p. 250°. *β-Methoxy-β-3 : 4-methylenedioxyphenylethylamine hydrochloride*, m. p. 162°, is described. β-Methoxy-β-3 : 4-dimethoxyphenylethylamine is transformed by homoveratryl chloride into the *amide*, $C_6H_3(OMe)_2{\cdot}CH(OMe){\cdot}CH_2{\cdot}NH{\cdot}CO{\cdot}CH_2{\cdot}C_6H_3(OMe)_2$, m. p. 147—148°, which with phosphoric oxide affords papaverine, m. p. 146·5—147°. H. Wren.

Alkaloids of the *Calumba* root. VI. *Corydalis* alkaloids. VIII. Synthesis of tetrahydrojatrorrhizine, tetrahydrocolumbamine, and corypalmine. E. Späth and E. Mosettig (Ber., 1927, **60**, [*B*], 383—389; cf. A., 1926, 963, 965).—The base (I) (R=R′=H), obtained by the action of



phloroglucinol and sulphuric acid on *r*-tetrahydroberberine (*loc. cit.*), is converted by partial methylation with diazomethane in methyl-alcoholic solution into tetrahydropalmatine (R—R′=Me), tetrahydrojatrorrhizine (R=H, R′=Me), and tetrahydrocolumbamine (R=Me, R′=H), together with unchanged material. The mono- and di-phenolic bases are separated from one another by means of their hydrochlorides. Partial methylation of the dextrorotatory form of base (I) affords *d*-tetrahydropalmatine and a mixture of phenolic bases from which corypalmine is isolated by fractional extraction of the chloroform solution with dilute hydrochloric acid. H. Wren.

Derivatives of dibenzoarsenole [*oo′*-diphenylylenearsine]. H. Gottlieb-Billroth (J. Amer. Chem. Soc., 1927, **49**, 482—486).—In the preparation of 3 : 3′-dimethoxydiphenyl from *o*-dianisidine by treatment of the tetrazo-hydrochloride with alcohol, the yield of the former is increased to 60% if a trace of copper powder be added previously to the alcohol, but there are formed, at the same time, small proportions of *4-chloro-3 : 3′-dimethoxydiphenyl*, m. p. 74°, and *4 : 4′-dichloro-3 : 3′-dimethoxydiphenyl*, m. p. 130°. When boiled with arsenious chloride, 3 : 3′-dimethoxydiphenyl yields *3 : 6-dimethoxy-9-chloro-oo′-diphenylylenearsine* (I), m. p. 198—



199°. This is unattacked by molecular silver in xylene at 100°, but yields, on oxidation with hydrogen peroxide in pyridine, *3 : 6-dimethoxy-oo′-diphenylylenearsinic acid*, decomp. 220°, whilst treatment with 10% aqueous sodium hydroxide for 6 hrs. at 150—160° affords an amorphous *substance*, softening at about 85°, apparently isomeric with the corresponding dimethoxy-*oo′*-diphenylylenearsenious oxide. Nitration of the above arsinic acid with concentrated nitric and sulphuric acids at the ordinary temperature yields *2 : 4 : 5 : 7-tetranitro-3 : 6-dimethoxy-oo′-diphenylylenearsinic acid*, yellow, decomp. 265°, which turns reddish when exposed to light (cf. Aeschlimann, A., 1925, i, 319). F. G. Willson.

Reaction between Grignard reagents and 10-chlorophenoxarsine or 10-chloro-5 : 10-dihydrophenarsazine. J. A. Aeschlimann (J.C.S., 1927, 413—417; cf. Roberts and Turner, A., 1926, 852).—An extension of previous work (A., 1925, i, 706). *10-Methylphenoxarsine*, b. p. 185°/20 mm., yields a *dihydroxide*, m. p. 94°, with hydrogen peroxide, and reacts with bromoacetic acid to give *10-methyl-10-carboxymethylphenoxarsonium bromide*, m. p. 199°. 10 : 10-Dimethylphenoxarsonium iodide has m. p. 225° when heated quickly (cf. Roberts and Turner, *loc. cit.*). *10-Ethylphenoxarsine sulphide*, m. p. 109°, is formed by the action of sulphur in carbon disulphide, or from the corresponding oxide and hydrogen sulphide. *10-Phenylphenoxarsine*, m. p. 107°, b. p. 270°/30 mm., forms a *hydroxide*, m. p. 93°, and an *oxide*, m. p. 184°. *10-Phenyl-10-methylphenoxarsonium iodide* has m. p. 175°.

10-Methyl-, m. p. 105° (*acetyl* derivative, m. p. 154°); *10-ethyl-*, m. p. 75°; and *10-phenyl-5 : 10-dihydrophenarsazine*, m. p. 142°, react with 1 mol. of methyl iodide only, even at 100°, to give the corresponding *dihydrophenarsazonium iodides*: *10 : 10-dimethyl-*, m. p. 259° (slow heating) or 268° (rapid heating), which regenerates the dihydrophenarsazine when heated in a vacuum; *10-methyl-10-ethyl-*, m. p. 229° or 236°; *10-phenyl-10-methyl-*, m. p. 158° (decomp.). J. M. Gulland.

Types of linking in the protein molecule. W. S. Sadikov (Biochem. Z., 1926, **179**, 326—331).—An investigation of suggested types of linkings between amino-acids based on a study of the stability or otherwise of collagen, glutin (from gelatin), keratin, and peptone towards pepsin and trypsin. Collagen is labile to pepsin, stable to trypsin, glutin is labile to both pepsin and trypsin, keratin is stable to pepsin and to trypsin, whilst peptone is stable to pepsin and labile to trypsin. It is suggested that pepsin attacks ether, ester, or anhydride linkings, whilst trypsin acts on peptide linkings. J. Pryde.

Determination of halogens and sulphur in organic substances. A. Recsei (Chem.-Ztg., 1927, **51**, 96).—Sulphur and halogens are determined in non-volatile substances by the methods of Asboth (A., 1896, ii, 448) and of Warunis (A., 1911, ii, 927) respectively, using in each case 50—60 parts of a mixture of 2 parts of potassium sodium carbonate and 1 part of sodium peroxide. C. Irwin.

Determination of acetoacetic acid. L. Lorber.—See this vol., 372.

Biochemistry.

Fœtal blood-gas tensions and gas transfusion through the placenta of the goat. A. S. HUGGETT (J. Physiol., 1927, **62**, 373—384).—The oxygen and the carbon dioxide dissociation curves of the maternal and fœtal blood of the goat have been determined. The difference in oxygen tension between maternal arterial and fœtal venous blood was 45 mm. for oxygen and 18 mm. for carbon dioxide. The gradient for carbon dioxide can be reversed by asphyxiation of the mother. Diffusion of blood gases across the placenta satisfactorily explains these results.

R. K. CANNAN.

Uptake of dyes by red blood-corpuscles. P. J. JURISIC (Biochem. Z., 1927, **181**, 17—29).—The uptake of any given basic or acidic dye by red blood corpuscles, over a definite period, is proportional to the concentration of the dye in the solution; in general, the basic dyes are taken up to a greater extent from an isotonic sodium chloride solution than from one containing sucrose, the reverse being the case with the acidic dyes. In the case of two acidic dyes soluble in diamylamine, the uptake of the dye by the blood-corpuscles, especially from dilute solutions, was almost complete in experiments of long duration, indicating adsorption. The rate of uptake of the dyes was increased by a rise in temperature.

C. R. HARINGTON.

Spectrophotometric study of blood solutions. R. P. KENNEDY (Amer. J. Physiol., 1927, **79**, 346—361).—The determination of the hæmoglobin in blood solutions by measurement of the light absorption has been controlled by determinations of the oxygen capacity by the Van Slyke method. The absorption ratio of hæmoglobin has been determined over the visible spectrum. Precautions and limits of error in spectrophotometric measurements are discussed.

R. K. CANNAN.

Spectrophotometric studies on blood pigments and their derivatives. V. ZILZER (Biochem. Z., 1926, **179**, 348—363).—From the fact that the specific extinction coefficients of oxyhæmoglobin, hæmin, and hæmatoporphyrin increase with increasing thickness of solution, but with constant concentration, or with constant layer thickness and increasing concentration, it is inferred that the pigment molecules disperse as well as absorb light and that they follow in these respects different laws. When concentration and layer thickness are altered in opposite but equal senses, the specific extinction coefficients are unaltered and the Beer law holds. The spectrophotometric determination of these blood pigments will therefore be beset with inaccuracies until the laws of light dispersion as applied to them are more fully elucidated.

J. PRYDE.

Biochemistry of sulphur. I. Identity of ergothioneine from ergot with sympectothion and thiasine from blood. B. A. EAGLES and T. B. JOHNSON (J. Amer. Chem. Soc., 1927, **49**, 575—580).—Sympectothion (Hunter and Eagles, A., 1926, 85) and thiasine (Benedict, A., 1926, 421) are both identical with Tanret's ergothioneine (the betaine of thiolhistidine) (A., 1909, i, 671; cf. Barger and Ewins, J.C.S., 1911, **99**, 2336).

F. G. WILLSON.

Ammonium salts in circulating blood. J. K. PARNAS (Bull. Soc. Chim. biol., 1927, **9**, 76—90).—It is reaffirmed that a small but definite quantity of ammonium salts exists in the circulating blood (cf. Parnas and Heller, A., 1925, i, 323, 454; Fontes and Yovanovitch, *ibid.*, 1926, 85; Parnas and Klisiecki, *ibid.*, 536; Fontes, *ibid.*, 968).

F. L. HEWITT.

Ammonia content and formation in blood. VII. Ammonia formation in physiologically stagnant blood. A. KLISIECKI, W. MOZOLOWSKI, and M. TAUBENHAUS. **VIII. Is the ammonia content of the blood connected with the presence of cyanates?** W. MOZOLOWSKI and M. TAUBENHAUS (Biochem. Z., 1927, **181**, 80—84, 85—95).—VII. Blood obtained by producing a contraction in the resting spleen has a higher content of ammonia than systemic blood, whilst that obtained by allowing the spleen to fill with blood again and immediately producing a second contraction contains the same concentration of ammonia as the systemic blood. Ammonia must therefore accumulate during the physiological stagnation of the blood in the spleen.

VIII. Observation of the formation of ammonia in shed blood or in protein-free blood filtrates, with and without the addition of cyanates, affords no support to the view that the latter are present in normal blood and form the source of the ammonia which is produced.

C. R. HARINGTON.

Blood-ammonia. D. ADLERSBERG and M. TAUBENHAUS (Arch. exp. Path. Pharm., 1927, **121**, 35—66; cf. A., 1926, 855).—The blood-ammonia in normal and pathological subjects, and the effect on the normal value of varying conditions, have been determined. The normal actual ammonia-nitrogen content of circulating blood is less than 0·05 mg. %. This value is increased temporarily by intravenous injection of sodium dihydrogen phosphate or by greatly increased breathing. No alteration occurs during short periods of breathing mixtures poor in oxygen. Pathological conditions, with the exception of severe diabetic acidosis, show normal values. With rabbits, cutting off the kidneys from the circulation causes a gradual rise in the ammonia of the peripheral blood and a similar rise in the blood of the hepatic vein. After cutting off all the abdominal organs, no alteration occurs in the blood-ammonia, but a gradual rise in the precursor of ammonia results. Normal fresh rabbit's bile always contains ammonia, the value varying from 0·023 to 0·07 mg. %. Fresh human cerebrospinal fluid contains no ammonia.

A. WORMALL.

Determination of plasmal in blood-serum. R. FEULGEN and K. IMHAUSER (Biochem. Z., 1927, **181**, 30—48; cf. Pflüger's Arch., 1924, **206**, 389).—Blood-serum is treated with Schiff's reagent and with sufficient sulphur dioxide in aqueous solution to liberate the plasmal from its precursor; the solution so obtained is compared colorimetrically with another obtained by similar treatment of a second sample

of serum which contains, in colloidal solution, a known amount of plasmal thiosemicarbazone; by the use of Burker's colorimeter (A., 1923, ii, 694) the plasmalogen in the second sample of serum can be compensated for and that in the first sample calculated. Considerable variations were found in the plasmal content of the blood-serum of various species.

C. R. HARINGTON.

Plasmalogen. I. Occurrence of plasmalogen in body-fluids. W. STEPP, R. FEULGEN, and K. VOIT (Biochem. Z., 1927, **181**, 284—288).—A method is given for the detection of plasmalogen with fuchsin-sulphurous acid. Serum, saliva, the stromata of red blood-corpuscles, amniotic fluid, and pus gave a positive, cerebrospinal fluid, urine, and aqueous humour a negative reaction. With hen's eggs, the white gives a faint reaction, but the yolk is rich in plasmalogen. Milk gives a positive reaction, but colostrum is much richer. P. W. CLUTTERBUCK.

Decolorisation of light-green by male and female sera. H. B. VAN DYKE and A. SCHURMEYER (Biochem. Z., 1927, **180**, 353—356).—Contrary to Manoiloff and Ssentjurin, there is no specific sex difference in the rates of decolorisation of light-green by male and female sera of animals or man.

R. K. CANNAN.

Effect of potassium oxalate on electrolytes of blood and plasma. A. J. EISENMAN (J. Biol. Chem., 1927, **71**, 587—604).—Variations, which were outside the limits of experimental error, but were inconsistent in magnitude and direction, were observed between oxalated and defibrinated samples of the same blood, particularly in the electrolyte content and the carbon dioxide absorption curve. The hæmatocrit values of the oxalated blood were always lower than those of the defibrinated blood. The variations were present whether the blood was treated anaerobically or in the air; they were independent of the time which had elapsed since the addition of the oxalate, and they were not the same as those produced by an equivalent amount of sodium chloride. In view of these results, defibrination is recommended in preference to treatment with oxalate for the prevention of coagulation in blood required for accurate work on the concentration of electrolytes.

C. R. HARINGTON.

Anaerobic defibrination of blood. A. J. EISENMAN (J. Biol. Chem., 1927, **71**, 607—609).—A sampling bulb provided with a stopcock at either end, and connected at one end to a levelling bulb, is completely filled with mercury; blood is allowed to flow into the bulb until nearly all the mercury is displaced, the stopcocks are closed and the bulb is shaken; the fibrin adheres to the fine globules of mercury and the blood is readily separated. C. R. HARINGTON.

Determination of partition of phosphorus in blood. M. MACHEBŒUF (Bull. Soc. Chim. biol., 1927, **9**, 94—98).—Determination of the total phosphorus of whole blood, serum, and corpuscles, and of the inorganic phosphates of the serum may be carried out, using 10 c.c. of blood. For inorganic phosphate determination in serum, proteins are removed from 3 c.c. of serum by trichloroacetic acid; sulphuric acid, ammonium nitrate, and ammonium molybdate are added to the filtrate, the phosphomolybdate is collected, and the amount of standard sodium hydroxide required to displace the ammonia is determined, using phenolphthalein as indicator. Fractionation of the proteins with ammonium sulphate indicated that in 1 c.c. of horse serum, containing 0·077 mg. of total phosphorus, the inorganic phosphates accounted for 0·025 mg., the albumin contained 0·035 mg., and the globulin 0·014 mg. L. F. HEWITT.

Gasometric determination of p_H of blood. A. J. EISENMAN (J. Biol. Chem., 1927, **71**, 611—628).—Serum is separated from blood anaerobically and its carbon dioxide content determined; other samples of the same serum are saturated at known (higher and lower) tensions of carbon dioxide, and the resulting carbon dioxide content is determined; by means of the logarithmic chart of Peters (A., 1923, i, 1249), the carbon dioxide absorption curve of the serum is constructed from the last two observations; the first observed carbon dioxide content can then be located on the line so obtained and the corresponding p_H read off. By employing an experimentally-determined average value of 5·6 vol.-% to represent the difference in carbon dioxide content of the serum at 60 and 30 mm. tension of carbon dioxide, the method requires the determination of only one point on the curve; this modification is less accurate, since the above-mentioned average value is subject to variations which could not be definitely accounted for.

C. R. HARINGTON.

Micro-colorimeter. H. KLEINMANN (Biochem. Z., 1926, **179**, 276—286).—A description of the construction and method of using a micro-colorimeter made on the Duboscq principle and requiring only 1 c.c. of the solution. Depths up to 60 mm. are available, the angle of the field of view is 4·5°, and the error of the instrument is 0·5—1%.

J. PRYDE.

Micro-colorimetric determination of nitrogen. Total and residual nitrogen of blood-drops. H. KLEINMANN (Biochem. Z., 1926, **179**, 287—300).—A micro-Kjeldahl apparatus is described together with its application, in conjunction with the Nessler technique and the micro-colorimeter (see preceding abstract), to the determination of the total and residual nitrogen of minute quantities of blood (0·1—0·2 c.c.). J. PRYDE.

Nephelometric determination of neutral fat + cholesterol of the blood by Bing and Heckscher's method. H. HECKSCHER (Biochem. Z., 1927, **181**, 444—487).—Pure cholesterol suspensions are not suitable for nephelometric determination by the method of Bing and Heckscher (cf. A., 1925, i, 995, 999), but mixtures of triolein and cholesterol containing more than 10% of triolein can be determined quantitatively. In carrying out the method, temperature variations within 10° and 20° are unimportant, and the degree of cloudiness is constant from 15 to 45 min. after formation of the suspension. Further details are given in respect to the taking of samples of blood, drying, preserving, and extraction, and in this modified form the method gives results comparable with those obtained by Bang's method.

P. W. CLUTTERBUCK.

Determination of minute quantities of quinine in the blood. A. C. Roy (Indian J. Med. Res., 1926, **14**, 129—133).—Acidified 0·01*N*-iodine solution detects a difference of 0·002 mg. of alkaloid between 0·03 and 0·045 mg. per 5 c.c., and a difference of 0·001 mg. between 0·03 and 0·001 mg. With a total volume of 5 c.c. or 2 c.c., 0·0005 mg. or 0·0001 mg., respectively, can be detected by matching against saturated ammonium sulphate solution.

Chemical Abstracts.

Lithium citrate as anticoagulant in blood investigations. Systematisation of blood micro-analysis. G. de Toni (Biochem. Z., 1927, **181**, 289—295).—The determination of inorganic phosphorus, sodium, potassium, calcium, and magnesium in blood by the methods of Kramer and Tisdall (A., 1921, ii, 412, 595, 463) and of Kramer and Gittleman (A., 1925, i, 180) is not interfered with by the presence of lithium citrate, which can therefore be used to prevent clotting when the samples are taken. P. W. Clutterbuck.

Bile salt hæmolysis. I. Fixation of bile salts by serum as an absorption phenomenon. J. L. Donelly and A. G. Mitchell (Amer. J. Physiol., 1927, **79**, 297—304).—The amounts of bile salts which fix increasing volumes of serum are given by $K-X^n/C$, where X is the weight of bile salts, C is the volume of serum, and $n=2·175$. When a given addition of bile salts is spread over a period of time, more remains free than when the entire quantity is added at once.

R. K. Cannan.

Calcium and halogen content of an organism during gestation. H. Vignes and Coisset (Compt. rend., 1927, **184**, 472—474).—Determination of the calcium and chlorine content of pregnant guinea-pigs showed progressive decalcification throughout the period of gestation. There were slight indications of a corresponding increase in chlorine.

B. W. Anderson.

Combined cholesterol of the brain. L. Gassner (Biochem. Z., 1927, **180**, 359—362).—Practically the whole of the cholesterol of the brain is in the free state. The higher proportions of cholesterol esters hitherto reported may be due to the fact that precipitation of cholesterol by digitonin is not complete without long keeping. Drying brain tissue at 100° with calcium sulphate leads to a loss of 30% of the total free cholesterol. R. K. Cannan.

Chemistry of the brain. I. Nitrogen distribution in the fractions of horse brain soluble in light petroleum. K. Singer (Biochem. Z., 1926, **179**, 432—442).—The choline, total amino-, cerebroside, and residual nitrogen values of light petroleum extracts of horse brain have been determined. It is intended to apply the method to the brains of normal and mental (*e.g.*, progressive paralysis) cases. J. Pryde.

Characteristics of unvarying lipins. E. F. Terroine and P. Belin (Bull. Soc. Chim. biol., 1927, **9**, 12—48).—The fatty acid content of the brain does not depend on the diet, but that of all other tissues may be divided into two classes, one part affected by and the other independent of the diet. The variable portion disappears during starvation. The ratio of unvarying fatty acids to lipin phosphorus is constant, practically the same for all animals, and identical with that of lecithin. The iodine value of the unvarying fatty acids is higher than that of the variable acids and of the fat deposits. It is suggested that linoleic acid is a constituent of the extracellular phosphatides of the lungs and linolenic acid of the liver and kidneys. In the muscles, the phosphatides probably consist of two saturated and two unsaturated fatty acids, one of the latter being linolenic acid and the other a similar acid with four unsaturated linkings.

L. F. Hewitt.

Spectrochemical detection and identification of the natural porphyrins. O. Schumm (Z. physiol. Chem., 1927, **164**, 143—158).—Methods by which the natural animal porphyrins can be differentiated are described. The complex iron compounds of the porphyrins, which have very similar spectrochemical properties, are freed from iron and the porphyrin mixture is examined. A. Wormall.

Determination of the nucleic acid content of organs. N. Alders (Biochem. Z., 1927, **181**, 400—409).—The method of determination of the nucleic acid content of organs from their purine base content is critically examined and a new method described in which the nucleic acid content is obtained from a determination of the phosphorus remaining after the organ had been extracted continuously with ether to remove soluble phosphatides and subjected to repeated extraction with warm, very dilute acetic acid to remove inorganic phosphates. The method gives higher values than the purine base method and appears to be more trustworthy.

P. W. Clutterbuck.

Constitution and synthesis of spermidine. H. W. Dudley, O. Rosenheim, and W. W. Starling. —See this vol., 343.

Inorganic constituents of the pancreas and suprarenals. H. Marx (Biochem. Z., 1926, **179**, 414—425).—The ratio of potassium to calcium in the pancreas is much higher than that of the suprarenals. Magnesium is present in the former organ in greater amount than in the latter. J. Pryde.

Vaso-dilator constituents of certain tissue extracts. C. H. Best, H. H. Dale, H. W. Dudley, and W. V. Thorpe (J. Physiol., 1927, **62**, 397—417). —Histamine and choline have been isolated from alcoholic extracts of fresh liver and lung in quantities sufficient to account for the immediate vaso-dilator effects of such extracts. Anomalous chemical behaviour of these bases when present in crude tissue extracts has been demonstrated. The average amounts of histamine isolated were 1·58 mg. per kg. of liver and 27·64 mg. per kg. of lung. The physiological significance of the occurrence of histamine in the tissues is discussed. R. K. Cannan.

Ovarian residue. II. Alcohol-insoluble, water-soluble nitrogeneous extractives. F. W. Heyl and B. Fullerton (J. Amer. Pharm. Assoc., 1926, **15**, 549—556).—The basic fraction (0·51%) from ovarian residue which has been extracted with ethyl alcohol and ether contains 0·098% of basic nitrogen, including 0·009% of creatinine nitrogen.

Adenine, arginine, and lysine were separated; a substance, not xanthine, having the formula $C_5H_4O_2N_4$ and possibly a trace of histidine were isolated. CHEMICAL ABSTRACTS.

Glucosamine compounds. Y. KOMORI (J. Biochem. [Japan], 1926, **6**, 1—20).—(1) Shells of cicad larvæ were decalcified with hydrochloric acid and well washed, the protein then being destroyed by boiling with 20% potassium hydroxide solution. The residue, decolorised by means of 0·5% potassium permanganate followed by oxalic acid, contained 0·13% of ash, 46·09% C, 6·76% H, 6·50% N. The hydrolysed substance contained 59·70% of acetic acid, equivalent to 2 acetyl groups per nitrogen atom. The glucosamine content of the ash-free material was 85·13% (N : glucosamine= 1 : 1·02); the glucosamine was obtained by boiling with concentrated hydrochloric acid (osazone, m. p. 203°). (2) Ovomucoid was digested with trypsin (2%) at 38°. After removal of tyrosine by evaporation and filtration, leucine was removed after precipitation with mercuric chloride and lead acetate. Decomposition of the lead precipitate afforded a substance containing 4·59% of ash, 44·46% C, 6·77% H, 7·55% N. When hydrolysed with hydrochloric acid and stannous chloride, it yielded 27·5% of glucosamine; the acetic acid content of the ash-free substance was 37·54% (N : AcOH=1 : 1·15). (3) The fluid from the egg-sac of gastropods, when boiled with a slight excess of acetic acid, yielded a substance containing 17·75% of ash and 8·08% of nitrogen. It contained 51·24% of acetic acid and yielded glucosamine hydrochloride by the above method. CHEMICAL ABSTRACTS.

Proximate composition of Pacific Coast crabs. C. R. FELLERS and C. F. PARKS (Univ. Wash. Pub. Fish., 1926, **1**, No. 7, 130—156).—*Cancer magister* and *Paralithodes camtschatica* contain 102 and 362 " parts per billion " of iodine, respectively; both contain struvite ($MgNH_4PO_4,6H_2O$) crystals. Fresh crab flesh contains tyrosinase; blue discolorations are probably due to the interaction of biuret and copper, both from the blood, and ammonia. The decomposition of the meat is investigated.

CHEMICAL ABSTRACTS.

Chemical composition of the cerebrospinal fluid. H. B. WILCOX, J. D. LYTTLE, and J. E. HEARN (Amer. J. Dis. Children, 1926, **30**, 513—540).—The normal chloride content of cerebrospinal fluid is 690—720 mg. %, low values being obtained in acute and tuberculous meningitis; the normal protein content is 30—80 mg. %, high values being obtained in inflammations of the meninges and brain substance. The normal sugar value is 40—60% of that of the blood, abnormal values being obtained in certain pathological conditions. CHEMICAL ABSTRACTS.

Determination of pepsin in gastric juice. H. CITRON (Deut. med. Woch., 1926, **52**, 1781—1782).—Pepsin is allowed to act on fibrin, dyed with carmine, and the resulting colour compared with that obtained from a standard pepsin preparation of known composition. CHEMICAL ABSTRACTS.

Liver function. VI. Determination of cholesterol and alcohol-soluble and -insoluble bile pigments of the duodenal contents. C. W. MCCLURE and M. HUNTSINGER (Boston Med. Surg. J., 1926, **194**, 811—814). CHEMICAL ABSTRACTS.

Individual differences in the isoelectric point of the caseinogen of human milk. F. TRENDTEL (Biochem. Z., 1927, **180**, 371—376).—The p_H of maximum flocculation of the caseinogen of human milk varies in different women, but is constant in any one subject. The addition of 5% of sodium chloride shifts the isoelectric point towards the alkaline side, but the individual differences persist.

R. K. CANNAN.

Iodine and milk secretion. V, VI. Administration of small doses to goats. VII, VIII. Administration to cows. K. SCHARRER (Biochem. Z., 1927, **180**, 300—306, 307—312, 313—333, 334—340).—V. [With A. STROBEL.] The daily administration of 7·5 or 15 mg. of iodine to goats was without striking effect on the milk yield or its fat content.

VI. [With J. SCHWAIBOLD.] The milk of normal goats contains traces of iodine. Study was made of the rate of secretion in the milk of small doses of iodine administered as sodium iodide.

VII. [With A. STROBEL and W. SCHROPP.] VIII. [With J. SCHWAIBOLD.] Similar studies to the above were carried out on cows. R. K. CANNAN.

Enzymes of cow's milk. I. Effect of diet. II. Diastase of the milk in disease. T. CHRZASZCZ and C. GORALOVNA (Biochem Z., 1927, **180**, 237—262, 263—271).—I. The diastase, catalase, peroxydase, and aldehydase (determined by the nitrate method) are but little affected by the feed of the cow. The first three enzymes are found chiefly in the cream.

II. The diastase and catalase activities are notably increased in milk of unhealthy cows. The former increase may be found to be of diagnostic value.

R. K. CANNAN.

Bacteriological detection of the sugars in urine. M. BENJASCH (Deut. med. Woch., 1926, **52**, 1733).—A discussion of the method of Klein and Soliterman (*ibid.*, 959). Parallel determinations with *Bacillus coli* and *B. typhosus* allow a differentiation of dextrose and lactose. The method is inapplicable to urine in cases of icterus. Phloridzin sugar is fermented more slowly than diabetic.

CHEMICAL ABSTRACTS.

Semi-micro-method of determining orthophosphoric acid applied to urine. R. F. LE GUYON (Bull. Soc. Chim. biol., 1927, **9**, 59—75).—Organic matter in the urine is destroyed by treating with nitric acid and magnesium nitrate, the liquid is neutralised, a known amount of 0·1*N*-silver nitrate and sodium acetate added, the precipitated silver phosphate is filtered off, dissolved in dilute nitric acid, and the silver determined by titration with potassium thiocyanate. Phosphates may be determined simultaneously with the chlorides by measuring the amount of silver nitrate employed, the excess of silver in the filtrate, and the amount in the dilute nitric acid solution. Five c.c. of urine are sufficient for a determination. L. F. HEWITT.

Determination of acetoacetic acid. L. LORBER (Biochem. Z., 1927, **181**, 366—374).—Acetoacetic

acid is determined by a macrotitrimetric method, in which the acid is exactly neutralised and heated with excess of standard sulphuric acid, when the difference in titre before and after warming gives the acetoacetic acid value, and by a microcolorimetric method which is an adaptation of the Rothera test and is applied to its determination in urine and blood.

P. W. CLUTTERBUCK.

Quantitative proportion of acetone and acetoacetic acid in urine as obtained by qualitative tests. L. LORBER (Biochem. Z., 1927, **181**, 375—382).—The nitroprusside test and Lieben's test detect in so-called acetone-containing urine, not acetone, but acetoacetic acid. Lieben's test is modified to detect acetone and the method of using Gerhardt's test is specified. P. W. CLUTTERBUCK.

Tautomeric enol and keto-forms of acetoacetic acid. L. LORBER (Biochem. Z., 1927, **181**, 383—390).—The nitroprusside and the ferric chloride tests on acetone urines yield completely parallel results, both tests detecting the enol form of acetoacetic acid, which form is predominantly present both in pure solutions of the acid and in urine. Quantitative determination by Gerhardt's method of acetoacetic acid in pure solutions and in urine is described.

P. W. CLUTTERBUCK.

Spectrophotometric analysis of blood-serum in normal and pathological conditions. I. T. B. MAGATH and C. SHEARD (Arch. Int. Med., 1927, **39**, 214—225).—A large number of sera have been examined by spectrophotometric methods, and in all cases the type of curve is like that of bile, and corresponds with the spectral analysis of bilirubin. This yellow pigment is present in normal serum and in the sera of patients suffering from slight anæmia, malaria, pernicious anæmia, hæmolytic icterus, and obstructive jaundice. The bilirubins in the sera appear to be identical, and the amount present is least in the normals and increases in the order named. An increased destruction of erythrocytes, a diminished excretion of bile, or a combination of these two factors leads to a retention of bilirubin in these pathological conditions. A. WORMALL.

Catalase content of blood in experimental anæmia. A. BERNSTEIN (Biochem. Z., 1926, **179**, 304—312).—In experimental anæmia, produced in rabbits by injection of phenylhydrazine hydrochloride, the catalase content of the blood is diminished, whilst the catalase index is increased. The increase in the latter value is more marked than, but runs parallel to, that of the colour index. The change of the catalase index in simple anæmia is much less than that in phenylhydrazine anæmia. J. PRYDE.

Influence of muscular work on blood lactic acid, alkali reserve, acidity of the urine, etc. in circulatory diseases. B. GROAG and H. SCHWARZ (Arch. exp. Path. Pharm., 1927, **121**, 23—34).—Experiments carried out on the fasting patients showed a definite rise in the blood lactic acid after muscular exercise, in some cases up to double the resting value, in contrast to normals, where the rise was extremely small. At the same time, a distinct lowering of the alkali reserve occurred, but there was no absolute relationship between this fall and the rise in lactic acid. The urine, under these conditions, became slightly more acid and there was a slight decrease in the ammonia excretion. The significance of these results, in the light of the theories of muscle contraction and the possibility of a decreased buffering power of muscle in circulatory diseases, is discussed. A. WORMALL.

Unknown substance in urine from a case of diabetes insipidus. A. B. ILLIEVITZ (J. Biol. Chem., 1927, **71**, 693—694).—On long keeping, under sterile conditions in the cold, of the urine from a case of diabetes insipidus, an ether-soluble purple pigment was produced; it was soluble in alkalis, insoluble in acids, showed no characteristic absorption spectrum, and could not be related to indican.

C. R. HARINGTON.

Existence of insulin-like material in fusocellular sarcoma of white rats. A. H. ROFFO and L. M. CORREA (Rev. Soc. Argentina Biol., 1926, 2, 567).—In a preliminary investigation, insulin-like material equivalent to 8—12 clinical units was obtained from 500 g. of the sarcoma.

G. W. ROBINSON.

Post-mortem blood-sugar determinations. J. R. PAUL (Bull. Ayer Clin. Lab. Penn. Hosp., 1926, **10**, 34—43).—Within 2 hrs. after sudden death, the dextrose content of the blood was 73—143 mg. per 100 c.c. (4 cases). In a series of general hospital cases, it was below 60 mg. in 14 cases, below 40 mg. in 8 cases, below 10 mg. in 4 cases, below 1 mg. in 1 case, and 0 in 2 cases. In 2 cases, the dextrose content of blood drawn 0·5 hr. after death was 100 mg. less than that drawn 8 hrs. before death. The results suggest the rather frequent occurrence of terminal or agonal hypoglycæmic states in a wide variety of conditions. CHEMICAL ABSTRACTS.

Metabolism of transplanted tissues and their growth in the absence of oxygen and carbohydrate. F. WIND (Biochem. Z., 1926, **179**, 384—399).—Rous sarcoma can grow temporarily under anaerobic conditions in Carrel's culture medium. Normal 5- to 10-day embryonic heart cells, spleen cells, and monocytes may also grow under anaerobiosis, but not so well as sarcoma cells. On removing dextrose from the culture media by dialysis, anaerobic growth ceases. Rous sarcoma is not more sensitive to anaerobic conditions than is yeast. J. PRYDE.

Inorganic salt metabolism of dogs. III. Deposition and resorption of bone. M. R. JONES (Amer. J. Physiol., 1927, **79**, 694—705).—A study is reported of the bone changes in puppies in relation to the calcium, phosphorus, and alkali of the diet. By sufficient increase in the alkali of a diet on which calcification was efficient, a resorption of bone may be induced. Metabolism and blood studies indicate that the cause lies in the metabolism within the cells. Calcification is primarily dependent on the inherent metabolic state of the animal modified by any factor—*e.g.*, diet—which influences the metabolism of the bone cells so as to alter the balance of ions between the cells and the surrounding medium. R. K. CANNAN.

Calcification. I. Pigs fed different protein supplements. II. Rats fed menhaden oil and

various menhaden fish meals. L. A. MAYNARD and R. C. MILLER (Amer. J. Physiol., 1927, 79, 615—625, 626—632).—I. Calcification was measured by the ash content of the femurs. Fish meal or a mixture of blood meal and caseinogen (which required to be enriched by the addition of calcium and phosphate) were better protein supplements than linseed oil meal.

II. Both meal and oil of menhaden fish contain the calcifying factor. R. K. CANNAN.

Lactic acid formation in red and white muscle of birds. C. SCHMITT-KRAHMER (Biochem. Z., 1927, 180, 272—287).—The post-mortem production of lactic acid by various red and white muscles of the hen and pigeon has been determined. The amount is related to the functional activity rather than to the colour of the muscles, the least active muscles giving the highest values. Striated muscle of these birds gave values exceeding those for frog's muscle and approximating to those for mammalian muscle.

R. K. CANNAN.

Decomposition of β-hydroxybutyric acid in the liver. I. SNAPPER and A. GRUNBAUM (Biochem. Z., 1927, **181**, 410—417).—After perfusing dog's liver with blood to which β-hydroxybutyric acid has been added, almost the whole of the acid may be recovered from the blood and liver (16—32% as acetoacetic acid). A considerable amount of β-hydroxybutyric acid is adsorbed by the liver tissue, which after perfusion contains about four times as much acid as would be expected from the β-hydroxybutyric acid content of the blood in the liver. The possibility that the liver decomposes some of the acid is not excluded, since the normal liver perfused with normal blood forms small amounts (50 mg.) of acetoacetic and β-hydroxybutyric acids, but the amount recovered from both liver and blood never exceeds the amount added.

P. W. CLUTTERBUCK.

Decomposition of acetoacetic acid during liver perfusion. I. SNAPPER and A. GRUNBAUM (Biochem. Z., 1927, **181**, 418—424).—The amount of ketonic substances found in the blood and liver of a dog after perfusion with normal blood to which acetoacetic acid had been added was, in five experiments, 77, 128, 91, 87, 103% of the added amount, the greater part (50—60%) being present as β-hydroxybutyric acid. A considerable amount of the β-hydroxybutyric acid formed is adsorbed by the liver-tissue, the amount present in the liver after perfusion being 4—9 times the liver-blood content. The power of the surviving liver to reduce acetoacetic acid is great, but its power to break it down further is small.

P. W. CLUTTERBUCK.

Citric acid metabolism. E. B. WOODS (Amer. J. Physiol., 1927, 79, 321—340).—On prolonged feeding with citric acid, the pig develops remarkable powers of oxidation. The total organic acid, calcium, and phosphorus excretion bear no simple relation to the citric acid or acetone excreted. There is no evidence of a direct antiketogenic action of citric acid. R. K. CANNAN.

Behaviour of alanine and pyruvic acid in the surviving diabetic liver. V. LAUFBERGER (Biochem. Z., 1927, **181**, 220—224).—On perfusion, in solution in ox-blood, through the surviving liver of a diabetic dog, neither alanine nor pyruvic acid is converted into lactic acid, as is the case with the normal liver. The values observed for the acetone of the blood in these experiments were very low, which is ascribed to the anti-ketogenic action of the alanine and pyruvic acid. C. R. HARINGTON.

Fate of glycuronic and galacturonic acids in the animal organism. R. HURTHLE (Biochem. Z., 1927, **181**, 105—108).—Administration of glycuronic acid to dogs and rabbits in amounts greater than 0·2 g. per kg. leads to excretion of a large part of the substance unchanged. A dog failed to oxidise as little as 0·06 g. per kg. of galacturonic acid.

C. R. HARINGTON.

Relation between the excretion of urinary phosphorus and the consumption of carbohydrates. G. PIAZZA (Arch. Farm. sperim., 1926, **42**, 85—92).—The results of experiments on dogs and on a diabetic patient show that, contrary to the conclusions of various authors, the urinary excretion of phosphorus in normal animals bears no relation to the amount of carbohydrate consumed, and that the increased tolerance towards carbohydrates induced in diabetics by insulin therapy leads to diminution in the excretion of urinary phosphorus. T. H. POPE.

Behaviour of glycæmia and of phosphorus content of the blood during muscular work. G. PIAZZA (Arch. Farm. sperim., 1926, **42**, 93—96).—The performance of either moderate or severe work is accompanied usually by a very slight diminution of the proportion of inorganic nitrogen in the blood, although in one case a slight increase occurred. The acid-soluble phosphorus shows no regular change in either direction, but the free sugar of the blood tends to increase (cf. Embden and Grafe, A., 1921, i, 529; Heinelt, Deut. Ges. inn. Med., 1925, 396).

T. H. POPE.

Physiological value of five carbohydrates based on growth and fæcal analysis. H. S. MITCHELL (Amer. J. Physiol., 1927, 79, 537—541, 542—544).—I. The intestinal flora of rats fed on a diet containing 60% of lactose changed from the putrefactive to the aciduric type. The growth of the rats was poor, owing to excessive diarrhœa. With lactose and other sugars there was a close relation between the loss of carbohydrate in the fæces and the predominance of the aciduric type in the fæces.

II. Normal growth together with a change of the fæcal flora to the aciduric type was effected by feeding 30% of lactose in the diet. R. K. CANNAN.

Nutritive value of malt. M. RUBNER and A. SCHITTENHELM (Biochem. Z., 1927, **180**, 426—453).—In metabolism studies on men and on dogs the meat of a normal diet was replaced by a mixture of yeast and malt. The absorption, partition in the urine, and the nutritive balance of nitrogen were followed and observations are recorded on the phosphorus, carbohydrate, and fat metabolism.

R. K. CANNAN.

Nutritive value of dried yeast preparations. A. SCHITTENHELM, MASSATSCH, and WARNAT (Biochem. Z., 1927, **180**, 453—470).—Dried yeast preserved its nutritive value after roasting. The protein was

good and the vitamin value high. The growth of the feathers of young pigeons as an index of general growth (Abel) is confirmed as a method of testing for vitamin. R. K. CANNAN.

Diet and body fat. L. B. MENDEL and W. E. ANDERSON (Science, 1926, **64**, 384—386).—Starvation of rats, after feeding soya-bean oil, largely removes the "soft" oily fat, permitting the deposit of a "hard" fat. A. A. ELDRIDGE.

Has the actual reaction of the urine any influence on the extent of synthesis of hippuric acid? C. E. KOCH (Arch. exp. Path. Pharm., 1927, **121**, 83—88).—Subcutaneous injection into a rabbit of 1 g. of sodium benzoate, dissolved in physiological saline, results in the excretion in the urine of an amount of hippuric acid which is independent of the reaction of the urine, the range of the latter being p_H 5·5—8·2. With dogs, the excretion of hippuric acid after injection of 2 g. of sodium benzoate was somewhat greater in the more alkaline urines, but this is attributed to the fact that starved dogs were used to give an acid urine. Thus the extent of synthesis of hippuric acid in dogs, as in rabbits, is independent of the p_H of the urine. Part of the benzoic acid administered to dogs is excreted in combination with glycuronic acid. A. WORMALL.

Influence of nutrition on the synthesis of hippuric acid in man. E. M. P. WIDMARK (Biochem. Z., 1926, **179**, 272—275).—In the human subject receiving sodium benzoate *per os*, the hippuric acid : benzoic acid ratio of the urine falls markedly when carbohydrate is excluded from the diet, but returns to a normal value on restoration to a full *régime*. J. PRYDE.

Comparative metabolism of aromatic acids. XII. Fate of triphenylacetic acid, triphenylmethane, and triphenylcarbinol in the animal body. S. R. MIRIAM, J. T. WOLF, and C. P. SHERWIN (J. Biol. Chem., 1927, **71**, 695—698).—After feeding triphenylacetic acid to rabbits and dogs, 30—65% was recovered unchanged from the urine; a small quantity of triphenylmethane was found in the fæces. After feeding triphenylmethane, the unchanged material was recovered to the extent of 30%; triphenylcarbinol was more completely oxidised. *Triphenylacetylglycine* has m. p. 202—204°. C. H. HARINGTON.

Skatoxylsulphuric acid in urine. G. SCHEFF (Biochem. Z., 1926, **179**, 364—375).—The organic sulphates of dog's urine are increased by the administration of skatole. J. PRYDE.

Intermediate purine metabolism. I. Enzymic formation of uric acid precursors in the blood. W. A. ENGELHARDT (Biochem. Z., 1927, **182**, 121—130).—On keeping rabbit's blood, substances are formed which, under the action of oxido-reducing enzymes, give rise to uric acid. The formation of these precursor substances, which takes place in the corpuscles, is not observed at 0°, is most rapid at 37°, and diminishes at 56°. The process is not appreciably affected by the addition to the blood of fluoride, oxalate, or cyanide, nor by hæmolysis. It is suggested that the same process may lie at the basis of the formation of ammonia and inorganic phosphoric acid when blood is kept *in vitro*. J. PRYDE.

Static effort and the excretion of uric acid. R. C. GARRY (J. Physiol., 1927, **62**, 364—372).—Static effort and ordinary muscular exertion increase the excretion of uric acid. The increase extends over the two days following the work. The output of total nitrogen is similarly increased. R. K. CANNAN.

Physiological effect of massage. F. A. CAJORI, C. V. CROUTER, and R. PEMBERTON (Arch. Int. Med., 1927, **39**, 281—285).—Vigorous muscular and abdominal massage, under fasting conditions following a standard meal, leads to no appreciable alteration in the excretion of nitrogenous and other constituents in the urine. The benefits of massage appear to result from changes in the circulation, and not from any specific effect on general metabolism. A. WORMALL.

Action of physiologically equilibrated salt solutions. D. L. RUBINSTEIN (Biochem. Z., 1927, **182**, 50—64).—The sodium ion when present alone in solution has a double toxic action on turbellariæ, polychætes, and crabs. Potassium antagonises the one, and calcium the other, of these two toxic actions, but their behaviours in this respect are independent and do not summate. J. PRYDE.

Carbon monoxide poisoning in the absence of hæmoglobin. J. B. S. HALDANE (Nature, 1927, **119**, 352).—Experiments with the wax-moth, *Galleria mellonella*, and the cress plant, *Lepidium sativum*, suggest that oxygen, before it can be utilised for at least some of the oxidative processes in the cell, must combine with a substance possessing a smaller but well-marked affinity for carbon monoxide, these two gases combining with the same group in its molecule. The substance is probably a nearly universal cell constituent. A. A. ELDRIDGE.

Cytolysis of tissue-cells. V. LAUFBERGER. Conditions of tissue cytolysis. F. HORA (Biochem. Z., 1927, **181**, 225—229, 230—249).—Addition of small amounts of potassium cyanide, of formamide, or of saccharin to aqueous suspensions of normal cells caused a more or less extensive cytolysis of the latter within 24 hrs. Numerous other substances were found to be devoid of this effect. The cytolytic activity of the three compounds mentioned is thought to be connected with their high dielectric constant.

The cytolytic activity can be inhibited by addition of a variety of salts and other compounds, but neither the activity of the original substance nor the inhibition caused by the added substance is dependent on the concentration, the curves relating degree of cytolysis to concentration of cytolytic agent or of inhibitor showing a succession of maxima and minima. The inhibitors lose their characteristic effect on keeping in contact with the cells for 24 hrs. C. R. HARINGTON.

Physiological action of alcohol. I. Alcoholic content of the blood of a fasting man following ingestion of alcoholic liquor. II. Variations of glycæmia and alcoholæmia following ingestion of alcoholic liquors and of sucrose. S. BAGLIONI,

L. Bracaloni, and A. Galamini (Atti R. Accad. Lincei, 1926, [vi], 4, 545—551; 1927, [vi], 5, 34—39).—I. The course followed by the curve expressing the proportion of alcohol in the blood as a function of the time reckoned from the consumption of alcoholic liquor is different according as the subject is a habitual drinker or not. In the former event, the alcohol content of the blood reaches a maximum, and also vanishes, more rapidly than with an abstainer.

II. Experiments on human beings disclose a connexion between glycæmic and alcoholæmic variations which appears to support the view that sugar in the organism ultimately undergoes alcoholic scission.

T. H. Pope.

Action of narcosis on the chemical composition of the brain. M. Serejski (Biochem. Z., 1927, **182**, 188—192).—Chloroform narcosis in dogs leads to an increase in the lipin content of both the white and the grey matter of the brain. The white matter shows a greater increase in cholesterol and unsaturated phosphatides than the grey matter. The total nitrogen of the white and grey matter is not significantly altered, but there is a slight tendency to increase. J. Pryde.

Toxicity of local anæsthetics administered intra-arterially. T. Kuroda (Biochem. Z., 1927, **181**, 172—175).—The toxicity of anæsthetics of the cocaine group is less after intra-arterial than after intravenous administration, probably owing to a detoxication during passage through the capillary plexus. C. R. Harington.

Blood reactions of the alkaloids of *Ceanothus americanus*. C. E. Tharaldsen and J. Krawetz (Amer. J. Physiol., 1927, **79**, 545—552).—Both *in vitro* and when administered orally or subcutaneously, these alkaloids reduced the clotting time of blood. Their influence was probably on the action of the thromboplastin. R. K. Cannan.

[Pharmacology of] quinine. G. Weiss and R. A. Hatcher (J. Pharm. Exp. Ther., 1927, **30**, 327—333).—The toxicity of quinine is dependent on the rate of its intravenous injection. For the cat, the fatal dose of the hydrochloride falls from 140 mg. per kg. body-weight to 100 mg. as the rate of injection is increased from 2 to 5 mg. per kg. body-weight per min. Cats recover within about 3 hrs. from the toxic effects of 70% of the fatal dose. The exclusion of the kidneys from the circulation has little influence on the rate of recovery, and perfusion experiments show that the greater part of an intravenous dose is probably destroyed in the liver. E. A. Lunt.

[Pharmacology of] quinine. R. A. Hatcher and H. Gold (J. Pharm. Exp. Ther., 1927, **30**, 347—350).—Quinine is eliminated practically completely from human blood in 6—20 min. after intravenous injection. E. A. Lunt.

[Pharmacology of] quinidine. S. Weiss and R. A. Hatcher (J. Pharm. Exp. Ther., 1927, **30**, 335—345).—The toxicity of quinidine sulphate varies with the rate of intravenous injection. The average fatal dose for the cat, when injected at the rate of 5 mg. per kg. body-weight per min., is about 80 mg. per kg. About 95% of an intravenous dose leaves the blood within 5 min.; the elimination is practically complete in 3—4 hrs. Perfusion experiments indicate that the liver of the cat destroys quinidine and quinine at practically the same rates. The quinidine was determined by titration with bromine water.

E. A. Lunt.

Nephelometric determination of small quantities of arsenic. M. Delaville and J. Belin (Bull. Soc. Chim. biol., 1927, **9**, 91—93).—A mixture of 5 c.c. of the fluid investigated with 5 c.c. of a reagent containing sodium hyposulphite (10%) in hydrochloric acid is boiled and cooled, and the turbidity compared in a nephelometer with that of a standard arsenic solution. The error is $\pm 6\%$, using solutions containing 0·0005 mg. of arsenic per c.c. In biological fluids, organic matter is destroyed first by a mixture of nitric and sulphuric acids; the liquid is then evaporated and diluted. L. F. Hewitt.

Detection of small quantities of lead in organs by chemical and spectrographic means. M. Klostermann (Ver. Ges. deut. Naturforsch. Aerzte, 1926, **3**, 1116—1118).—Lead is obtained as dioxide by ordinary methods, and the formation of a deep blue colouring matter by the interaction of tetramethyldiaminodiphenylmethane, lead dioxide, and glacial acetic acid gives a colorimetric criterion for the quantity of lead present. The method has been calibrated by the addition of known amounts of lead to various organs and determining its quantity by the procedure described. The lead may be reconverted into the dioxide and then determined spectrographically. R. A. Morton.

Kinetics of the action of carboxylase. E. Hagglund and T. Rosenquist (Biochem. Z., 1927, **181**, 296—301).—The optimal phosphate concentration for the extraction of carboxylase from yeast is 0·3—0·35*M*, such extracts being four times as active as an aqueous extract. The variation of reaction velocity with concentration of substrate and with amount of enzyme is studied.

P. W. Clutterbuck.

Catalase. I. H. von Euler and K. Josephson (Annalen, 1927, **452**, 158—181).—By a modification of the method of Hennichs (A., 1926, 756), the authors have obtained an exceedingly active preparation of catalase from horse-liver. The first extraction of the liver with water does not remove all the enzyme, a second extraction yielding a solution practically identical with the first. Only a single precipitation of the combined extracts with a half volume of alcohol should be employed. The solution (C.F. 1500) so obtained was adsorbed with aluminium hydroxide and the enzyme eluted with 0·02*N*-ammonia solution, 46% of the activity being obtained. Dialysis of this solution (C.F. 7500) for 60 hrs. resulted in no loss of activity, and yielded a product with C.F. 14,600. Elution with sodium hydrogen phosphate removes only 29% of the activity together with a much larger amount of blood pigment, and in this case a loss of activity occurs during dialysis, the final product having C.F. 4600. After dialysis of the solution obtained from the ammonia elution, the enzyme was adsorbed on kaolin in a medium having 5, and again eluted with 0·02*N*-ammonia.

The solution (C.F. 26,000) after dialysis through a collodion membrane at 0° for 110 hrs. yielded a preparation having C.F. 43,000, which could be concentrated under diminished pressure without loss of activity. In agreement with Hennichs, it was found that there is no relation between the activity of the preparations and the percentage of iron present. Two preparations having C.F. 43,000 and 40,000, respectively, contained N 14·72 and 15·06%; S 0·78 and 1·25%; Fe 0·63 and 0·15%, respectively (phosphorus absent), the ash content of the two samples being only 1·4 and 0·94%, respectively.

J. W. Baker.

Collagen-dissolving enzyme (collagenase). W. S. Sadikov (Biochem. Z., 1927, **181**, 267—283).—Whereas freshly-prepared trypsin does not, many commercial preparations (especially when old) do attack tendon collagen. When minced pancreas is digested with 20% glycerol at the ordinary temperature for 24 hrs., an extract is obtained which attacks both fibrin and collagen, and the gland residue if further digested for 24 hrs. at 40° with glycerol gives an extract which attacks only collagen. Attempts were made to purify collagenase by adsorption methods. The enzyme is not precipitated by safranine, but it is adsorbed by kaolin (distinction from fibrinase). Charcoal adsorbs fibrinase partly, but does not adsorb collagenase. Kaolin and charcoal adsorbates of pepsin contain an enzyme which in acid solution converts collagen into a glue, but cannot further digest it (glutinase). When an old pancreatic solution was fractionated with kaolin and charcoal, whilst with charcoal no selective adsorption occurred, with kaolin the collagenase was destroyed. Collagenase is not injured by alcohol (distinction from trypsin). Collagen which has been treated with picric acid withstands the action of pepsin and trypsin, but is attacked by collagenase. Collagen and fibrin pretreated with formaldehyde are completely resistant to collagenase and trypsin, but fibrin, so treated, is attacked by pepsin. Glycerol extracts of spleen attack fibrin and collagen in alkaline solution and sodium carbonate extracts contain glutinase. Glycerol and sodium carbonate extracts of pancreas act equally well on collagen and fibrin, but those of liver are inactive. Pure pancreatic juice without addition of enterokinase digests fibrin both in acid and alkaline solution, but acts only faintly on collagen. In presence of enterokinase, collagen is attacked in both acid and alkaline solution, but fibrin only in alkaline solution. Enterokinase alone possesses to a slight extent the properties of collagenase and glutinase. Glycerol extracts of the fæces of various animals were shown to contain tryptase, collagenase, α-glutinase (glutinises in acid solution), and β-glutinase (glutinises in alkaline solution). Diphtheria toxin contains α-glutinase, but no collagenase, peptase, or tryptase.

P. W. Clutterbuck.

Glycerophosphatase. H. Kobayashi (J. Biochem. [Japan], 1926, **6**, 261—274).—The optimum acidity for the activity of glycerophosphatase is at p_H 5·56. The rate of hydrolysis of glycerophosphate is proportional to the enzyme quantity, *i.e.*, the time necessary for equal degrees of hydrolysis is inversely proportional to the amount of enzyme. The affinity between the enzyme and the substrate is not influenced by the acidity of the medium.

Chemical Abstracts.

Peroxydase. IV. Influence of the substrate on the optimum p_H. H. Ucko and H. W. Bansi (Z. physiol. Chem., 1927, **164**, 52—57).—Horseradish peroxydase has different optimum reactions for the substrates, pyrogallol, guaiacol, and *o*-cresol (cf. A., 1926, 1275). The activity–p_H curve and the optimum p_H are not specific properties of an enzyme, but depend on the substrate.

A. Wormall.

Stereochemical specificity of lipases. Effect of poisons on fat-splitting enzymes. P. Rona and R. Ammon (Biochem. Z., 1927, **181**, 49—79).—The course of hydrolysis of various esters by different preparations of lipase was followed electrometrically, periodic measured additions of alkali being made in sufficient amount to maintain a constant p_H; in all cases the course of reaction was linear. When the substrate was *r*-methyl mandelate, the lipases from pig- and ox-liver and from taka-diastase attacked the *d*-ester preferentially, whilst those from human liver, guinea-pig serum, and pig-pancreas attacked the *l*-ester first (cf. Willstatter, A., 1924, i, 1144). The lipase from pig-liver behaved abnormally in that it hydrolysed the pure *l*-ester more rapidly than the pure *d*-ester, although its action on the *r*-ester was to bring about a preferential hydrolysis of the *d*-form; on further purification, this enzyme tended to lose its optical specificity. Whilst the concentration of enzyme had little effect on the hydrolysis of tributyrin by pig-liver lipase, it had a large effect on the rate of hydrolysis of the mandelic esters; further, methyl mandelate was hydrolysed much more rapidly than ethyl mandelate. The inhibiting effect of various alkaloids, of atoxyl, of trypaflavine, and of adrenaline on these enzymes is described.

C. R. Harington.

Influence of the quinine group on enzymic functions of the organism. VI. Dependence on the p_H of the action of quinine and carbamide on pancreatic lipase. J. A. Smorodincev and V. A. Danilov (Biochem. Z., 1927, **181**, 149—157).—Quinine accelerates the hydrolysis of triacetin by pancreatic lipase over the range p_H 4·5—6·0, but retards it at p_H 8, which, under normal conditions, is the optimum reaction for this enzyme. Carbamide has no effect on the enzyme at any reaction; carbamide nitrate has no action beyond that due to its effect on the p_H of the solution.

C. R. Harington.

Papain. H. Kraut and E. Bauer (Z. physiol. Chem., 1927, **164**, 10—36; cf. A., 1924, i, 467; 1925, i, 739).—The adsorption curves of papain and invertase on alumina show significant differences. Small amounts of the adsorbent remove a relatively large amount of papain and a small amount of invertase, but with further additions the amount of the former decreases, whilst that of the latter increases. Simple peptides are not integral constituents of papain, but it is not possible to separate the peptones and polypeptides from the enzyme.

Crude papain contains an inhibitory substance, which is probably a peptide, since digestion with erepsin leads to an increase in activity. Substances associated with the enzyme act as stabilisers and as co-adsorbents, for purified papain is much less readily adsorbed than the original preparation. Purification results in the removal of nine-tenths of the original impurities, and the methods of purification include extraction with chloroform, precipitation of part of the impurities with lead phosphate, adsorption on alumina, and elution with dilute acetic acid. Yeast-gum is added as a stabiliser and co-adsorbent. Dialysis causes a loss in activity, probably due to the loss of a specific stabiliser with buffer properties. Some chemical properties of the preparation are given. Millon's reaction becomes somewhat stronger during the course of purification, whilst Molisch's and the ninhydrin reactions remain fairly constant. A study of the stability at different hydrogen-ion concentrations shows that there is a maximum stability at p_H 5—6, approximately the same as the optimum reaction. A. WORMALL.

Influence of the reaction on the proteolytic power of papain. II. W. E. RINGER and B. W. GRUTTERINK (Z. physiol. Chem., 1927, 164, 112—142; cf. A., 1926, 977).—A purified water-soluble papain shows two optimum reactions (p_H 2·5 and 11·3) for the dissolution of fibrin. Similar optima are found when heat-coagulated egg-white and serum proteins are used as substrates, although the optimum on the acid side varies somewhat with the protein. The influence of electrolytes on this action depends on the p_H of the medium, for small quantities of a large number of anions and cations have a strong inhibitory action, except in neutral or faintly acid solutions, where they have a strong activating action. Variations in the amount of electrolyte, with constant p_H, produce alterations in the velocity of the reactions, and also in the range of p_H, over which the action takes place. The further digestion of serum proteins by papain in neutral solution, as measured by the liberation of amino-nitrogen, is also accelerated by electrolytes. Papain and serum proteins appear to form compounds in neutral solution. A. WORMALL.

Purification and properties of pepsin. J. C. FORBES (J. Biol. Chem., 1927, 71, 559—585).—On treatment of an aqueous solution of commercial pepsin with safranine, the enzyme was quantitatively precipitated; the precipitate was dissolved in 20% alcohol containing a little oxalic acid and the dye removed by extraction with butyl alcohol. In this way, enzyme preparations were obtained having twenty times the activity of the original material. Such an active preparation had C 45·24, H 6·19, N 11·50, S 1·79%; figures are given for the nitrogen distribution; traces only of purine derivatives were found. The isoelectric point was at p_H 2·5; the preparation had no immediate effect when added to dilute hydrochloric acid, but on prolonged incubation of such a solution a decrease was observed both in the conductivity and the hydrogen-ion concentration. Extraction of the dried preparation with ether left the enzymic activity unchanged; addition of alcohol and ether to aqueous solutions of the pepsin caused inactivation when the concentration of acid was high, but had little or no effect when it was low. C. R. HARINGTON.

Intensification of enzymic action by minimal amounts of known substances. M. JACOBY (Biochem. Z., 1927, 181, 194—206).—The activity of urease is increased by the presence of as little as 0·0001 mg. of potassium cyanide, or by even less of acetaldehydecyanohydrin; the activating effect is independent of the p_H. Urease which has been inactivated by mercuric chloride can be reactivated by treatment with cyanide. The action of urease is also accelerated by very small amounts of histidine, histamine, and hæmoglobin; arginine and lysine have a slight accelerating effect, whilst other amino-acids have practically no effect, Histidine, therefore, apparently belongs to a second group of accelerating substances of the same order of activity as cyanides. C. R. HARINGTON.

Fermentations with yeast regarded from the biological point of view. II. Fermentability of glyceraldehyde and dihydroxyacetone by living yeast. H. HAEHN and M. GLAUBITZ (Ber., 1927, 60, [*B*], 490—493).—Pure glyceraldehyde is not fermented by bottom beer yeast, top yeast *M*, or *Saccharomycodes Ludwigii* in 1% solution or in a solution of p_H 7·37—7·73, and only slightly if boiled previous to the addition of the yeast. The yeast-cells become damaged to some extent. Pure dihydroxyacetone is vigorously fermented by *S. Ludwigii* after a pronounced period of induction, but not by the other two varieties of yeast. With technical, bimolecular dihydroxyacetone, the action is somewhat less vigorous. The yeast-cell does not suffer damage in any case. H. WREN.

Fermentability of free and phosphorylated hexoses and a polarimetric proof of their fixation in the yeast-cell. C. NEUBERG and M. KOBEL (Biochem. Z., 1926, 179, 451—458).—Robison's hexosemonophosphate and the two monophosphates prepared by Neuberg—one by partial hydrolysis of hexosediphosphate, the other by hydrolysis of synthetic sucrosemonophosphate—are all fermented by top and bottom yeasts, but more rapidly by yeast juice. In no case is the fermentation as rapid as that of dextrose and lævulose. Lævulose shows an increased lævorotation, and hexosemonophosphate (Robison's and that from the diphosphate) an increased dextrorotation when they are added to yeast juice which has lost its fermentative power through keeping. It is suggested that a combination of sugar or sugar phosphate with yeast protein or protein degradation products may lie at the basis of this phenomenon (see also Neuberg and Kobel, A., 1926, 151, 1061). J. PRYDE.

Phosphorylation and oxido-reduction [in fermentation]. R. NILSSON and T. LOVGREN (Z. physiol. Chem., 1927, 164, 61—68).—The addition of small quantities of methylene-blue to dried bottom yeast *H* in a phosphate solution containing sugar decreases considerably the induction of the fermentation process as measured by the evolution of carbon dioxide, but subsequently the fermentation curves, with and without methylene-blue, are approximately

parallel. Large quantities of methylene-blue, however, entirely suppress the evolution of carbon dioxide. The action of small amounts of methylene-blue, by which the induction period is shortened, is attributed to the participation of this substance in the oxido-reduction reactions. Addition of methylene-blue also increases the rate of disappearance of inorganic phosphate from the solution during the first stages. A. WORMALL.

Fermentation of dextrose and pyruvic acid. E. HAGGLUND and L. AHLBOM (Biochem. Z., 1927, **181**, 158—171).—The relative rates of fermentation of dextrose and of pyruvic acid by yeast and yeast extracts vary with the nature of the enzyme preparation. Acceptance of the theory that the action of carboxylase on pyruvic acid is an essential part of yeast fermentation involves the further assumption of the existence of a co-enzyme which renders the pyruvic acid susceptible to the action of carboxylase, and, in those cases in which pyruvic acid is not fermented, must have been inactivated. No evidence of the existence of such a co-enzyme has so far been obtained. C. R. HARINGTON.

Velocity of fermentation of pyruvic acid and the theory of fermentation. C. NEUBERG (Biochem. Z., 1927, **180**, 471—490).—Living yeast ferments dextrose more rapidly than pyruvic acid. With dry yeast, acetone yeast, and maceration juice, on the other hand, pyruvic acid is the more rapidly fermented in acetate buffers at p_H 4·8—5·0. The pyruvic acid theory of fermentation finds further support in these results. The fermentation of pyruvic acid and of dextrose in alkaline solution is discussed, and it is suggested that the inability of yeast to ferment added pyruvic acid in alkaline media may find explanation in the selective permeability of the yeast and the effect of the hydrogen-ion concentration on the ionisation and enolisation of pyruvic acid. R. K. CANNAN.

Pyruvic acid as an intermediate product of alcoholic fermentation. F. TRAETTA-MOSCA (Annali Chim. Appl., 1927, **17**, 59—60).—Rimini's results (this vol., 279) are criticised (see A., 1926, 978). T. H. POPE.

Inactivation of some yeast enzymes by zinc and cadmium salts. S. KOSTYTSCHEV and G. MEDVEDEV (Z. physiol. Chem., 1927, **164**, 77—102).—Invertase and reductase of dried yeast are both inhibited by small amounts of zinc and cadmium salts, the reductase action being measured by the reduction of added acetaldehyde. Concentrations of these salts as low as $M/25{,}000$ decrease the activities of the two enzymes. The velocity coefficient is greatly reduced in both cases, but the reaction curve is unaltered in form. The velocity coefficient for inversion is approximately inversely proportional to the logarithm of the concentration of the zinc or cadmium salt. This inhibitory effect is due to a specific action of zinc and cadmium ions, since the anions of their salts have no effect, and also salts of magnesium, calcium, strontium, and barium have little or no inhibitory influence on the enzymes concerned. The significance of these results in relation to the effect of zinc and cadmium salts on the formation of acetaldehyde during fermentation of dried yeast is discussed. The salts of bivalent metals have no specific action on the carboxylase of dried yeast, although there is a decreased liberation of carbon dioxide in the first stages. A. WORMALL.

[Determination of] cytochrome in yeast cells. H. VON EULER and H. FINK (Z. physiol. Chem., 1927, **164**, 69—76).—The hæmochromogen in a pyridine extract of yeast can be determined by utilising the spectrophotometric method of Odencrants, which is described. A pyridine solution of hæmin is used as standard, and a quantitative comparison is made of the absorption of light at the main band (about 557 mμ). A. WORMALL.

Changes in hydrogen-ion concentration of natural waters produced probably by the growth of bacteria. V. ENEVOLDSEN (Biochem. Z., 1927, **181**, 251—266).—Considerable changes in the p_H of sea-water were observed while travelling through the Cattegat and up the Baltic and also in the pools near Roskilde. Investigations of the changes of p_H of sea-, fresh-, and ditch-water show that any such change of p_H is followed by a period of compensation. Sterilised sea-water after being kept for 8 days with frequent shaking, on inoculating with sea-water bacteria, shows changes of p_H daily. P. W. CLUTTERBUCK.

Formation of carbamide by bacteria. II. N. N. IVANOV and M. I. SMIRNOWA (Biochem. Z., 1927, **181**, 8—16).—Both in the case of bacteria which form carbamide in a gelatin–peptone medium and in the case of those which do so only in presence of free arginine, the carbamide production is completely inhibited by the introduction of carbohydrates or of mannitol into the medium. Urease could be detected in all organisms which fail, under any conditions, to produce carbamide. It is thought, therefore, that production of carbamide is dependent on more or less complete absence of urease, and that the synthesis of the latter enzyme may be favoured by the presence of carbohydrate. C. R. HARINGTON.

Biochemistry of asymmetry (asymmetric dismutation). C. NEUBERG and E. SIMON (Biochem. Z., 1926, **179**, 443—450).—*dl*-Methyl-*n*-butaldehyde is converted by *Bacterium pasteurianum*, and by acetone extracts of the bacteria, into the corresponding dextrorotatory amyl alcohol and optically active valeric acid (cf. Neuberg and Simon, A., 1926, 1062). J. PRYDE.

Tissue-digesting enzyme (histase) of streptococci. M. FOBISHER (J. Exp. Med., 1926, **44**, 777—785).—The extracellular proteolytic enzyme, *histase*, present in many strains of beta-type, aerobic and facultative hæmolytic streptococci, is partly inactivated in about 45 min. at 60°. It is present in sterile filtrates of cooked meat cultures. No correlation was found between hæmolysis and proteolysis. The enzyme resembles trypsin in its action. CHEMICAL ABSTRACTS.

Mixed acid fermentation. Fermentative sugar dissimilation by micro-organisms of the coli group. W. C. DE GRAAF (Nederland. Tijdschr. Hyg. Microbiol. Serol., 1926, **1**, 43–70).—A discussion. CHEMICAL ABSTRACTS.

Reduction of *l*-cystine by *Bacillus coli*. H. YAOI and S. HOSOYA (Japan Med. World, 1926, **6**, 81—83).—When *B. coli communis* is incubated in protein-free synthetic media containing *l*-cystine, cysteine is produced by reduction. The daily increase reaches the optimum after the 15th or 18th day. Anaerobic conditions yield larger quantities of cysteine than aerobic conditions. CHEMICAL ABSTRACTS.

Effects of alkylresorcinolcarboxylic acids and their dependence on the constitution of the alkyl side-chains. L. BLEYER (Biochem. Z., 1927, **181**, 350—365).—Suspensions of gram-negative cells (*Bacillus coli, dysenteriæ, proteus, prodigiosus, pyocyaneus*, etc.) were homogenised by sodium hexyl- and heptyl-resorcinolcarboxylates, but gram-positive cells (staphylococcus, pneumococcus, *B. diphtheriæ*, etc.) were unaffected. Red blood-corpuscles were hæmolysed and coagulated opaque serum-protein was clarified. Toxins were deprived of their toxicity and of their antigenic function, 0·25—0·5% of the hexyl compound producing this effect with the toxins of dysentery and tetanus. Diphtheria toxin was, however, more resistant. The reaction depends on the size of the alkyl group. The sodium salt of resorcinolcarboxylic acid and its ethyl derivative have little or no effect, the cytolytic, toxin-destroying, and homogenising power first appearing in the amyl derivative and increasing in the hexyl and heptyl derivatives. P. W. CLUTTERBUCK.

Cystine content of peptones for bacteriological use. H. YAOI (Japan Med. World, 1926, **6**, 114—116).—Commercial peptones vary greatly as to cystine content: Witte contains most, Difco least. Some samples of gelatin also contain cystine in minute amounts. CHEMICAL ABSTRACTS.

Use of saponin in protection of insulin against enzymes. F. LASCH and S. BRÜGEL (Biochem. Z., 1927, **181**, 109—116).—The physiological activity of solutions of insulin to which small amounts of saponin had been added was not affected by exposure to the action of pepsin or of trypsin. It is suggested that this observation may form the basis of a method for the oral administration of insulin.
C. R. HARINGTON.

Replacement of sugar by other substances in the removal of hypoglycæmic symptoms caused by insulin. F. SILBERSTEIN, J. FREUD, and T. RÉVÉSZ (Biochem. Z., 1927, **181**, 327—332).—Administration of dihydroxyacetone and especially of alanine, either perorally or subcutaneously, prevents hypoglycæmic symptoms after insulin. Lactates proved untrustworthy, and acetaldehyde, salts of pyruvic acid, glycerol, and alcohol were also unsuitable. P. W. CLUTTERBUCK.

Action of insulin on enzymes. U. SAMMARTINO (Arch. Farm. sperim., 1926, **42**, 17—27).—Experiments made with a more highly purified insulin confirm the previous conclusion (Atti R. Accad. Lincei, 1923, [v], **32**) that insulin has no influence on the velocity of reaction of enzymes such as diastase, catalase, and lipase. T. H. POPE.

Variations in the phosphorus content of muscular tissue during insulin hypoglycæmia. G. PIAZZA (Arch. Farm. sperim., 1926, **42**, 28—32).—No increase in the inorganic phosphorus content is detectable in muscle during hypoglycæmia produced by administration of insulin. No hydrolysable phosphorus fraction exists in muscle either before or after the action of insulin. Insulin hypophosphatæmia cannot be due to displacement of phosphorus or a phosphorus compound from the blood into the muscular tissue. T. H. POPE.

Influence of insulin on the mammalian heart. M. B. VISSCHER and E. A. MULLER (J. Physiol., 1927, **62**, 341—348).—Insulin has no intrinsic effect on the oxygen consumption of the heart in the heart–lung preparation. R. K. CANNAN.

Sugar, inorganic phosphorus, and lactic acid of blood after administration of insulin and dextrose. I. KATAYAMA and J. A. KILLIAN (J. Biol. Chem., 1927, **71**, 707—722).—Both in rabbits and in normal and diabetic human beings, insulin in large doses causes an increase in the lactic acid of the blood; the increase is, however, small in comparison with the fall in concentration of dextrose. A similar, but less marked, rise in concentration of lactic acid follows ingestion of dextrose. The fall in the inorganic phosphorus of the blood, which follows administration of insulin, precedes the rise in the lactic acid content. The rise in lactic acid is greater in the normal than in the diabetic subject, and the results, in general, are in favour of the view that the lactic acid is an intermediate product in the utilisation of carbohydrate under the influence of insulin. C. R. HARINGTON.

Blood calcium and tolerance for magnesium. Hypercalcæmia induced by the parathyroid hormone. S. A. MATTHEWS and W. C. AUSTIN (Amer. J. Physiol., 1927, **79**, 708—718).—From studies of the fatal dose of magnesium sulphate when injected into normal and parathyroidectomised dogs and into dogs injected with parathyroid extract, it was concluded that the toxicity of magnesium sulphate is closely proportional to the calcium concentration in the blood. The effect of the parathyroid hormone on the heart and vascular system is antagonised by magnesium sulphate. R. K. CANNAN.

Action of iodine and iodine preparations, thyroidectomy, and administration of thyroid gland on blood catalase *in vitro* and *in vivo*. A. TIMOFEJEWA (Biochem. Z., 1927, **180**, 35—45).—A relationship exists between the functioning of the thyroid gland and the catalase activity of the blood. This is not a direct effect, since iodine, iodide ions, iodised protein, and active thyroid extracts do not increase catalase activity *in vitro*. On the other hand, catalase is activated or mobilised by feeding with thyroid extract or by pretreatment for some time with iodine or potassium iodide. P. W. CLUTTERBUCK.

Thyroxin. III. Constitution and synthesis. C. R. HARINGTON and G. BARGER.—See this vol., 358.

Diuretic-antidiuretic action of pituitary. R. L. STEHLE (Amer. J. Physiol., 1927, **79**, 289—296).—Urine secreted after pituitary injection is extraordinarily rich in phosphorus, calcium, potassium, and magnesium, which presumably arise from the

cells. It is suggested that the antidiuretic action of pituitary is due to increased capacity of the cells to hold water as a result of electrolyte changes. The diuretic effect is a salt effect due to the necessity for the kidney to excrete the salts thrown into the blood by the cells. R. K. CANNAN.

Internal secretions of the ovary. IV. A. S. PARKES and C. W. BELLERBY (J. Physiol., 1927, 62, 385—396).—Details are given of the extraction and the yields of œstrus-producing hormone from placenta, uterus, fœtus, and amniotic fluid. It is improbable that the hormone is elaborated in the placenta. R. K. CANNAN.

Cell respiration. VI. Function of the suprarenal cortex and the substance C_{XII}. A. VON SZENT-GYORGYI (Biochem. Z., 1927, 181, 433—437).—A substance, C_{XII}, having the properties of a thiophenol derivative, is isolated from the suprarenal cortex. It is soluble in acetone, water, and methyl alcohol, slightly soluble in ether, insoluble in light petroleum. It gives no nitroprusside reaction, reduces iodine, *p*-phenylenediamine, neutral silver nitrate, and ferric salts, and gives colour reactions with ferrous and ferric salts. It does not reduce permanganate (cf. A., 1925, 93, 708; 1926, 99). P. W. CLUTTERBUCK.

Function of the suprarenal cortex. I. Blood changes following bilateral suprarenalectomy in cats. II. (With A. J. EISENMAN.) Acid-base equilibrium. W. W. SWINGLE (Amer. J. Physiol., 1927, 79, 666—678, 679—688).—I. The blood becomes more concentrated, resulting in a rise in the concentration of protein, non-protein nitrogen, and carbamide. The blood-sugar falls to a level characteristic of insulin hypoglycæmia. There is albuminuria and a diminished secretion of urine. Death may be attributed either to hypoglycæmia or to acid intoxication.

II. There is a fall in the p_H, carbon dioxide tension, and total acid of the blood and in the serum hydrogen carbonate. There is evidence of an uncompensated acidosis due to phosphoric and organic acids. R. K. CANNAN.

Cellular oxidation in certain tissues of dogs deprived of suprarenals. O. P. ESTRADA and S. M. NEUSCHLOSZ (Rev. Soc. Argentina Biol., 1926, 2, 597—598).—The oxidative power of different tissues of dogs was determined after extirpation of the suprarenals. There was a general diminution in the case of muscular tissues which was compensated by addition of cortical substance. Addition of thyroid from normal animals caused compensation, but the thyroid from animals deprived of suprarenals had the contrary effect. Cortical substance slightly inhibits oxidation by normal muscle. The effect of suprarenal extirpation in the case of organs was slight, but there was an inconstant increase in the oxidative power of the pancreas. G. W. ROBINSON.

Disappearance of intravenously injected dextrose, formation of glycogen, and arterial and venous sugar content in dogs deprived of suprarenals. O. P. ESTRADA (Rev. Soc. Argentina Biol., 1926, 2, 544—547).—Dogs from which the suprarenals had been removed showed a decrease in blood-sugar content in the first 4 hrs. after removal. The blood-sugar was then maintained at 0·05—0·085% for some time, subsequently falling to 0·025—0·055% at death. The disappearance of sugar was delayed by intravenous injection of dextrose in four cases out of five, and the subsequent hypoglycæmia did not occur. Hepatic and myocardial glycogen were greatly diminished. A less evident diminution in muscular glycogen took place. Hepatic glycogen was not increased by injection of dextrose, but there was an increase in myocardial and muscular glycogen which did not, however, reach the normal figure. Removal of the suprarenals tended to cause the sugar content of venous blood to equal and exceed that of arterial blood. The effect still persisted after injection of dextrose. G. W. ROBINSON.

Effect of irradiation on vitamin-*A*. S. G. WILLIMOTT and F. WOKES (Pharm. J., 1927, 118, 217—218).—Cod-liver oil, rich in vitamin-*A*, was irradiated in an open evaporating basin 3 inches from a quartz mercury vapour lamp. The temperature of the oil rose from 20° to 70° in 90 min. Data are given showing the diminution in vitamin-*A* content with time in an oil irradiated under these conditions. The determinations were made in a Lovibond tintometer, using the arsenious chloride and antimony chloride tests. One third of the vitamin was destroyed in the first hr., and the whole in 2 hrs.; irradiation of the oil for a few min. results in the subsequent slow destruction of the vitamin over a long period. E. A. LUNT.

Feeding of xanthophyll to rats on a diet deficient in vitamin-*A*. S. G. WILLIMOTT and T. MOORE (Biochem. J., 1927, 21, 86—88).—Pure crystalline xanthophyll prepared from nettle leaves cannot replace vitamin-*A* in the diet of rats. S. S. ZILVA.

Absorption spectrum of cholesterol and its biological significance with reference to vitamin-*D*. I. I. M. HEILBRON, E. D. KAMM, and R. A. MORTON (Biochem. J., 1927, 21, 78—85).—In the fractional crystallisation of cholesterol (from brain and from cod-liver oil) from ethyl acetate a small quantity of a compound accumulates in the least soluble fraction which shows well-defined absorption bands at 293 $\mu\mu$, 280 $\mu\mu$, and 269 $\mu\mu$. Cholesterol itself shows only general absorption. These bands disappear on irradiation with ultra-violet light. The unknown substance is therefore closely connected with the precursor of vitamin-*D*. S. S. ZILVA.

Relation of cholesterol to vitamin-*D*. O. ROSENHEIM and T. A. WEBSTER (Biochem. J., 1927, 21, 127—129).—Cholesterol purified by way of the dibromide shows no longer the absorption spectrum in the ultra-violet region characteristic of ordinary cholesterol (cf. preceding abstract) and cannot be activated antirachitically by irradiation with ultra-violet light. Ergosterol (or some similar sterol) is the parent substance of vitamin-*D*. S. S. ZILVA.

Antirachitic value of fresh spinach. M. H. ROSCOE (Biochem. J., 1927, 21, 211—215).—A slight but definite influence upon calcification is demonstrated by introducing fresh green leaves of summer

spinach into the diet of young rats and rabbits (cf. Chick and Roscoe, A., 1926, 437; Boas, *ibid.*, 437). The effect is more marked in the case of the rabbits. S. S. ZILVA.

Effect of excessive irradiation with ultra-violet light upon the growth of rats. J. L. LEIGH-CLARE (Biochem. J., 1927, **21**, 208—210).—Provided that the eyes are shielded, exposure of young growing rats to ultra-violet radiation for periods up to 30 min. daily has no deleterious effect on growth and well-being of the rats. An exposure for 30 min. is no more beneficial than that for shorter periods. S. S. ZILVA.

Antirachitic value of cod-liver oil concentrate injected subcutaneously. B. KRAMER, S. D. KRAMER, D. H. SHELLING, and M. J. SHEAR (J. Biol. Chem., 1927, **71**, 699—706).—The unsaponifiable fraction of cod-liver oil, after removal of cholesterol, cured rickets in rats when injected subcutaneously in ethereal solution, but was inactive when injected in solution in palmitin. C. R. HARINGTON.

Isolation of the anti-beri-beri vitamin. B. C. P. JANSEN and W. F. DONATH (Proc. K. Akad. Wetensch. Amsterdam, 1926, **29**, 1390—1400).—A method is described for extracting from fine rice polishings the vitamin which protects rice-birds and pigeons from polyneuritis. From 100 kg. of the rice polishings a residue of 1·4 g. was obtained which appeared to contain about one quarter of the vitamin originally present. The product was apparently the hydrochloride of a base, possibly $C_6H_{10}ON_2,HCl$. Its chemical behaviour suggests the presence of a glyoxaline nucleus. M. S. BURR.

Gaseous metabolism in the initial stages of *B*-avitaminosis in birds. B. A. LAVROV and S. N. MATZKO (Biochem. Z., 1926, **179**, 332—347).—From experiments on hens kept on a diet deficient in vitamin-*B* it is concluded that the specific effects of lack of the latter are not related to the lowered oxidative processes of the organism. The drop in gaseous metabolism in *B*-avitaminosis appears only when symptoms of starvation have set in. J. PRYDE.

Influence of nutrition on the blood catalase content. A. BERNSTEIN (Biochem. Z., 1926, **179**, 313—325).—The catalase content of pigeon's blood is less than that of other animals, but in different animal species it is found to vary within wide limits, up to 1000%. In a single animal species variations up to 50% may be encountered. In starvation and during lack of vitamin-*B*, the catalase content does not fall below normal values. The catalase content of the organism cannot serve as an index of the total metabolism. J. PRYDE.

Serum-calcium in vitamin-*B* deficiency. A. UNGAR (Biochem. Z., 1927, **180**, 357—358).—The serum-calcium of normal and of beri-beri pigeons showed no differences sufficient to support the view that beri-beri convulsions are due to a deficiency in the secretion of the parathyroid. R. K. CANNAN.

Water-soluble vitamins-*B* and -*C* in malt and malt extract. L. RANDOIN and R. LECOQ (Bull. Soc. Chim. biol., 1927, **9**, 49—58).—Malt and malt extract do not possess anti-scorbutic activity, but they contain vitamin-*B*, and hence promote growth and alleviate polyneuritic symptoms of pigeons and rats. The beneficial effect of malt extract in human scurvy is attributed to the high content of vitamin-*B*, thus partly replacing vitamin-*C*. L. F. HEWITT.

Can administration of sodium hydrogen carbonate or active iron oxide influence the course of avitaminosis in pigeons? D. BANERJEE (Biochem. Z., 1927, **180**, 27—29).—The course of avitaminosis is unaffected by administration of these substances. P. W. CLUTTERBUCK.

Relation between vitamin-*C* content of diet and milk in the cow. J. S. HUGHES, J. B. FITCH, H. W. CAVE, and W. H. RIDDELL (J. Biol. Chem., 1927, **71**, 309—316).—No relationship could be observed between the vitamin-*C* content of the cow's food and that of its milk. C. R. HARINGTON.

Protoplasm. II. Chemical constituents of the plasmodium of *Lycogala epidendron* and alterations during spore differentiation. A. KIESEL (Z. physiol. Chem., 1927, **164**, 103—111).—The methods used are those previously described (A., 1926, 204). Tables are given showing the various constituents present in the dry material, and a complete analysis has been made of the ether-soluble matter, which represents more than one third of the dry substance. Cholesterol is present to the extent of 2·97% of the fat soluble in light petroleum. The unsaturated fatty acids include much oleic acid, a smaller quantity of linoleic acid, and unsaturated hydroxy-acids, whilst the saturated fatty acids include those from C_{16} to C_{20}. Spore differentiation is accompanied by appreciable decreases in the percentages of protein, glycogen, and fatty substances, and increases in plastein and myxoglucosan. A. WORMALL.

Action of amino-acids on the germination of *Phycomyces nitens*, Kunze and Schmidt. D. TITS (Bull. Acad. roy. Belg., 1926, [v], **12**, 545—554).—Using solutions of graded alkalinity containing 2% of peptone, germination took place only in those containing less than 0·1% of potassium hydroxide, the optimum solution containing 0·1% of tartaric or 0·5% of citric acid. With a series of solutions each containing 1% of tartaric acid and 0·7% of sucrose, together with 1% of one of a selected number of amino-acids, no germination was produced until 5 parts per 100,000 of peptone were added. The latter acted catalytically, since the minimum quantity producing germination in the absence of the amino-acids is 7 parts per 100,000. The activity of the amino-compounds in producing germination is in the descending order leucine, glutamic acid, histidine, cystine, and glucosamine. S. J. GREGG.

Acid formation by fungi. W. S. BUTKEWITSCH (Biochem. Z., 1927, **182**, 99—109).—Gluconic acid, as well as citric and oxalic acids, is formed by *Aspergillus* from sugars, and when nitrogen is lacking or in the presence of calcium carbonate, it is produced in larger amounts than the two last-mentioned acids. In cultures of *Mucor stolonifer*, under the same

conditions, only fumaric and oxalic acids were found. J. PRYDE.

Two kinds of carbamide formation in mushrooms. N. N. IVANOV and A. TOSCHEVIKOVA (Biochem. Z., 1927, **181**, 1—7).—On keeping cut mushrooms for some days with the cut end of the stem dipping into solutions containing ammonium carbonate or arginine nitrate, an increase in the carbamide content of the cap of the mushroom was observed; the expressed juice of mushrooms caused a formation of carbamide when added to a solution containing arginine, but not when added to one of ammonium carbonate. The formation of carbamide from the latter would therefore seem to be a function of the living cell. C. R. HARINGTON.

Fungus chitin. DOUS and ZIEGENSPECK (Arch. Pharm., 1926, **264**, 751—753).—*Boletus edulis* was dried, ground, extracted with alcohol and ether, then with alcoholic potassium hydroxide, washed with cold 4% alcoholic hydrochloric acid, warmed with 0·5% aqueous hydrochloric acid to remove hemicelluloses and glycogen, washed with boiling water, and finally with alcohol and ether. The product contained 2·09% N. Crab shells were similarly treated to provide material for comparison, and the product contained 6·05% N. The two substances were subjected to hydrolysis with 1%, 5%, and 10% sulphuric acid. Differences were shown in the proportion of nitrogen removed and in the amounts of reducing sugar formed. The authors conclude that the product from *Boletus* is not chitin, and, following Ilkewitsch, term it mycetin. When mycetin is hydrolysed with fuming hydrochloric acid, it yields *mycetosamine*, which is different from the chitosamine obtained from crab chitin. The corresponding sugars are also different. Mycetosamine yields a methylpentose, termed *mycetose*. Chitosamine hydrochloride has $[\alpha]+87·4°$; mycetosamine hydrochloride has $[\alpha]+70·2°$. W. A. SILVESTER.

Bio-radioactivity of plants. E. BURKSER, I. BRUN, and K. BRONSTEIN (Biochem. Z., 1927, **181**, 145—148).—Only insignificant radium emanations could be detected in the fresh leaves and stems of various plants, and none at all in the dried material; the radium content of the ash of plants was also found to be very small except in the case of the grape. Thorium could not be detected in the ash of any plant. C. R. HARINGTON.

Constancy of the chemical composition of plants. N. N. IVANOV (Biochem. Z., 1927, **182**, 88—98).—The seeds of pea, lentil, and vetch plants grown under very variable conditions of soil, moisture, and climate contain the same constant amount of protein, carbohydrate, and ether-soluble material. The nitrogen intake of these plants is independent of the soil nitrogen. In contrast to other cereals, and in resemblance to these *Leguminosæ*, maize, which can utilise atmospheric nitrogen fixed by soil bacteria, shows the same stability with regard to chemical composition under varying conditions of growth. J. PRYDE.

Cell-membrane of plants. E. SCHMIDT, K. MEINEL, and E. ZINTL (Ber., 1927, **60**, [*B*], 503—526).—The cell-membrane of archegoniates and phanerogams is composed of cellulose, hemicellulose, and incrustation. Repeated treatment of it alternately with chlorine dioxide and sodium sulphite results in the isolation of a cellulose–hemicellulose complex which is not further affected by the reagents, and therefore appears to pre-exist in the cell-membrane, and hence is termed "skeleton substance," whereas the incrustation and a portion of the hemicellulose are removed. The existence of two types of hemicellulose, differentiated also by varying stability towards oxidising agents, is therefore postulated. Glycuronic acid occurs among the products of hydrolysis of the hemicellulose of flax, hemp, wheat straw, beech (cf. A., 1925, i, 1370), fern, spruce, pine, etc., and since these are systematically very distinct members of the series of archegoniates and phanerogams, it seems reasonable to conclude that a carboxylated polysaccharide (the precursor of glycuronic acid) is common to both series. Free glycuronic acid cannot, however, be present in the skeleton substance, since it cannot be removed by treatment with sodium hydrogen carbonate or sodium sulphite and hence an ester-like union of cellulose, acid, and hemicellulose is assumed. The method of Tollens and Lefèvre (determination of carbon dioxide liberated by the action of 12% hydrochloric acid) is not applicable to the polyglycuronic acids such as are derived from *Fucus serratus* (A., 1926, 939), but trustworthy results are obtained by treatment of the skeleton substance with $N/15$- or $N/10$-alkali hydroxide, followed by conductometric titration of the solution with $N/10$-hydrochloric acid. The results are independent of the presence or absence of the skeleton substance in the liquid during titration and, further, under the experimental conditions pure cellulose does not absorb appreciable quantities of alkali hydroxide. The form of the titration curves cannot be due to the production of alkoxides, to the presence of strong acids, or to adsorption phenomena at the solid phase. The presence of acids of medium strength must be postulated which with respect to dissociation constant are comparable with lactic acid, and considering the nature of the skeleton substance these can only be carboxylic acids. Treatment of the skeleton substance of beech with $N/10$-sodium hydroxide causes a loss in weight of 12·53%, whereas titration experiments indicate the presence of 12·86% of acid calculated as glycuronolactone. It is therefore probable that only the acid is removed from beech by the alkaline treatment, and this is confirmed by the observation that nothing further can be extracted by a fresh treatment. In the skeleton substance, the acid is regarded as present in esterified form. Further treatment with more concentrated alkali hydroxide causes the removal of the pentosans, so that by using alkali hydroxide of different concentrations it is possible to determine separately the polymeric acids and the acid-free pentosans. Pine does not suffer loss in weight when treated with $N/10$-alkali, although titration discloses the formation of acid. With 5% alkali hydroxide, acid and hemicelluloses are simultaneously removed, so that a more stable union of acid and hemicellulose in pine than in beech must be assumed. The behaviour of oxycellulose is similar to that of pine. H. WREN.

Cell respiration. V. Mechanism of some plant oxidations. A. VON SZENT-GYORGYI (Biochem. Z., 1927, **181**, 425—432).—The fruits, tubers, or roots of thirteen plants are divided by means of the guaiacum reaction into three groups, first, those which blue guaiacum directly, secondly, those which give only a blue colour after adding also pyrocatechol, and thirdly, those which do not blue guaiacum even in presence of pyrocatechol. The results are discussed in relation to the constitution of the plant oxidation systems. The browning of slices of plants in air is conditioned by the presence of tyrin, which, as with guaiacum, is not directly oxidised by the oxydase, but only by the *o*-quinone arising by the action of the oxydase. P. W. CLUTTERBUCK.

Plant oxidation: nature and reactions of the substance "tyrin." B. S. PLATT and A. WORMALL (Biochem. J., 1927, **21**, 26—30).—The oxidative properties of the preparation "tyrin" of Szent-Gyorgyi (A., 1926, 99) are due to the presence in it of free or combined amino-acids. It does not function as a respiratory pigment. The ether extract of potato oxydase after it has acted on a pyrocatechol solution for 10 min. yields a substance which gives a blue coloration with guaiacum and benzidine. Hydrogen peroxide is formed in addition to this oxidation product. This confirms Szent-Gyorgyi's hypothesis (*loc. cit.*) of the mechanism of the blueing of guaiacum by the pyrocatechol–oxydase system (cf. Onslow and Robinson, A., 1926, 1176).

S. S. ZILVA.

Relationship between catalase activity and seed vitality. M. GRACANIN (Biochem. Z., 1927, **180**, 205—210).—Further determinations of the catalase activity of seeds (cf., A., 1926, 432) show that the catalase content cannot always serve as an index of the vitality of a plant. The catalase activity of *Pisum sativum*, *Lupinus angustifolius*, *Zea mays*, and *Triticum vulgare* decreases with age, and etiolated leaves of *Beta vulgaris*, *Juglans regia*, and *Althæa officinalis* contain but little catalase compared with green leaves. On the other hand, both green and etiolated leaves of *Papaver somniferum*, *Daucus carota*, and *Sinapis alba* contained the same amount of catalase. Leaves of *Mnium undulatum*, *S. alba*, *P. sativum*, *Secale cereale*, and *Medicago sativa*, dipped in distilled water, 0·05*M*-sodium chloride, or 0·001*M*-zinc sulphate showed high catalase activity, in 0·001*M*-copper sulphate a less activity, and in 0·001*M*-ferric chloride or iodine no activity. It appears, therefore, that concentrations of sodium chloride and zinc sulphate which can kill these plants have but little effect on their catalase activity. P. W. CLUTTERBUCK.

Effect of juice of potato-tubers on biological reduction of o-dinitrobenzene. A. PIETSCH (Biochem. Z., 1927, **181**, 183—191).—The reduction of *o*-dinitrobenzene by potato-tubers themselves, by the higher plants, and by the muscles of animals, is inhibited by the juice of potato-tubers, whilst the reduction by yeast and by bacteria is stimulated by the tuber juice. The reduction by yeast is stimulated by 5% dextrose, whilst that by potato-tubers is inhibited by 5—10% dextrose; the dextrose content of the tuber juice may therefore account for its effect on the reduction. The reduction is, in general, retarded by 0·1% of camphor and completely inhibited by 0·1% of mercuric chloride.

C. R. HARINGTON.

Yield of carbon compounds in photosynthesis under natural conditions. S. KOSTYTSCHEV, K. BAZYRINA, and G. VASSILIEV (Biochem. Z., 1927, **182**, 79—87).—The method of investigating photosynthesis in a stream of atmospheric air suffers from the disadvantage that the velocity of the air current in relation to the leaf surface and the capacity of the leaf container is too low. This is regarded as explaining the discrepancies between the amount of photosynthesis as observed in the above methods and in the indirect method (Blatthalftenmethode of Sachs, Arb. bot. Inst., Wurzburg, 1884, **3**, 1). With increase in the velocity of the air-stream, increasing synthesis is observed, rising eventually to the high values obtained by the indirect methods. J. PRYDE.

Influence of potassium and sodium salts on the metabolism of reserve materials in young barley plants grown in darkness. A. BOBROWNICKA-ODRZYWOLSKA (Bull. Acad. Polonaise, 1925, *B*, 801—846).—Utilisation of the reserve materials of the seed by young barley plants has been studied by comparing the composition of the seed with that of plants grown in darkness to the point of exhaustion of the reserve materials, in culture solutions without nitrogen, and with and without sodium and potassium. In presence of potassium, a smaller amount of carbohydrate is required for the formation of a unit of cellulose. Sodium has a similar effect if accompanied by other necessary mineral salts. Potassium also reduces the loss of organic matter and the percentage of starch decomposed for respiration processes. The young plants made poorer growth in pure potassium or sodium chloride solutions than in distilled water; none the less, in pure potassium chloride solution, a smaller percentage of starch was decomposed for respiration than in distilled water. Plants grown in solutions of mineral salts including potassium always contained more nitrogen than when potassium was withheld. In pure potassium or sodium chloride solutions, there was a greater loss of "unidentified" material, but no greater loss of nitrogen, than in the other culture solutions. C. T. GIMINGHAM.

Nitrate utilisation by asparagus in the absence of light. G. T. NIGHTINGALE and L. G. SCHERMERHORN (Science, 1926, **64**, 282).—Quantitative experiments indicate that asparagus can take up nitrates in the dark, and that so long as there is a carbohydrate supply present, plants are able to build up nitrates to higher forms of nitrogen compounds. The assimilation of nitrates occurs as rapidly in the dark as in the light. A. A. ELDRIDGE.

Specificity of proteins in different rice varieties. T. TADOKORO (Proc. Imp. Acad. Tokyo, 1926, **2**, 498—501).—It is reported that samples of oryzanin prepared from common and from glutinous rice vary in isoelectric point, in nitrogen, sulphur, and phosphorus content, in free amino-nitrogen, in optical activity and refractive index, and in other ways. No experimental data are given. E. A. LUNT.

Bacterial decomposition of tobacco as leading to the formation of bases in presence of water. A. FAITELOWITZ (Biochem. J., 1927, **21**, 262—264; cf. Fodor and Reifenberg, A., 1925, i, 1519).—The formation of pyridine and amino-bases from nicotine with resulting basic reaction does not occur to any appreciable extent in the dry fermentation process. In presence of moisture, on the other hand, the decomposition of tobacco leads to a basic reaction. This change is most probably due to bacterial decomposition. S. S. ZILVA.

Relation of nitrates to tobacco frenching. W. D. VALLEAU and E. M. JOHNSON (Science, 1926, **64**, 278—279).—Frenching of tobacco plants appears to occur when the rate of carbohydrate metabolism proceeds relatively more rapidly than nitrogen absorption. Leaf-tissue is thus produced which, in the absence of sufficient available nitrogen, cannot sufficiently rapidly develop chlorophyll and other essential cell constituents; hence the new leaves of diseased plants are chlorotic.

A. A. ELDRIDGE.

Changes in fresh and dried tobacco leaves before and during fermentation. C. NEUBERG and M. KOBEL (Biochem. Z., 1926, **179**, 459—490).—In fresh tobacco leaves small quantities of acetaldehyde and ethyl alcohol are present. Treatment of the fresh leaves with steam liberates methyl alcohol from the pectic esters present. In a pulp of fresh leaves digested with calcium hydrogen sulphite the amount of acetaldehyde is considerably increased. Very active invertase, amylase, hexosediphosphatase, and aldehyde-mutase are present in a pulp of the fresh leaves. The last-mentioned enzyme converts phenylglyoxal into *l*-mandelic acid. Air-dried leaves and trade tobacco contain furoid substances in the form of pectins, and the fresh, dried, or fermented leaves all yield furfuraldehyde and carbon dioxide when treated with hydrochloric acid. The presence of uronic acids is inferred. Of the methyl alcohol which is liberated from fresh tobacco leaves, some 7—9% is present in the form of esters, the dried leaves contain some 30% more of the ester form than do fresh leaves, whilst dark (cigar) tobaccos contain only 1%, and light (cigarette) tobaccos 5—7%. In ungerminated tobacco plant seeds, phosphatase and aldehyde-mutase are present. It is concluded that a part of the carbohydrate exchange of the tobacco leaf is produced by self-contained agents. J. PRYDE.

Role of boron in the growth of plants. W. E. BRENCHLEY and K. WARINGTON (Ann. Bot., 1927, **41**, 167—187; cf. Warington, A., 1923, i, 1274).—The necessity of small quantities of boron for the growth of certain plants is evident in sand as well as in water cultures, and is independent of the composition and p_H value of the nutritive solution and of the conditions of aeration at the roots. Of 52 other elements tested, none proved capable of replacing boron for plants which require it. Boron is shown to be essential for a number of species of *Leguminosæ* and for melon, whereas various cereals and some other plants completed development in its absence. If the nutritive solution is frequently or continuously renewed, evidence of boron deficiency is considerably delayed and the total quantity required is lessened. The concentration, if not high enough to be toxic, appears to be of little importance. The boron is actually absorbed and does not act as an ordinary catalyst; it appears to be associated with absorption or utilisation of calcium.

C. T. GIMINGHAM.

Chemical stimulants of plant growth. A. ZLATAROFF (Bull Soc. Chim. biol., 1926, **8**, 1198—1207).—The effects of chlorides, oxidising and reducing compounds, amines, and uranyl acetate on plant growth are described. Seeds were immersed in a dilute solution of the compound to be tested and then allowed to germinate; in most cases a stimulating effect was observed. W. O. KERMACK.

Relation of leaf area to growth and composition of apples. M. H. HALLER and J. R. MAGNESS (Proc. Amer. Soc. Hort. Sci., 1925, 189—196).—A higher percentage of dry weight, sugars, and acids is associated with apples grown with a large leaf area as compared with those of the same variety grown with a small leaf area. CHEMICAL ABSTRACTS.

Carbon dioxide nutrition of the forest. D. FEHER (Biochem. Z., 1927, **180**, 201—204).—The carbon dioxide content of the air in woods, being conditioned by the simultaneous respiration of the soil, decreases from the soil upwards and is considerably influenced by the acidity of the soil; the greater the acidity, the greater the effect on soil bacteria and the lower the soil respiration and carbon dioxide content of the air. The optimal soil respiration and carbon dioxide content of the air are obtained during rainy periods.

P. W. CLUTTERBUCK.

Respiration processes in different varieties of potatoes. K. G. SCHULZ (Landw. Versuchs-Stat., 1926, **105**, 23—73).—The rate of uptake of oxygen by tubers of late varieties of potatoes was greater than in early varieties. Absorption of oxygen remained fairly steady over a period of 3 months. Individual tubers of the same variety showed considerable variation in respiratory activity. The rate of elimination of carbon dioxide from the leaves of growing potato plants per unit surface exposed was greater for late than for early varieties. Respiration was irregular, but appeared to bear a relationship to the rate of development of leaf-surface. A general uniformity existed between the rate of oxygen uptake by the tubers and the rate of carbon dioxide elimination from the leaves of different varieties. No relationship was apparent between the intensity of the respiratory changes and the size and number of sprouts developing from the tubers.

A. G. POLLARD.

Water-soluble content of calcium and phosphorus in cabbage. W. H. PETERSON and C. B. PETERSON (J. Agric. Res., 1926, **33**, 695—699).—In samples of cabbage grown on two types of soil, the average percentage of calcium in the fresh material was 0·046, and of phosphorus, 0·028; 60% of the total calcium and 61% of the total phosphorus were soluble in water. The proportion of water-soluble calcium and phosphorus decreased as the plants matured. C. T. GIMINGHAM.

Ether-soluble substances of cabbage-leaf cytoplasm. I. Preparation and general characters. II. Calcium salts of glyceride-phosphoric acids. A. C. Chibnall and H. J. Channon (Biochem. J., 1927, **21**, 225—232, 233—246).—I. The minced leaves are extracted with water and the aqueous extract is coagulated by heating at 70°. The residue is then pressed out in a Buchner press until no more liquid is expressed and extracted with ether for 40 hrs. The crude extract is evaporated to dryness in a vacuum and extracted again with dry ether. The fat constants of several such preparations from cabbage leaves are given.

II. On adding acetone to an ethereal solution of the ether-soluble substances of the cytoplasm from the leaf cells, no phospholipins are precipitated. All the phosphorus of this fraction is present in combination with calcium, glycerol, and fatty acids. Nitrogen is virtually absent. The main constituent was identified as the calcium salt of a *diglyceridephosphoric acid*, which pre-exists in the leaf cell and is a product of phospholipin decomposition. The preparation and properties of the free acid (decomp. 100°) and of its *calcium*, *lead*, and *barium* salts are given. Since the acid on boiling with barium hydroxide yields an optically active barium glycerophosphate, it is concluded that the phosphoric acid is in the α-position. Indication of the possible presence of the calcium salt of a monoglyceridephosphoric acid has also been obtained. S. S. Zilva.

Myrosin and sinigrin. A. Heiduschka and C. Pyriki (Arch. Pharm., 1926, **264**, 692—698).—Guignard's method of extracting myrosin from white mustard seed is improved by carrying out the digestion at 40° instead of at 70°. The myrosin is precipitated from the aqueous extract by alcohol, and so is obtained in much higher yield and of considerably greater activity. The products were tested by their action on sinigrin and the allylthiocarbimide obtained was determined by the German official method. Myrosin can be purified by repeated reprecipitation from aqueous solution by alcohol, followed by dialysis; the product so obtained is nearly twice as active as the original material. The purified substance still contains 4·09% of ash; corrected for this, it has the composition C, 43·52%; H, 6·33%; N, 14·96%; S, 2·62%; P, 1·21%. A number of *Cruciferæ* have been examined touching their content of myrosin and sinigrin. *Brassica Rapa esculenta*, Koch, *Brassica Napus esculenta*, DC., *Cochlearia Armoracia*, L., *Raphanus sativus*, L., v. *niger*, DC, and *ibia*, v. *alba*, DC. all contain allylthiocarbimide and myrosin, but no sinigrin. The amounts vary according to the species, *Cochlearia* containing the most, both of enzyme and allylthiocarbimide. *Beta vulgaris* contains neither sinigrin nor myrosin. W. A. Silvester.

Soluble enzymes contained in black mustard (*Brassica nigra*, K.). A. Astruc and M. Mousseron (Compt. rend., 1927, **184**, 126—128).—Black mustard seeds are shown to contain, in addition to myrosin, easily detectable quantities of invertase, amylase, maltase, emulsin, and an anaerobic oxydase. Sucrose is present, but no raffinose or stachyose. C. Hollins.

Rubichloric acid and asperuloside. H. Hérissey (Bull. Soc. Chim. biol., 1926, **8**, 1208—1210; cf. Annalen, 1851, **80**, 321; A., 1925, i, 1369; 1926, 547).—Rubichloric acid obtained by Rochleder in an impure condition from madder root is considered very probably to be identical with the glucoside, asperuloside, which has been isolated from odoriferous *Asperula* and from *Galium Aparine*. W. O. Kermack.

Chemistry of oleander. H. Tauber and J. Zellner (Arch. Pharm., 1926, **264**, 608—693; cf. Straub, A., 1918, i, 368).—Air-dry oleander leaves contain a paraffinic *hydrocarbon*, $C_{34}H_{70}$, m. p. 70°, resembling that found in *Alchemilla* by Vogl (A., 1923, i, 990), together with fats the isolated acids of which form a mixture of m. p. 55—60° and acid value 190. These substances are soluble in light petroleum; the original treatment of the plant material with trichloroethylene also extracted an amorphous resin *compound* (C, 66·76%; H, 9·76%), m. p. 245° (decomp.), insoluble in light petroleum (amorphous *nitro*-derivative, decomp. 185°).

When the dry leaves are extracted with water, the chief product is a glucoside "Oleandrin-6." This compound (cf. Straub, *loc. cit.*) crystallises in prisms and has the composition $C_{24}H_{34}O_7$, m. p. 230° (in a sealed tube filled with carbon dioxide). It gives the reactions of digitalis strongly; it is not hydrolysed by emulsin, but when treated with sulphuric acid (0·5%) it is resolved into a brown, resinous *compound* and an unidentified dextrorotatory sugar which reduces Fehling's solution but neither yields glucosazone nor gives the reactions of a pentose.

"Oleandrin-4" (Böhringer & Söhne) was not isolated in the above extraction of oleander leaves, but is obtained by this firm by a method of which a description is given. It differs from "Oleandrin-6" in being insoluble in a mixture of ether and alcohol, also in crystal form and composition; thus it forms leaflets of m. p. 224–225° (in sealed tube) and has the composition $C_{33}H_{46}O_8$ or This difference from "Oleandrin-6" is not due to water or alcohol of crystallisation. Moreover, whereas "Oleandrin-6" is decomposed when heated with acetic anhydride, "Oleandrin-4" yields a (*tri-* or *tetra-*)*acetyl* derivative (m. p. 210°). The mother-liquors of the above separation yield a mixture (m. p. 98—120°) which may or may not contain a third glucoside of the same group. Besides the above compounds, oleander leaves contain tannin-like substances. W. A. Silvester.

Plant chemistry. XVII. *Rhododendron hirsutum*. E. Feyertag and J. Zellner (Monatsh., 1926, **47**, 601—609).—The leaves of *Rhododendron hirsutum* have been examined by the usual methods. The light petroleum extract on hydrolysis with alcoholic potassium hydroxide yields a portion not hydrolysed from which were isolated a *hydrocarbon*, m. p. 65°, a *resin alcohol*, m. p. 226—227°, and a *substance* $C_{30}H_{52}O$, m. p. 205°, $[\alpha]_D$+63·9° (in chloroform), which could not be acetylated, and for which full crystallographic data are given. Acidification of the hydrolysed portion gave only resin acids. The small ether extract gave a *substance*, m. p. 234°. The

water-soluble portion of the alcohol extract yielded a tannin which on treatment with 3% sulphuric acid in a current of carbon dioxide gave a phlobaphen, the analytical data for both, however, not agreeing with that of Rochleder and Schwarz ("Phytochemie," 1854, p. 168). The water-insoluble portion yielded a natural phlobaphen, invert-sugar, and choline. Distillation of the leaves with steam yields an oil, d^{21} 0·8780, n_D^{20} 1·4807, $[\alpha]_D$ −29·0° (in ether), which consists, in all probability, of the *hydrocarbons* $C_{10}H_{18}$ and $C_{10}H_{16}$. J. W. Baker.

Plant chemistry. XV. Chemistry of barks. V. J. Zellner [with K. Knie, E. Rosenbluh, M. Stein, and J. Richling] (Monatsh., 1926, 47, 659—679).—The light petroleum extract (2·10%) of the bark of *Acer pseudoplatanus*, L., contains ceryl alcohol and an inactive phytosterol similar to that of elm-bark (A., 1926, 646), but differing from it in crystalline form. On hydrolysis, the saponifiable material yields glycerol and palmitic, stearic, arachidic (?), and phosphoric acids. Hydrolysis of the ether extract (0·94%) gives resin acids, ceryl alcohol, and a *resin alcohol*, $C_{32}H_{54}O_3$, m. p. 175—176°, but no octadecyl alcohol (cf. A., 1924, i, 814). The alcohol extract (11·50%) contains phlobaphens, tannin (3·47%), and invert-sugar. The water-soluble matter (20·66%) contains mineral matter (3·10%). Free acid (as KOH), 1·23%; soluble polysaccharides, 0·69%; crude fibre, 50·50%; pentosans, 11·39%; total ash, 10·54%; and total nitrogen, 1·99%, are also present.

The unsaponifiable portion of the light petroleum extract of *Crataegus oxyacantha*, L., contains compounds (*a*), m. p. 75°, probably impure ceryl alcohol, and (*b*), m. p. 212°, [α]+25° (acetyl derivative, m. p. 216°), probably identical with lupeol (A., 1922, i, 826); the saponifiable fraction contains stearic and palmitic acids. The ether extract yields, on hydrolysis, alnuresinol (*loc. cit.*), a *substance*, $C_{26}H_{44}O_2$(?), m. p. 170°, and a substance, $C_{22}H_{38}O_3$, m. p. 278°, previously obtained from lime-bark (A., 1926, 983), together with amorphous resin acids. The bark also contains phlobaphens, pyrocatechol-tannins, invert-sugar, water-soluble polysaccharides, oxalates, and tartrates.

The bark of *Pavia rubra*, Lam., yields: light petroleum extract, 3·91%; ether extract, 2·53%; alcohol extract, 18·46%; water-soluble matter, 28·94%; soluble polysaccharides, 2·33%; free acid (as KOH), 3·23%; reducing sugar, 2·67%; soluble mineral matter, 0·54%; total ash, 5·83%; total nitrogen, 1·96%; crude fibre, 30·22%. The light petroleum extract contains a *hydrocarbon*, m. p. 74°, ceryl alcohol, almost pure sitosterol, and saponifiable matter which yields myristic and oleic acids. The alcohol extract contains phlobaphens, tannins, aesculin, and dextrose. Enzymes were present in the cold aqueous extract.

The water-soluble portion of an alcoholic extract of the bark of *Picea excelsa*, Lk., contains tannins and invert-sugar. The insoluble portion, freed from terpenes by steam distillation, contains an *ester* (?), m. p. 116°; ceryl alcohol, and a *substance*, m. p. 70—71°. Arachidic acid and smaller amounts of palmitic and stearic acids are present, principally as glycerides. The large resin acid fraction contains a small quantity of a *substance*, m. p. 105—107°. Sterols appear to be completely absent. H. E. F. Notton.

Chemistry of halophytes. J. Zellner (Monatsh., 1926, 47, 611—618).—Complete analyses of the mineral matter present in various plants which grow in soils containing more salts than is usual have been carried out. The following summary gives, respectively, the water content, amount of mineral matter in the fresh plant and in the dried plant, for the examples studied: *Salicornia herbacea*, 76·58, 5·02, 21·42; *Suæda salsa*, 75·94, 5·74, 23·86; *Scorzonera parviflora*, 86·98, 2·23, 16·98; *Plantago maritima*, 80·46, 2·85, 14·58; *Aster Tripolium*, 73·15, 2·80, 10·43; *Erythræa tinariæfolia*, 61·87, 1·65, 4·32%. Determination of the osmotic pressure in the cells by the depression of the f.-p. method shows that this is exceedingly high, the value for *Salicornia* being 35 atmospheres, and for *Aster*, 16·4 atmospheres. J. W. Baker.

Philippine ginger. P. Valenzuela (J. Amer. Pharm. Assoc., 1926, **15**, 652—661, 734—744).—Fresh specimens of *Zingiber officinale* Roscoe contained: moisture 79·5, 80%; ash 6·29, 6·10%; acid-insoluble ash 2·3, 2·4%. The cortex was the most pungent and the parenchyma the least. The volatile oil had: acid value 2·22, ester value 32·8, ester value after acetylation 88·3. Aldehydes were present, but phenols were absent; a semicarbazone, m. p. 144—145°, was obtained. The residue after distillation with steam had d^{20} 1·0694, saponification value 41·41. From the fatty acids, oleic, linoleic, and stearic acids were obtained. A small quantity of vanillyl alcohol was obtained; the presence of melissyl alcohol was suggested. About 0·14% of dextrose was isolated. Chemical Abstracts.

Histochemical detection of santonin. E. Herndlhofer (Mikrochem., 1927, **5**, 21—26).—For the detection of santonin in parts of a plant, the crushed substance is extracted with a few c.c. of benzene under a reflux condenser and the filtered extract is evaporated to dryness. The residue is heated in the Klein-Werner sublimation apparatus and the sublimate is again extracted with benzene. In the presence of santonin evaporation of this solution yields yellow columnar crystals (m. p. 171°); these crystals yield characteristic greenish-brown cubes or plates (m. p. 113°) when treated with hydriodic acid containing iodine. Of the varieties of *Artemisia* tested only *A. cina* Berg and *A. cæresculens* contained santonin in the flowers and seeds. A. R. Powell.

Kirondrin, toxic principle from seeds of *Perriera madagascariensis* (*Simarubaceæ*). Volmar and Samdahl (Compt. rend., 1927, **184**, 393—395).—*Kirondrin*, the bitter, toxic principle of seeds of *Perriera madagascariensis*, is extracted by alcohol and occurs to the extent of 0·75% in the seeds; α- and β-kirondrin, m. p. 220—221° and 237—240°, respectively, have been isolated by fractional crystallisation and are similar in properties. The principle contains no nitrogen, sulphur, or halogen, but gives alkaloidal reactions, reduces Fehling's reagent, but does not give a phenylhydrazone, even after hydrolysis.

Subcutaneous injection of 4 mg. produces death of mice in 10 hrs. L. F. HEWITT.

Pine wood lignin. E. HAGGLUND and T. ROSENQVIST (Biochem. Z., 1926, **179**, 376—383).—Lignin prepared by the action of hydrochloric acid on pine wood, when distilled with 12% hydrochloric acid, yields about 3% of a volatile substance, similar to, but distinct from, furfuraldehyde, methylfurfuraldehyde, and hydroxymethylfurfuraldehyde. The usual methods for determining pentosans in lignins therefore give high results. Lignin prepared by alkali treatment also yields on distillation with hydrochloric acid, in addition to furfuraldehyde, volatile substances forming phloroglucides. Lignosulphonic acid precipitated by β-naphthylamine yields no substances which condense with phloroglucinol. Neither pine wood nor the lignin prepared from it contains methylpentosans. Friedrich's primary lignin contains ethoxyl groups. Lignin yields but small quantities of vanillic acid or vanillin. J. PRYDE.

Origin of humic matter. C. E. MARSHALL and H. J. PAGE (Nature, 1927, **119**, 393).—The view that humic matter is derived from lignins is supported. By means of aqueous sulphur dioxide under pressure, a true fractionation of humic and hymatomelanic acids of natural origin is effected; the substances dissolved are closely analogous to the lignosulphonic acids obtained from wood pulp. The close relationship between natural humic acids and lignins may, however, be due to the presence of unchanged lignins in natural humic acid preparations. A. A. ELDRIDGE.

Source of trilaurin: Mahuba seed, *Acrodiclidium Mahuba*, A. J. Sampaio. E. ANDRE (Compt. rend., 1927, **184**, 227—229).—Extraction of the seed with light petroleum and crystallisation of the crude product from ether yields trilaurin (45—50% of the weight of the seed). J. W. BAKER.

Distribution of dihydrositosterol in plant fats. R. J. ANDERSON, F. P. NABENHAUER, and R. L. SHRINER (J. Biol. Chem., 1927, **71**, 389—399; cf. A., 1924, i, 1153).—Dihydrositosterol has been isolated from the unsaponifiable matter of the oils from rice bran, maize, and wheat germ, but not from cotton-seed or linseed oils. The various preparations had m. p. 141—146°, $[\alpha]_D$ +23—25°; the *acetyl* derivative had m. p. 137—141°, $[\alpha]_D$ +13—14°. C. R. HARINGTON.

Distribution of saponins and tannins in plants. G. LUFT (Monatsh., 1926, **47**, 259—284).—An investigation of the occurrence of saponins, tannins, and other pharmaco-dynamic materials in the leaf, stem, and bark of the members of various families of plants. W. ROBSON.

Nutrition and statistical variations. IV. Chemical properties of various sorts of wheat. L. BERCZELLER and H. WASTL (Biochem. Z., 1927, **181**, 117—132).—Statistical comparison of the variations in content of protein, cellulose, fat, and ash of different wheats over a period of 5 years indicates, in general, that the nature of the season has a greater influence than the species in determining the chemical composition of wheat. As between the different species of wheat, the greatest variations were observed in the content of cellulose and the least in that of fat. C. R. HARINGTON.

Potential differences in the apple. L. JOST (Biochem. Z., 1926, **179**, 400—409).—Electro-potential concentration effects are observed in living and dead apples. In the former instance, the cell protoplasm forms the best membrane; in the latter, the cell membrane of the parenchymatous cells and the cuticle. Beutner's views are criticised. J. PRYDE.

Digestion of starch in vegetable cells. A. MAIGE (Compt. rend., 1927, **184**, 391—393).—Two modes of digestion of starch grains in vegetable cells, viz., peripheral and internal, are ascribed to the existence of stromata. In peripheral digestion, the amylase remains on the edge of the starch granule, whilst in internal digestion either the amylase penetrates the cortex or else the cortex is already destroyed. Heating at 55—60° destroys the vitality of the stroma and converts peripheral into internal digestion. L. F. HEWITT.

Effect of eosin on the growth of roots. F. BOAS (Ber. deut. bot. Ges., 1927, **45**, 61—64).—Seeds of *Sinapis alba*, *Lupinus luteus*, *L. angustifolius*, *Vicia faba*, and *Zea mays* after being soaked for 17 hrs. in solutions of eosin (0·1, 0·01, and 0·001%, respectively) were planted in soil. On germination of the seeds, the roots grew at first perpendicularly out of the soil. G. W. ROBINSON.

Colorimetric micro-determination of iron. L. LORBER (Biochem. Z., 1927, **181**, 391—394).—A micro-colorimetric method for the determination of iron in tissues, based on the yellow colour obtained with iron, sulphosalicylic acid, and excess of ammonia, is described and used to determine both inorganic and organically bound iron. P. W. CLUTTERBUCK.

Colorimetric determination of silicon in tissues by Isaacs' method. J. H. FOULGER (J. Amer. Chem. Soc., 1927, **49**, 429—435).—The work of Isaacs (Bull. Soc. Chim. biol., 1924, **6**, 157) is confirmed. The reduction of silicomolybdates by sodium sulphite is retarded by a sufficiently high concentration of phosphate; when this concentration is low (*e.g.*, in the ash from animal tissue) this inhibition may be prevented by slightly increasing the acidity of the system (cf. Bertrand, *ibid.*, 656). S. K. TWEEDY.

Gasometric micro-Kjeldahl determination of nitrogen. D. D. VAN SLYKE (J. Biol. Chem., 1927, **71**, 235—248).—The nitrogenous material is incinerated with a mixture of sulphuric and phosphoric acids and potassium persulphate; the resulting solution is neutralised, transferred to the apparatus of Van Slyke and Neill (A., 1924, ii, 872), and treated with sodium hypobromite; the liberated nitrogen is determined gasometrically. The error of the method is ±1%. C. R. HARINGTON.

Apparatus for rapid dialysis. L. AMBARD (Bull. Soc. Chim. biol., 1926, **8**, 1219—1221).—An apparatus is described in which dialysis can be carried out much more rapidly than with a simple collodion sac. W. O. KERMACK.

BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

MAY, 1927.

General, Physical, and Inorganic Chemistry.

Excitation of spectra by atomic hydrogen. F. L. MOHLER (Physical Rev., 1927, [ii], 29, 419—425).—When hydrogen from a Wood discharge tube is passed into a tube containing the metallic vapour, sodium and cadmium strongly emit their first resonance lines, potassium faintly emits the first resonance doublet, mercury gives the complete hydride spectrum and faint emission of the line 2537 Å., cæsium, magnesium, thallium, and zinc give no line spectra. Atomic hydrogen is evidently formed, but it is considered that two atoms cannot radiate away the energy of recombination, the presence of a third substance being necessary. A three-body collision of two hydrogen atoms and a metal atom may accomplish this, with excitation of the metal atom, or a metal hydride may first be formed, yielding a hydrogen molecule and an excited metal atom in a two-body collision with a hydrogen atom.

A. A. ELDRIDGE.

Relativistic fine structure of spectral lines. F. PASCHEN (Ann. Physik, 1927, [iv], 82, 689—696).—Leo (this vol., 82) found the value 0·3459 cm.$^{-1}$ for $\Delta\nu_H$ for the 4686 He II line, whereas on the basis of Sommerfeld's theory the value 0·3647 cm.$^{-1}$ was to be expected, and is now actually observed within the limits of error. The author's earlier measurements (Ann. Physik, 1916, [iv], 50, 913) are shown to be in agreement with theory in regard to wave-length. Leo's work with reference to the 3203 line is discussed.

R. A. MORTON.

Some infra-red spectra. H. G. SMITH and (MISS) M. E. WESTMAN (Trans. Roy. Soc. Canada, 1926, [iii], 20, III, 323—325).—The spectrum of beryllium has been studied from 4000 to 10,500 Å. and that of gold from 7000 to 10,500 Å., using a spark source. Some new air lines of wave-length greater than 8000 Å. have also been observed.

R. CUTHILL.

Structure of arc spectra of germanium and carbon. J. C. MCLENNAN and A. B. MCLAY (Trans. Roy. Soc. Canada, 1926, [iii], 20, III, 355—363).—The Ge I spectrum has been analysed from the point of view of the Heisenberg–Hund theory by the method previously described (A., 1926, 874), and its structure found to be similar to those of the arc spectra of silicon, tin, and lead, as Bohr's arrangement of the periodic table would require. The C I spectrum is also apparently of the same type.

R. CUTHILL.

Spectrum of the third order of oxygen. C. MIHUL (Compt. rend., 1927, 184, 874—875; cf. this vol., 177).—Five new multiplets, ($^3D'$—$^3P'$), ($^3D'$—D), (a^3D—$^3D'$), (a^3P'—$^3D'$), and (a^3P'—a^3P), have been discovered in the third order spectrum of oxygen, and are described.

J. GRANT.

Red and blue argon spectra in extreme ultra-violet. H. B. DORGELO and J. H. ABBINK (Z. Physik, 1927, 41, 753—768).—The red and blue spectra of argon between 1800 and 400 Å. have been examined with a vacuum spectrograph. The results are discussed in relation to theory and to other experimental results.

W. E. DOWNEY.

Measurements of the *P.D.* between the positive strata [in a discharge tube] of argon and neon. F. M. PENNING (Z. Physik, 1927, 41, 769—774).—The *P.D.* between stationary positive strata in argon and neon is almost independent of the pressure of the gas and of the current strength. The value of the difference for argon was found to be 11·9 volts, approximately the excitation potential of the 1*s* state, whilst for neon it is 18·5 volts, approximately the excitation potential of the 2*p* state. The *P.D.* between moving positive strata in argon is proportional to the current strength.

W. E. DOWNEY.

Spectrum of doubly-ionised scandium. S. SMITH (Proc. Nat. Acad. Sci., 1927, 13, 65—67).—Twelve lines between 730 and 4070 Å. in the Sc III spectrum are given, together with their intensities, wave-numbers, separations, and term combinations. Assuming for 4*F* the value 62,570, which is suggested by the values of the 4*F* terms of K I and Ca II, term values have been calculated. It is concluded that the lines 2012 and 1993 Å., which were considered by Gibbs and White (A., 1926, 1185) as $4^2P_{1,2}$—5^2S_1, together with the line 2011, form a triplet in which the line 2012 is the satellite of the strongest member 2011. The triplet at 2011 is considered to be the first normal member of the diffuse series of Sc III.

J. S. CARTER.

Multiplets in two-electron systems of the first long period. R. C. GIBBS and H. E. WHITE (Physical Rev., 1927, [ii], 29, 426—432).—Multiplets appearing when an electron in a 4*p* orbit jumps to a 4*s* orbit in the presence of another valency electron in a 3*d* orbit have been observed for V IV and Cr V, and the wave-lengths of the lines have been measured. The regular and irregular doublet laws hold fairly accurately for two-electron systems when one of the electrons jumps between two orbits, *p* and *s*, having the same total quantum number.

A. A. ELDRIDGE.

Spark spectrum of copper (Cu II). A. G. SHENSTONE (Physical Rev., 1927, [ii], 29, 380—390).—The spark spectrum of copper consists of a set of

terms ^3D and ^1D from the electron structure (d^9s), the letters denoting the k-values of the orbits and the indices the numbers of electrons, only the last eleven being given, since the others remain in closed groups; a set ^3P, $^3D'$, ^3F, ^1P, $^1D'$, ^1F due to the configuration (d^9p); a set ^3D, ^1D, from the configuration (d^9,s), the notation indicating that the s-electron is in an excited level; and probably ^1S (d^{10}). All but the last have been identified. The value of ^1S is about 22,224 wave-numbers lower than $^3D_3$. A comparison is made with corresponding terms in Ni I and Pd I. An ionisation potential for Cu II is computed to be about 20·5 volts.

A. A. Eldridge.

Arc spectrum of zinc. N. K. Sur (Z. Physik, 1927, 44, 791—793).—The absorption spectrum of zinc measured by Zumstein (A., 1926, 453) is explained in terms of Hund's theory of spectra.

W. E. Downey.

Spectra of doubly-ionised gallium and indium. K. R. Rao (Proc. Physical Soc., 1927, 39, 150—160).

Investigation of the second spark spectra of indium and gallium has been extended for long wave-lengths. The spark spectra of the elements in hydrogen and in air under different conditions of excitation were studied, and lines corresponding with the second series in the spectra of doubly-ionised indium and gallium identified. The results obtained are in excellent accord with the quantum theory of spectral line emission. C. J. Smithells.

Spectrum of ionised tin (Sn III). K. R. Rao (Proc. Physical Soc., 1927, 39, 161—168).—A search for regularities in the spectrum of Sn III has been made. Varying conditions of excitation revealed a strong triplet at 5100. The detection of two more triplets confirms this identification. A member of the first fundamental series was also found with the aid of the corresponding members in In II and Ga II (see preceding abstract). C. J. Smithells.

Arc and spark spectra [of yttrium, zirconium, lanthanum, cerium, neodymium, and beryllium] in the lower quartz spectral region. (Miss) M. C. McDonald, (Miss) E. E. Sutton, and A. B. McLay (Trans. Roy. Soc. Canada, 1926, [iii], 20, III, 313—322). The arc and spark spectra of the above elements in the region between 1850 and 2300 Å. have been investigated and the results tabulated. Most of the important wave-lengths are apparently in the visible region of the spectrum. R. Cuthill.

Arc and spark spectra of rare elements in the fluorite region. J. C. McLennan and M. J. Liggett (Trans. Roy. Soc. Canada, 1926, [iii], 20, III, 377—383). The arc and spark spectra of yttrium, niobium, lanthanum, cerium, neodymium, praseodymium, beryllium, scandium, and gold in the fluorite region have been investigated and the results obtained tabulated. R. Cuthill.

Flash arc spectrum of cæsium. F. H. Newman (Phil. Mag., 1927, [vii], 3, 843—848).—With an applied potential of 100 volts and at a pressure less than 10^{-4} mm., an intermittent arc could be struck between iron electrodes. The radiation obtained contained none of the iron lines, and in addition to the ordinary arc spectrum of cæsium showed 149 lines between 6648 and 2267·8 Å. All these lines, with the exception of those at 6648, 6078, 5845, 5664, 5102, 5086, 4622 Å., and some very faint lines are included in the induction spectral lines observed by Dunoyer (A., 1922, ii, 729). The spectrum also includes all the lines found by Mohler (A., 1926, 877) to be excited at 24 volts. The flash arc spectrum can be divided into two groups. The first group extends from 5400 to 3780 Å., contains practically all the first spark spectral lines, and has an optical centre at 4350 Å. It is much more intense than the second group, which extends from 3700 to 2268 Å., and contains many lines of a second spark spectrum found by Mohler to be excited between 40 and 80 volts. The two groups are analogous to the two different types of xenon arc spectra, and point to a similarity in structure between the singly-ionised cæsium and the normal xenon atoms.

A. E. Mitchell.

Fine structure of the spark spectrum of cæsium. A. Filippov and E. Gross (Z. Physik, 1927, 42, 77—80).—The fine structure of the following cæsium lines has been determined: 5371, 5274, 5249, 5227, 4953, 4830, 4604, and 4527 Å.

R. W. Lunt.

New lines in the arc spectrum of europium at normal pressure between 3100 and 2200 Å. S. Pina de Rubies (Anal. Fís. Quím., 1927, 25, 47—51; cf. this vol., 82).—A description of the arc spectrum of europium at normal pressure between the above limits, including some new lines.

G. W. Robinson.

Arc spectrum of gadolinium. Measurements made at normal pressure between 3100 and 2200 I.Å. S. Pina de Rubies (Compt. rend., 1927, 184, 593—596).—A list of 250 new lines found in the arc spectrum of gadolinium oxide is given, with their intensities. J. Grant.

Radiations of mercury, krypton, and xenon from the point of view of their meteorological applications. A. Pérard (Compt. rend., 1927, 184, 681—683; cf. this vol., 285).—Exact measurements of the wave-lengths of the most intense rays in the spectra of mercury, krypton, and xenon have been made with the object of enabling them to be used for meteorological purposes. Correction curves have been constructed as for neon and helium (*loc. cit.*). The wave-lengths measured (in mμ) are as follows: mercury, 435·8325, 491·60686, 546·07430, 576·95996, 579·06638; krypton, 557·02892, 587·09154; xenon, 462·4275, 467·1225, 473·4154. For xenon, the rays were feeble, and situated in a portion of the spectrum to which the eye is insensitive. J. Grant.

Arc spectrum of lead. N. K. Sur (Phil. Mag., 1927, [vii], 3, 736—739).—An explanation of the arc spectrum of lead from the point of view of Hund's theory of complex spectra. A. E. Mitchell.

X-Ray spectrometer with which wave-lengths are read directly on an ordinary micrometer screw. W. W. Nicholas (J. Opt. Soc. Amer., 1927, 14, 61—70; cf. A., 1926, 215).—The accuracy and some details of construction of the instrument are discussed. L. F. Gilbert.

Selective displacement of 0·0153 Å. in *X*-ray spectral lines. III and IV. F. H. LORING (Chem. News, 1927, **134**, 130—131, 193—194).—III. Explanatory.

IV. In view of the different values recorded for the Cu $K\beta_1$ line, revised tables have been prepared showing the deviations of certain *X*-ray spectral lines of a number of the elements from the values calculated on the basis of a selective displacement of 0·0153 Å., or a multiple of this, from a standard *x*-value (cf. this vol., 87, 287). M. S. BURR.

Chemical constitution and *K* absorption spectra. IV. Chloro-compounds. O. STELLING (Ber., 1927, 60, [*B*], 650—655; cf. A., 1924, ii, 139; 1925, ii, 935, 936).—Determinations are recorded of the *X*-ray *K* absorption spectra of lithium, sodium, potassium, rubidium, cæsium, cuprous, silver, ammonium, magnesium, calcium, strontium, barium, manganese, ferrous, nickel, cerium, cobalt, and cupric chlorides, of a series of cobalt and chromium ammines, and of the chlorates and perchlorates of sodium and potassium. Attention is directed to the characteristic effect of water of crystallisation and to the different action of ionic and non-ionic chlorine. The results are interpreted in accordance with the deformation theory. H. WREN.

Intensity dissymmetry for the Stark effect in hydrogen. R. WIERL (Ann. Physik, 1927, [iv], 82, 563—575).—The long-wave and short-wave components in the hydrogen Stark effect exhibit intensity differences which are reversed when the field is reversed both with moving hydrogen particles and with "stationary" hydrogen excited by means of nitrogen canal-rays. In the same field, the intensity difference of the components in the "stationary" emission is the reverse of that found in the "moving" light. To explain these results, it is assumed that the emission centres of the long-wave and short-wave components are on different sides of the nucleus of the atom and that the orientation depends on the electric vector. The components of the emission from retarding hydrogen are symmetrically resolved in the field, and although unequal intensities are observed if the canal ray is projected in nitrogen in a direction transverse to the field, a symmetrical resolution is obtained if the last few mm. of its trajectory occur in a high vacuum. R. A. MORTON.

Intensity dissymmetry for the Stark effect in hydrogen. F. G. SLACK (Ann. Physik, 1927, [iv], 82, 576—584).—An explanation of Wierl's work (preceding abstract) in terms of Schrödinger's wave-mechanics. R. A. MORTON.

Ionisation and resonance potentials in gallium and indium. C. W. JARVIS (Physical Rev., 1927, [ii], 29, 442—450).—Ionisation potentials (probably $\pm$0·5 volt) were observed in gallium vapour at 5·8 and 13·2 volts, and in indium vapour at 6·3 and 14·1 volts. Critical potentials below ionisation were observed in gallium vapour at 3·07, 4·22, 2·70, and 3·8 volts, and in indium vapour at 0·30, 3·03, 4·07, and 2·8 volts. A. A. ELDRIDGE.

Relation between ionisation potential and certain physico-chemical properties. N. PERRAKIS (J. Chim. phys., 1927, 24, 120—128).—The ionisation potential varies approximately inversely with the atomic radius, and thus also inversely with the cube root of the atomic volume, since the work required to remove the valency electron will diminish as its distance from the nucleus increases. A marked periodic relationship also exists between the ionisation potential and the atomic number; this also applies to the "atomic number" of some compounds, since hydrogen chloride, hydrogen bromide, and hydrogen iodide have ionisation potentials which are identical respectively with those of argon, krypton, and xenon, in agreement with the respective identity of atomic numbers. With the rare gases and oxygen and nitrogen, the ionisation potential diminishes as the critical temperature and pressure increase, since the work required to remove an electron decreases as the gas becomes further removed from the ideal state. For the same gases, the ionisation potential $V=28{\cdot}57e^{-0{\cdot}07147T}$, where T is the b. p. on the absolute scale, whilst for elements boiling between 200° and 2200° Abs., the relationship between T and V is linear. For elementary gases of n atoms per molecule, each having an ionisation potential V_i, the molecular ionisation potential V_m (*i.e.*, the *P.D.* necessary to remove one optical electron from the molecule) is given by $V_m=nV-D$, where D is the dissociation potential for the molecule. S. J. GREGG.

Photo-electric ionisation of mercury vapour. F. G. HOUTERMANS (Z. Physik, 1927, 41, 619—635).—The ionisation of saturated mercury vapour in the temperature range 19—170° (0·002—5 mm.) varies as the square of the intensity of the exciting radiation for the line 2537 Å. In the temperature range 65—150°, the addition of hydrogen greatly reduces the ionisation, the reduction being approximately 50% for a partial pressure of 10^{-2} mm. of hydrogen. The results are held to demonstrate a linear relationship between the ionisation and the number of mercury atoms in the 2^3P_0 state. R. W. LUNT.

Photo-electric properties of thoroughly outgassed platinum. L. A. DUBRIDGE (Physical Rev., 1927, [ii], 29, 451—465).—The photo-electric emission from platinum foil heated at 1200—1400° at 10^{-8} mm. decreased to a minimum value which could not be further reduced; this value is characteristic of the gas-free platinum. The long wave-length limit reached a final steady value of 1958$\pm$15 Å. The photo-electric effect is independent of the temperature only in the region below 500°. At higher temperatures up to 1200°, the photo-electric currents increase with rise of temperature, and the threshold shifts slightly towards the red. A. A. ELDRIDGE.

Photo-electric emission, thermionic emission, and Peltier effect from the point of view of dual electric conduction. E. H. HALL (Proc. Nat. Acad. Sci., 1927, 13, 43—46).

Comparison of the thermionic and photo-electric work functions for clean tungsten. A. H. WARNER (Proc. Nat. Acad. Sci., 1927, 13, 56—60).—The thermionic and photo-electric work functions for clean tungsten are identical within the experimental error. J. S. CARTER.

Electron scattering in helium. E. G. DYMOND (Physical Rev., 1927, [ii], 29, 433—441).—The velocity and angular distribution of electrons scattered by single collisions in helium have been measured. For initial velocities of not less than 100 volts, the principal energy loss is due to the excitation of the 2^1S state, corresponding with 20·5 volts. For still higher velocities, the energy change probably ceases to be quantised. A. A. ELDRIDGE.

Energy loss of slow electrons in collisions with molecules. W. HARRIES (Z. Physik, 1927, 42, 26—42).—An apparatus is described in which determinations with an estimated accuracy of 3% have been made of the energy loss suffered by electrons, of a velocity corresponding with 5·2 volts, in collisions with gas molecules. For a hundred collisions, the values 0·26 and 0·83 volt have been obtained for the energy loss in nitrogen and carbon monoxide, respectively. The values correspond with the absorption of one vibration quantum in 110 collisions in nitrogen, and with 31 in carbon monoxide; this result is to be anticipated from the fact that carbon monoxide has an electric moment and nitrogen has none. R. W. LUNT.

Cluster-formation in gas ions. W. BUSSE (Ann. Physik, 1927, [iv], 82, 697—712).—A detailed reply to Nolan's criticisms. R. A. MORTON.

Potential gradient in the positive column of the glow discharge. I. Nitrogen, hydrogen, neon. A. GÜNTHER-SCHULZE (Z. Physik, 1927, 41, 718—736).—The usual methods of examining the connexion between the gradient in the positive column of a glow discharge and the pressure of the gas fail to show any law. The two quantities are not connected. The mean free path l is taken as the variable, and is calculated from the measured pressure and from the partly measured, partly calculated rise in temperature of the discharge space. It is found, for a glow discharge in nitrogen or hydrogen, for constant l, that the gradient is independent of the current strength. In neon, for higher current densities, the gradient slightly decreases for increasing current strength. The equation, gradient $\propto 1/r^m$ where r is the radius of the tube, deduced on theoretical grounds, applies to all three gases. For nitrogen and hydrogen, $m=\frac{1}{2}$; for neon, $m=1$. Thus, for neon the gradient is independent of both l and the gas pressure. The relations between potential gradient and r agree with the equation, gradient $=C/r$, which Schottky deduced from his theory of the ambipolar diffusion of the positive column. The relationship fails, first, with decrease of gas pressure when the mean free path is large compared with the diameter of the tube, so that the diffusion law no longer holds, and, secondly, when the pressure is so great that the positive column detaches itself from the walls of the vessel and becomes an independent tube or thread-like structure. Thus, the law applies between the same pressure limits as give a true glow discharge. W. E. DOWNEY.

Effect of velocity distribution on the deflexion of atoms in an inhomogeneous magnetic field. W. H. RODEBUSH (Proc. Nat. Acad. Sci., 1927, 13, 50—52).

Definition of an element according to the International Commission on Chemical Elements. G. URBAIN (Bull. Soc. chim. Belg., 1927, 36, 124—136).—A *resume* of the discoveries which in 1923 led the International Commission to define an element in terms of an atomic number. J. S. CARTER.

Density of boron trichloride and the suspected variation in the atomic weight of boron. H. V. A. BRISCOE, P. L. ROBINSON, and H. C. SMITH (J.C.S., 1927, 282—290).—The densities of samples of boron trichloride derived from different sources have been determined by the method of calibrated glass floats (A., 1926, 771). The boron trichloride in each case was the same as that used in the determination of the ratio $BCl_3 : 3Ag$ (A., 1925, ii, 346), and was subjected to further purification. The densities so determined reveal a real difference of approximately 0·01 in the mean atomic weights of boron from California and from Asia Minor. W. E. DOWNEY.

Constitution of mercury derived from coal tar. F. W. ASTON (Nature, 1927, 119, 489).—Mercury obtained from coal tar, where it is present in the lightest fractions, gives isotopic lines indistinguishable from those of ordinary mercury. A. A. ELDRIDGE.

Straggling of α-particles from radium-C. G. H. BRIGGS (Proc. Roy. Soc., 1927, A, 114, 313—340).—By means of the magnetic deflexion method, measurements have been made of the distribution of the velocities for α-particles from radium-*C* after passing through sheets of mica of varying thickness. The stopping power of the mica, measured by the scintillation method and expressed as the air equivalent, ranged from 0·315 to 5·056 cm. The distribution of density in the deflected and undeflected bands produced on a photographic plate was measured with a microphotometer, applying the null method of Dobson and measuring the density directly in terms of a neutral grey wedge; results are given for emergent velocities from 0·98 to $0·22V_0$. The distribution of energies on emergence is very approximately Gaussian in form, as indicated by Bohr's theory of the phenomenon. From the data for the energy distribution, it is shown that the straggling of the ranges can be calculated at any point in the region investigated, and the contribution to the total straggling of various parts of the range can be determined. It is found that the straggling is proceeding at a maximum rate near the beginning of the range, half the total occurring in the first 2·4 cm. It is everywhere found to be about 1·4 times that predicted by Bohr's theory. This indicates that for a small element of path, ΣQ^2, where Q is the energy transferred to an electron, is approximately twice as great as in Bohr's theory. The experimental and theoretical results are compared, and it is suggested that the simplest explanation which accounts for the discrepancy between theory and experiment is that the large transfers of energy from the α-particles to the electrons, which account for nearly all the straggling, occur twice as frequently as predicted by Bohr's theory of the stopping of α-particles. L. L. BIRCUMSHAW.

Decrease in velocity of α-particles from radium-C. G. H. BRIGGS (Proc. Roy. Soc., 1927, A, 114, 341—354; cf. preceding abstract).—Using the apparatus employed in the investigation of the straggling of α-particles in radium-*C* (*loc. cit.*), data can be obtained on the photographic plates from which the mean value of V/V_0 for the beam of α-particles can be calculated. The values of V/V_0, over a range of velocity from 0·98 to $0{\cdot}22V_0$, have been deduced from values of r/r_0 (r being the radius of curvature of the path), which were calculated from the appropriate formula for the deflexion in terms of r and the dimensions of the apparatus. For velocities less than $0{\cdot}55V_0$, the decrease in velocity was much more rapid than that found by Marsden and Taylor (*ibid.*, 1913, A, 88, 443), but was in good agreement near the end of the range with the results found by indirect methods by Kapitza (*ibid.*, 1924, A, 102, 48) and by Curie (A., 1925, ii, 834). The ratio λ_2/λ_1 the number of singly- to doubly-charged α-particles at various velocities is given by the ratio of the areas of the density curves of the corresponding bands, and from the values obtained it is deduced that $\lambda_2/\lambda_1=5{\cdot}3\times10^{-3}V^{-4{\cdot}3}$. The homogeneity of the initial velocities of the α-particles was also investigated by means of the same apparatus. No evidence was found of velocities greater than the average by more than 1 in 3000. Velocities of less than the maximum were present, probably due to absorption in the source. L. L. BIRCUMSHAW.

Relation between the atomic weight of the isotopic radio-elements and the speed of the α-particles they emit. G. FOURNIER (Compt. rend., 1927, 184, 878—880).—If the atomic weights (A) of the isotopic radio-elements are plotted as a function of the speeds of the α-particles they emit (v), all the points (except that of polonium) fall on five parallel straight lines, each of which corresponds with a determined atomic number, *i.e.*, with a group of isotopes. Thus, the speeds of the α-particles decrease proportionally with their atomic weights to the same extents for the different isotopic groups. This is expressed by the relation $v=v_0-kA$, where v_0 varies with the group of isotopes and k is a constant. An atomic weight of 227 is indicated for actinium, which is probably derived from an isotope of uranium ($A=239$). Possibly v depends on the force existing between the α-particle and the layer from which it is emitted. J. GRANT.

Passage of α-rays and β-rays through matter. E. J. WILLIAMS (Nature, 1927, 119, 489—490).—Much of the discrepancy between the results of the application of classical mechanics to the calculation of possible energy transfers during encounters between the moving particle and the atomic electrons and the corresponding experimental results disappears when the motion of the atomic electrons is allowed for. For primary ionisation in hydrogen, the values agree to within 5%. A corrected value for the stopping power is given. A. A. ELDRIDGE.

Relative intensities of the groups in the magnetic β-ray spectra of radium-B and radium-C. C. D. ELLIS and W. A. WOOSTER (Proc. Roy. Soc., 1927, A, 114, 276—288).—Previous work on β-ray spectra of radioactive substances has been concerned almost entirely with the energies of the individual groups forming the spectra, but many important questions are connected with relative intensities. These have been measured for radium-*B* and radium-*C* by photometric measurement of the density of the lines recorded photographically by the standard focussing method. Intensities of the groups in the two spectra are measured on the same scale, and refer to equal numbers of disintegrating atoms. It is found that the ratio of the intensities of the groups due to conversion of the same frequency γ-ray in the K and L levels is independent of the frequency and approximately equal to that occurring in the ordinary external absorption of X-rays. The bearing of this result on the mechanism of emission of the groups is discussed. From Gurney's measurements of the number of electrons in the stronger groups of radium-*B* and radium-*C* (A., 1926, 5), the numbers of electrons in the other groups are deduced.

L. L. BIRCUMSHAW.

Ionising powers of radium-B and radium-C. H. JEDRZEJOVSKI (Compt. rend., 1927, 184, 596—598).—The ratio of the amounts of radium-*B* and radium-*C* in an active deposit of radium is constant when these are in equilibrium with the radon, but varies with the time when they are separated from it. A formula is deduced for the determination of the percentage, due to each of these constituents, of the total ionisation produced by γ-rays from such a deposit. The method has been confirmed by measurements of the ionising power of the deposit when that due to radium-*B* is excluded by lead screens. A table also is given for the decrease in ionising power when screens of increasing thicknesses of aluminium are used. The action of the γ-rays of radium-*B* cannot be detected through aluminium screens more than 60 mm. thick. J. GRANT.

Discoloration and luminescence due to Becquerel rays. II. K. PRZIBRAM (Z. Physik, 1927, 41, 833—847; cf. A., 1924, ii, 85).—The discoloration produced in various salts of the alkali metals when exposed to β- and γ-radiations is discussed at length from the point of view of the author's theory (*loc. cit.*). Following an account of the effect of pressure on these phenomena, an equation, involving four constants, is developed relating the absorption coefficient (assumed proportional to the density of neutral atoms produced by the radiation) with the intensity of the radiation and the time of exposure. By a suitable choice of constants, this equation can be used to represent the data of Bělař on the coloration produced in rock-salt; for a constant intensity, the coloration increases logarithmically with the time to a limiting value. Data are tabulated referring to the coloration, the absorption maximum, and the stability of the coloration of the hydrides and halides of sodium, potassium, rubidium, and cæsium.

R. W. LUNT.

Experiments to test the possibility of transmutation by electronic bombardment. M. W. GARRETT (Proc. Roy. Soc., 1927, A, 114, 289—292; cf. A., 1926, 1015).—Negative results were obtained in an attempt to transmute tin into indium in a

quartz tube apparatus with sealed-in tungsten leads similar to that used with mercury (*loc. cit.*). It was found impossible to obtain tin free from all traces of indium, the most persistent line in the spectrum being the 4102. Unsuccessful attempts were made to transmute titanium into scandium by bombardment in a vacuum with high-speed electrons capable of penetrating the innermost electronic orbits of the titanium atom. L. L. BIRCUMSHAW.

Existence of sub-electrons. F. EHRENHAFT (Z. Physik, 1927, **41**, 708—709).—A reply to Mattauch's criticism (this vol., 87) of the author's paper (A., 1926, 880). R. W. LUNT.

The Main Smith-Stoner scheme of atomic orbits. M. N. SABA and B. B. RAY (Physikal. Z., 1927, **28**, 221—225).—Theoretical. A combination of Bohr's scheme of atomic orbits with Pauli's principle of electron-orbit synthesis gives better agreement with experimental results than those obtained by the use of the scheme of Main Smith and Stoner. W. E. DOWNEY.

Atomic number and atomic structure. G. PICCARDI (Atti R. Accad. Lincei, 1927, [vi], **5**, 169—174).—It is suggested that the difference between the atomic weight and twice the atomic number in the higher elements is to be attributed to a neutral zone of protons and electrons exterior to the nucleus, and therefore relatively easily detached. Attempts are made on this basis to explain the occurrence of hydrogen in positive-ray apparatus, and in the experiments of Rutherford and Chadwick. R. W. LUNT.

Quantum theory of the emission and absorption of radiation. P. A. M. DIRAC (Proc. Roy. Soc., 1927, **A**, **114**, 243—265).—The problem is considered of an assembly of similar systems satisfying the Einstein–Bose statistics, which interact with another different system, a Hamiltonian function being used to describe the motion. The theory is applied to the interaction of an atom with an assembly of particles moving with the velocity of light, and it is shown that it gives Einstein's laws for the emission and absorption of radiation. The interaction of an atom with electro-magnetic waves is also considered, and it is shown that by taking the energies and phases of the waves to be q-numbers satisfying the proper quantum conditions instead of c-numbers, the Hamiltonian function takes the same form as in the light-quantum treatment. The theory gives the correct values for Einstein's A's and B's. L. L. BIRCUMSHAW.

Theoretical prediction of physical properties of many-electron atoms and ions. Mole refraction, diamagnetic susceptibility, and extension in space. L. PAULING (Proc. Roy. Soc., 1927, **A**, **114**, 181—211).—The wave mechanics of Schrodinger provides an atomic model which suggests that the method of treatment used to evaluate the screening constant s_0 (cf. this vol., 88) can be adapted to derive theoretical values of screening constants to be used in the equations representing the mole refraction or polarisability, diamagnetic susceptibility, extension in space, and other properties of atoms and monatomic ions. In following this procedure, the assumption is made that the nuclear charge is large in comparison with that of an electron shell. Since this requirement is not fulfilled by actual atoms and ions, an empirical correction is introduced, obtained from a consideration of the mole refraction and mole refraction-screening constant of the rare gases and of some ions in aqueous solution. Theoretical values are thus obtained for the mole refraction and diamagnetic susceptibility of a large number of atoms and ions, the values being in good agreement with such experimental data as are available. A third screening constant is also evaluated, which permits the calculation of the electronic distribution in atoms and ions and the determination of inter-atomic distances. It is shown in this connexion that the study of the diffraction of X-rays by crystals provides a method for the direct experimental verification of the form of Schrödinger's *eigen* functions. It is stated that the general method followed in this communication is capable of refinements which should render possible the accurate prediction of the properties of any atom or ion. L. L. BIRCUMSHAW.

Ionised hydrogen molecule and [Schrödinger's] wave mechanics. W. ALEXANDROV (Ann. Physik, 1927, [iv], **82**, 683—688).—An extension of previous work (this vol., 5). R. A. MORTON.

Radiation and the photo-electric effect. F. H. LORING (Chem. News, 1927, **134**, 129—130).—An extension of some theoretical considerations on the fundamental ideas of radiation. R. A. MORTON.

Spinning electron in wave mechanics. A. CARRELLI (Nature, 1927, **119**, 492—493).—Mathematical. A. A. ELDRIDGE.

Structure of an atom of nitrogen. H. COLLINS (Chem. News, 1927, **134**, 209—212, 273—277).—Speculative.

Photographic method of spectrophotometry in the red and infra-red. A. L. SCHOEN (J. Opt. Soc. Amer., 1927, **14**, 179—186, and Z. wiss. Phot., 1927, **24**, 326—336).—A method is described which permits the use of suitable photographic plates for spectrophotometric measurements throughout the range 200—900 mμ. L. F. GILBERT.

Electronic states and band spectrum structure in diatomic molecules. III. Intensity relations. R. S. MULLIKEN (Physical Rev., 1927, [ii], 29, 391—412).—The correspondence principle predicts definite intensity relations for P, Q, and R band lines in molecules having a rotational energy term $F(j)-B(j--\sigma^2)+\ldots$, provided σ is an electronic quantum number correlated with a precession about the internuclear axis (along which the angular momentum $\sigma h/2\pi$ is directed). Hönl and London's equations for the three possible cases $\Delta\sigma=0$, ±1, have been altered in form. Theoretical and experimental results are in qualitative agreement for various electronic emission bands, and for oscillation–rotation absorption bands corresponding with $\sigma'=\sigma''=0$. A. A. ELDRIDGE.

Bands in the secondary spectrum of hydrogen. H. S. ALLEN and I. SANDEMAN (Proc. Roy. Soc., 1927, **A**, **114**, 293—313; cf. A., 1925, ii, 909).—The band with head at 4582·58 Å., comprising a P, Q, and R combination, which was described in

a previous communication (*loc. cit.*) and attributed to triatomic hydrogen, has been found to be one of a large number of similar bands. These bands occur in groups, the bands of a group being spaced out at intervals of about 92 wave-numbers, the spacing being in some cases approximately constant and in others conforming to a quadratic law. The bands are found both in the range of wave-lengths measured by Merton and Barratt (A., 1922, ii, 461) and by Tanaka (A., 1925, ii, 909), and also in the infra-red region investigated by Allibone (A., 1926, 873). Two groups occurring in the latter region have been considered in detail. Experiment has shown that in some cases the lines of the group are enormously enhanced in the spectrum of the arc in hydrogen at higher pressures. The bands must originate in molecules with large moments of inertia, and other considerations are advanced which support the view that they are due to triatomic hydrogen.

L. L. Bircumshaw.

Structure and origin of the Swan band spectrum of carbon. R. C. Johnson (Phil. Trans., 1927, A, **266**, 157—230).—The Swan band spectrum has been studied both experimentally and theoretically. The sources used were a carbon arc burning in hydrogen and the discharge through a vacuum tube containing traces of carbon gases and filled with 20—50 mm. of one of the inert gases. The spectrum was photographed in the second order of a twenty-one foot grating, and about 2000 lines were measured. Eleven bands have been assigned to series and the rotational energy functions evaluated. The moments of inertia and internuclear distances deduced therefrom have values appropriate to an HC·CH molecule. The bands consist each of a *P* and *R* branch typical of a dipolar emitter. The fine structure multiplicity classes the bands as of the Heurlinger triplet type. The distribution of energy among the vibrational states shows the Swan bands to be a high-temperature, non-thermal system. A new band system with its strongest head at 4770 Å. was found associated with the Swan bands.

The analysis of the spectrum points to an HC·CH molecule as the emitter. Experimental evidence is also adduced to show that the earlier view that the Swan bands are due to carbon monoxide is extremely improbable; the fine structure analysis indicates that two carbon atoms are present; the singlet character of the levels classes the Swan emitter as an even-valency electron model; the close analogy to the second positive nitrogen bands (due to neutral $_2$ molecule) points to its origin in an HC·CH molecule. It is probable that in the molecule each carbon atom retains its *K*-electrons, which are shared by the CH group and move in 1_1 orbits. Common the whole molecule is the complete *L*-shell of the our 2_1 electrons and four 2_2 electrons. Outside, ut penetrating to between the nuclei, are the two valency electrons in 3_1 orbits. The ground level is as in the magnesium atom. W. E. Downey.

Spectra excited by active nitrogen. A. E. Uark, P. D. Foote, P. Rudnick, and R. L. Chenault (J. Opt. Soc. Amer., 1927, **14**, 17—27).—The acts bearing on the constitution of active nitrogen are discussed, and it is concluded that the balance of evidence is in favour of the older view that the active gas is composed of neutral unexcited atoms, and not, as has been recently suggested, of excited diatomic molecules. Full references are given, and the following new facts adduced. (1) Active nitrogen has no absorption spectrum between 6500 and 3200 Å.; absorption in this region would be expected from an activated molecule, but not necessarily from an atom. (2) Mercury atoms can receive at least 10 volts energy from active nitrogen. This energy corresponds with the lower limit for the heat of association of two nitrogen atoms. It was also observed that the usual intensity rules for the mercury multiplets do not hold for after-glow spectra; and two new bands of the β-system of nitric oxide, near 2400 and 2300 Å., are recorded. The nitrogen was excited by the electrodeless discharge, and an apparatus is described suitable for the introduction of metal vapours into the active gas.

The after-glow spectra of zinc, magnesium, platinum, sodium, cadmium, and thallium, and of silicon and titanium tetrachlorides, are discussed.

S. Barratt.

Absorption bands of nitrogen. H. Sponer (Z. Physik, 1927, **41**, 611—618).—The absorption of nitrogen has been examined in the range 1700—1200 Å. by a vacuum grating spectrograph. Two different band systems are observed, commencing at 1544 and at 1450 Å. The results are discussed at length, with particular reference to the spectra of carbon monoxide and of nitric oxide. R. W. Lunt.

[Spectrochemistry of compounds containing nitrogen. II.] K. von Auwers and W. Ernst (Z. physikal. Chem., 1926, **124**, 464).—A concession of priority to Colson (J.C.S., 1917, **111**, 554) in the application of spectrochemical methods to the question of the structure of cyanamide (cf. A., 1926, 994), and a correction. R. Cuthill.

Rotational terms in the MgH bands. W. W. Watson and P. Rudnick (Physical Rev., 1927, [ii], **29**, 413—418).—Wave-numbers for the first six branches in the band 5211 Å., to which are assigned the vibrational quantum numbers $n'=n''=\frac{1}{2}$, are tabulated, together with values of ΔF for initial and final electron levels and several vibrational levels. The Kratzer, Kramers, and Pauli formula is applied.

A. A. Eldridge.

Ultra-violet absorption spectra of nickel, cobalt, and tellurium. J. C. McLennan and R. F. B. Cooley (Trans. Roy. Soc. Canada, 1926, [iii], **20**, III, 349—353).—The absorption spectra of the vapours of the above elements in the lower quartz and fluorite regions have been examined. In the region 2402—1524 Å., 26 wave-lengths of nickel, and possibly 4 additional ones, were shown to be absorbed by the normal vapour of nickel. Between 2000 and 1448 Å., 15 wave-lengths of the spectrum of cobalt were found to be totally absorbed and 10 partly so by cobalt vapour. Between 2000 and 1650 Å., 11 wave-lengths were found to be absorbed by tellurium vapour. R. Cuthill.

Absorption spectra of metallic vapours. J. C. McLennan, (Miss) E. Cohen, and M. J. Liggett

(Trans. Roy. Soc. Canada, 1926, [iii], 20, III, 365—376).—The absorption spectra of the vapours of manganese, nickel, palladium, platinum, lanthanum, neodymium, praseodymium, and uranium have been mapped between 1450 and 6000 Å. Numerous new lines are recorded. No absorption by the vapour of cerium or thorium could be detected. R. CUTHILL.

Ultra-violet spectrograms of carbohydrates. P. NIEDERHOFF (Z. physiol. Chem., 1927, 165, 130—139).—Ultra-violet absorption curves are given for dextrose, lævulose, galactose, and lactose; sucrose shows no absorption in the ultra-violet. The results are in general agreement with those of Bielecki and Henri (Ber., 1914, 46, 3627). The form of the curve for dextrose suggests the presence of a carbonyl group. C. R. HARINGTON.

Spectrochemical studies of hydroxyazo-compounds. III. T. UEMURA, N. YOKOJIMA, and T. ENDO (Bull. Chem. Soc. Japan, 1927, 2, 48—51; cf. this vol., 238, 291).—The following substances have been examined spectrochemically, and possess the forms assigned: benzeneazopyrogallol, *A*-form in neutral solution, a mixture of the *A*- and *R*-forms in alkaline solution; *p*-nitrobenzeneazopyrogallol, *A*-form in neutral solution, *R*-form in alkaline solution; benzeneazophloroglucinol, *A*-form in both solutions; *p*-nitrobenzeneazophloroglucinol, *A*-form in neutral solution, *R*-form in alkaline solution.

S. J. GREGG.

Absorption spectra and the constitution of benzene derivatives. IX. Dihydroxybenzaldehydes. Theory of auxochromes. N. VALASCHKO (Ukraine Chem. J., 1926, 2, 183—235).—It has been shown (A., 1910, ii, 1015; 1913, ii, 367) that the isomeric hydroxybenzaldehydes give two types of absorption spectra. These two types consist of the α_1 and α_2-bands characteristic of benzaldehyde, and the ϕ-band characteristic of phenol. When the hydroxyl group is in the *para* position, a phenolic type of absorption spectrum is produced; in the *ortho* or *meta* positions, the ϕ-line is very weak or is missing, and the spectra of the α-type are produced with a very strong α_2-band.

Curves of absorption spectra for 2 : 4-, 3 : 4-, 2 : 5-, and 2 : 6-dihydroxybenzaldehydes and their methoxy-derivatives have been compared in aqueous, alcoholic, alkaline, and acid solutions, with the corresponding curves for the hydroxybenzaldehyde derivatives. With the 2 : 4-dihydroxybenzaldehyde derivatives, the α_2-band is shifted towards the ultra-violet, and is greatly intensified as compared with the corresponding 2-hydroxybenzaldehyde. The ϕ-band in neutral or acid solution is shifted towards the ultra-violet as compared with 4-hydroxybenzaldehyde. In alkaline solution, the band is shifted somewhat towards the red end, whilst its intensification either remains constant or is slightly decreased. Both the neutral and alkaline solutions are colourless. In neutral or acid solution, 3 : 4-dihydroxybenzaldehyde derivatives give α-lines shifted either greatly towards the blue or slightly towards the red, as compared with 3-hydroxybenzaldehyde. In strong alkaline solution, the bands are shifted greatly towards the red and are very much intensified. The ϕ-band is shifted towards the blue in neutral solution; in alkalis, towards the red, with a great diminution of intensity. 2 : 3-Dihydroxybenzaldehyde derivatives show a great shift of the α_2-band towards the red, with no change of intensity. The ϕ-band is missing. The alkali solutions of the compounds are lemon-yellow. Derivatives of 2 : 5-dihydroxybenzaldehyde resemble the 2 : 3-derivatives.

On the basis of Auwers' work, (A., 1915, ii, 297) the probable mechanism by which the above results are obtained is discussed, and it is concluded that the various spectra are due to the different kinds of conjugation of the double linkings with the hydroxyl groups. The effects of placing the auxochromes in various positions as compared with the chromophores with regard to the formation of colour are discussed and various corrections to the rules formulated by Kauffmann and Franck (A., 1906, i, 841) are made. Finally, it is suggested that the presence of the three bands can be explained by attributing the α_2-band to the carbonyl group, the ϕ-band to the phenolic group, and the α_1-band to the benzene ring.

From the facts that in *o*-hydroxybenzaldehyde the α_2-band is increased in intensity 120 times, in *m*-hydroxybenzaldehyde 80 times, whilst in *p*-hydroxybenzaldehyde the α_2- and the α_1-bands disappear and the ϕ-band is increased 20 times, all the types of absorption spectra for the dihydroxybenzaldehydes can be explained. In the last case, the disappearance of the α_1-band is attributed to the fact that it has been shifted towards the ultra-violet and is lost in the much stronger ϕ-band. E. ROTHSTEIN.

Excitation of fluorescence in fluorescein. E. H. KENNARD (Physical Rev., 1927, [ii], 29, 466—477).—The fluorescence curves show a maximum at about 5240 Å.; the excitation curve shows a maximum at 5000 Å. for fluorescence at 5270 Å., and at shorter wave-lengths for other points in the fluorescence spectrum. Maximum absorption occurs around 4750 Å. A. A. ELDRIDGE.

Fluorescence of chlorine and of bromine. L. BLOCH and E. BLOCH (Compt. rend., 1927, 184, 744—746).—In the course of experiments on the effect of an oscillating electric discharge on sodium chloride and bromide (this vol., 178), a fluorescence characteristic of the anion of the salt employed has been observed to appear at a particular pressure. Photographs of the spectra have shown that the fluorescence of chlorine consists of groups of channelled bands of complicated structure situated chiefly between 3960 and 4920 Å., those in the middle of the spectrum being most intense. The intense orange fluorescence of bromine yielded 25 bands, similar in structure and arrangement to those of chlorine, between 6400 and 5100 Å. (cf. A., 1926, 884). The phenomena are attributed to the effect of soft *X*-rays, since the bands of nitrogen, water vapour, and the first and third negative groups of carbon are also present.

J. GRANT.

Intensity distribution in the *D*-line of the chemiluminescence of sodium vapour. R. L. HASCHE, M. PÓLANYI, and E. VOGT (Z. Physik, 1927, 41, 583—610).—Measurements of the absorption by sodium vapour of the *D*-line emitted from sodium

vapour, at pressures in the range 5×10^{-4}—10^{-2} mm., burning in mercuric chloride vapour have shown that the half width of the line varies from 0·055 to 0·08 Å.; this variation is attributed to absorption in the burning mixture. It has also been shown that the broadening of the line so observed is the same as that in the light emitted by sodium vapour at corresponding temperatures and pressures. The mechanism of the reaction is discussed on the basis of these results, and it is concluded that the observed light emission is excited by the vibrational energy of the sodium chloride molecules formed in the reaction.

R. W. Lunt.

Effect of *X*-rays on thermoluminescence. (Miss) F. G. Wick (J. Opt. Soc. Amer., 1927, **14**, 33—44; cf. A., 1924, ii, 714; 1925, ii, 262).—The effect of (*a*) variation of temperature on the rate of decay of the thermoluminescence of natural specimens of fluorite and calcite, natural specimens after exposure to *X*-rays, and specimens heated to remove all thermoluminescence before being exposed to *X*-rays, of (*b*) time of exposure to *X*-rays on maximum brightness of thermoluminescence and rate of decay, and of (*c*) keeping specimens for varying lengths of time after exposure to *X*-rays before observations were made has been investigated. Specimens of fluorite which were not naturally thermoluminescent became so to a greater or less degree on exposure to *X*-rays. Crystals which were naturally active had the intensity at a given temperature greatly increased, and many of them acquired, in addition to the luminescence of the original colour, a new and entirely differently coloured luminescence, which flashed up before the thermoluminescence characteristic of the natural crystal appeared. The results suggest a complicated mechanism.

L. F. Gilbert.

Effect of exposure to *X*-rays on the thermoluminescence of some synthetically prepared materials. (Miss) F. G. Wick and (Miss) M. K. Slattery (J. Opt. Soc. Amer., 1927, **14**, 125—132; cf. preceding abstract).—Small amounts (0·2—0·4%) of manganese mixed with calcium sulphate induce a green thermoluminescence on exposure to *X*-rays. The decay of luminescence at 120° is of the "persistent" type (cf. Nichols and Howes, Proc. Nat. Acad. Sci., 1918, **4**, 305). The brightness of the maximum after exposure increases linearly with the temperature. Saturation is reached at 260° with an exposure of 1 hr. Synthetic thermophosphors show an increase in activity on keeping a few minutes after exposure. Less energy is stored in a specimen of manganese calcium sulphate if the temperature of exposure is decreased slightly. L. F. Gilbert.

Ionic mobilities for ion rays. F. Koether (Ann. Physik, 1927, [iv], **82**, 639—663).—With a rge surface and high temperatures the emission of positive ions from salts is reasonably constant. Rutherford's alternating current method leads to mobilities of the order of a few cm. per sec. for the positive ions from silver and cadmium halides over the temperature range 325—425°. An increase of 20° in temperature brings about a roughly two-fold increase in mobility. Greater frequency corresponds with increased mobility, an effect which is connected with polarisation of the salt at the surface from which ions are being liberated. The mobilities of ions set free by other methods (volume ionisation) are of the order 10^{-2}, 10^{-3}, and the evidence points to charged complexes (cluster-theory) rather than to simple ions as the carriers in this work. R. A. Morton.

Ion-rays. G. C. Schmidt (Ann. Physik, 1927, [iv], **82**, 664—682; cf. A., 1926, 877).—The emission of ion-rays is very sensitive to the presence of impurities. Specially purified lead chloride emits negative ions exclusively, whilst silver chloride, silver iodide, and cadmium iodide emit only positive ions at moderate temperatures. The emission falls off with time, except at higher temperatures. Near the m. p. it is constant. The presence of impurities frequently causes the appearance of a maximum in the time–emission curve, although the occurrence of an emission increasing with time does not necessarily denote impurities. The falling off in the emission of a pure salt is due neither to polarisation of the electrode or of the salt nor to the formation of complexes as a result of sudden cooling. The conductivity of very quickly-cooled salts is greater than that of slowly-cooled salts. The change, although small, is real, and it is therefore inferred that the change in emission of ions is due to a surface effect akin to photo-electric fatigue and passivity. R. A. Morton.

Separation of molecular streams in magnetic fields. A. Leu (Z. Physik, 1927, **41**, 551—562).—Improvements are described in the technique of Gerlach and Stern. The principal error is thought to arise in the determination of the heterogeneous magnetic field. This measurement has been made by observing the magnetic moment of a bismuth wire in the field; the value so obtained for the susceptibility agrees within 3% of the accepted value, and no error greater than this arises in determining the magnetic moment in a molecular stream. Zinc and cadmium show no separation and have therefore no magnetic moment. A number of determinations have shown that the atoms of sodium and potassium are to be associated with one Bohr magneton (±3—4%) and those of thallium with one third of a Bohr magneton (±4%). R. W. Lunt.

Magnetic separation in hydrogen streams. E. Wrede (Z. Physik, 1927, **41**, 569—575).—A modification of the technique of Leu (cf. preceding abstract) has been adopted to determine the magnetic separation in a stream of unimolecular hydrogen. Tungstic oxide was found to be most sensitive as a target indicator, but molybdic oxide, silver nitrate, bismuth nitrate, and zinc chloride were also found to be satisfactory, particularly the last, although of slow reactivity. The separation observed corresponds with one Bohr magneton per hydrogen atom.

R. W. Lunt.

Electric double refraction in relation to the polarity and optical anisotropy of molecules. I. Gases and vapours. II. Liquids. C. V. Raman and K. S. Krishnan (Phil. Mag., 1927, [vii], **3**, 713—723, 724—735).—I. An attempt is made to correlate, on the basis of Born's theory of electrical birefringence, the available data on the Kerr effect of gases and vapours with the optical anisotropy

determined from measurements of light scattering and with the polarity of the molecules as determined from measurements of their dielectric constants. With electrically polar molecules, the orienting action of an electrostatic field is found to be due chiefly to the couple exerted on the permanent electric doublet present and to be much larger than would be the case if the molecules were non-polar. With the aid of the simplifying assumptions of Gans (Ann. Physik, 1921, [iv], **45**, 97) regarding the relationship between the constants of electrical and optical anisotropy, values of the Kerr constant have been calculated for several non-polar molecules from the factor of depolarisation of scattered light. These values are in good agreement with those observed. It is shown that in the case of polar molecules having an axis of optical symmetry, to which the permanent moment is parallel or is inclined at a known angle, it is possible to calculate the value of the moment from the Kerr constant and the depolarisation constant. Such calculations have been made for hydrogen chloride, methyl chloride, and ethyl chloride molecules. The value for the hydrogen chloride molecule is in exact agreement with that obtained by Zahn from dielectric constant measurements. Alternatively, if the value of the moment is known, its direction can be calculated from the same data, and the applicability of the method to simple benzene derivatives is indicated. The significance of the negative value of the Kerr effect in the case of di- and trichloromethane and the positive value in the case of monochloromethane is discussed, and is shown to be in agreement with Born's theory.

II. The work has been extended to an examination of the Kerr effect in liquids. As in the case of vapours, all the compounds exhibiting large Kerr effects are electrically polar. The influence of the polarity on the magnitude of the Kerr effect is greater in liquids than in vapours. In the case of non-polar molecules, the moments induced in the molecules by an external electrostatic field are sufficient to account for the observed double refraction. In the case of liquids where sufficient data are available, the observed Kerr constant is in numerical agreement with that calculated on the basis of Born's theory. The theory is supported also by the available measurements on the variation of the electrical birefringence of liquids with temperature. A. E. Mitchell.

Electric double refraction of benzopurpurin. T. Wereide (Z. Physik, 1927, **41**, 857—863).—The electric double refraction of aqueous solutions of benzopurpurin (wt. concentration 5·9—95 $\times 10^{-6}$) increases less rapidly than the concentration, and is diminished by high concentration of electrolytes. R. W. Lunt.

Electrical anisotropy of crystalline liquids. M. Jezevski (Bull. Acad. Polonaise, 1926, A, 263—271).—See this vol., 92.

Magnetic rotation of solutions of certain ferric salts. (Miss) C. E. Richards and R. W. Roberts (Phil. Mag., 1927, [vii], **3**, 770—784).—As previous work (A., 1925, ii, 478) on the magnetic rotatory dispersion of certain solutions of nickel and cobalt had shown that in order to obtain effects characteristic of the solute it was necessary to take into account the rotation due to the solvent, an extension has been made to solutions in which the paramagnetic rotation due to the ions in solution preponderates over the diamagnetic rotation of the solvent. With ferric sulphate solutions, whilst the rotation of the solution is positive, the effect due to the salt is distinctly negative. The rotatory dispersion curve indicates the presence of at least two absorption bands, one at 0·53 μ and the other at 0·57 μ. With ferric nitrate solutions, a similar result is obtained and an absorption band at 0·535 μ is indicated. With ferric chloride solutions, the rotation changes from positive to negative with increasing iron content. In the solution of d 1·092, the rotatory dispersion sion curve suffers a marked change in the neighbourhood of 0·57 μ. It is suggested that this is due to a partial dehydration of the ferric chloride molecule. All the indications are that ferric chloride and ferric sulphate solutions have the same magnetic absorption band. A solution of ferric ammonium chloride of d 1·091 gave a positive magnetic rotation and the rotatory dispersion curve gave indications of magnetic absorption bands at 0·57 and 0·53 μ. A. E. Mitchell.

Connexion between chemical valency, electron grouping, and crystal structure. W. Hume-Rothery (Phil. Mag., 1927, [vii], **3**, 301—305).—Some of the conclusions of Grimm and Sommerfeld (A., 1926, 560) are criticised. Examples are quoted in which the same atomic configuration can be produced by more than one method of binding together of the atoms or by more than one electronic configuration. It is therefore held to be unjustifiable to argue that the fact that similar space-lattices are formed by different elements indicates similar electronic structure. It is also pointed out that the deduction from X-ray evidence that silicon and the compounds carbon silicide, boron nitride, aluminium nitride, and beryllium oxide are non-polar in the solid state, and that the atoms are held together in the solid in the same way as the atoms of carbon in the diamond lattice, should be received with caution. A. S. Russell.

Electronic nature of isomeric transformations. II. F. I. Berezovskaya (Ukraine Chem. J., 1926, **2**, 250—276; cf. A., 1926, 887).—The effect of magnetic fields on the structures of fumaric and maleic acids has been re-examined. The maximum change of maleic into fumaric acid occurred in a field of 4750—5150 units, when 12·75% of the total change took place in 7 hrs. Thereafter, as the field was increased, a small amount of maleic acid was formed. In a field of 7000 units, fumaric acid broke down analogously to oxalic acid, which is known to break down into carbon dioxide and formic acid when exposed to a strong magnetic field.

It is shown that methylfumaric acid is a stronger acid than fumaric acid, owing to the attraction of the carbon atom of the methyl group for the electrons of the carbon atom of the carboxyl group. Methylmaleic acid, in which the methyl group acts in the opposite sense, should be a weaker acid, and therefore have less mobile electrons. Hence in a magnetic field methylfumaric acid will be converted into methyl-

maleic acid. This also explains why dimethylfumaric acid does not exist. The effect of magnetic fields on alkylated maleic and fumaric acids will be examined. E. ROTHSTEIN.

Electronic interpretation of the constitution of the boron hydrides and of compounds of boron, nitrogen, and hydrogen. M. ULMANN (Ber., 1927, 60, [*B*], 610—615; cf. Stock, A., 1926, 1218).—The position of boron in the periodic system renders equally possible the attainment of a stable electronic arrangement by the loss of three or the gain of five electrons. In the boron hydrides, the hydrogen atoms represent negative systems in the first case, in that each gains an electron, and positive systems in the second case, since each loses its single electron. In the former case, the hydrogen resembles that of the hydrides of the alkali and alkaline-earth metals, whereas in the latter case it is similar to that in the hydrides of elements on the right side of the periodic system. If it be assumed that gain and loss of electrons occur under similar energy conditions, it is possible to construct molecular models for boron hydrides and similar compounds from a uniform point of view. The hydride B_2H_6 contains a system of two boron atoms, one of which loses three electrons, whereas the other gains five. In each portion of the system, the stable, so-called "rare-gas" arrangement of electrons is present. The formula B_2H_6 can therefore be resolved into $BH_2{\cdot}BH_4$ or $\overset{-}{\underset{-}{-H-B=B=H_4}}$, and this is shown to be consistent with the chemical properties of the hydride. For the more complex compounds the following formulæ are developed on similar lines: $BH_2{\cdot}BH_3{\cdot}BH{\cdot}BH_4$, $BH_2{\cdot}BH_3{\cdot}BH{\cdot}BH_2{\cdot}BH_2$, $BH_2{\cdot}[BH_2{\cdot}B]_2{\cdot}BH_4$, and $BH_2{\cdot}[BH_2{\cdot}B]_4{\cdot}BH_4$. For the compounds of boron, hydrogen, and nitrogen the structures NH·B·NH·B·NH and $BH_2{\cdot}NH{\cdot}BH{\cdot}NH{\cdot}B{\cdot}NH$ are proposed.

H. WREN.

Constitution of boron [hydride] compounds. J. A. CHRISTIANSEN (Z. anorg. Chem., 1927, **160**, 395—403).—Stock ascribes to boron the valencies 3 and 4 in the various hydrides and their derivatives (A., 1926, 1218), but it is now shown that the behaviour of these compounds may be more satisfactorily explained on the assumption that boron has valencies of 3 and 5 and a co-ordination number of 4. On this basis, B_2H_6 would be formulated as $H_3B{:}BH_3$, and the ammonia compound either as the salt $[H_2B{:}BH_2][NH_4]$, or as the dipolar compound $[H_3B{:}NH_3]$, the former being the more probable in view of its analogy to the salt-like compound $B_2H_6Na_2$. The hydride B_4H_{10} may be written as $H_3B{:}BH_2{:}BH_2{:}BH_3$; on hydrolysis, this yields hydrogen and the acid $B_2H_6O_2$, the potassium salt of which is obtained by treating B_2H_6 with potassium hydroxide and may be written as $[H_2(OH)B{\cdot}B(OH)H_2]K_2$. The comparatively great stability of hydrides with 5, 6, boron atoms is most satisfactorily explained by the adoption of ring formulæ as follows:

$BH_2{-}{-}BH_2$ $BH_2{:}BH{:}BH_2$ $BH_2{:}BH{\cdot}B{:}BH_2{:}BH_2$
$BH_2{\cdot}BH{\cdot}BH_2$ $BH_2{:}BH{:}BH_2$ $BH_2{:}BH_2{\cdot}B{\cdot}BH{:}BH$
(I) (II) (III)

Formula (I) accounts for the fact that B_5H_9 combines with 4 mols. of ammonia to give $B_5H_9(NH_3)_4$, which with hydrogen chloride evolves 4 mols. of hydrogen rapidly and a further 3 mols. more slowly. The naphthalene formation of (III) is in agreement with its chemical properties and with its high m. p.

A. R. POWELL.

Sizes of ions and the structure of ionic crystals. L. PAULING (J. Amer. Chem. Soc., 1927, **49**, 765—790).—Theoretical. With the aid of an atomic model derived from Schrodinger's wave mechanics (Ann. Physik, 1926, [iv], **81**, 109), radii are calculated for ions in a crystal having a small mutually-deforming force. The sum of the radii of two ions is equal to the interionic distance in a "normal" crystal composed of these ions with the sodium chloride structure, a "normal" crystal being one in which strong repulsion occurs only between adjacent anions and cations, and in which there is only so much deformation as is shown by the alkali halides. The calculated radii agree fairly well with the empirical values of Wasastjerna (A., 1923, ii, 593) and account satisfactorily for the experimental results both for "normal" crystals and for crystals in which the above additivity rule does not hold. Thus in some crystals (*e.g.*, lithium chloride, magnesium sulphide) the interatomic distances depend on the anion radius only, since the anions are in mutual contact. Double repulsion (*i.e.*, anion–anion as well as anion–cation) in sodium chloride, magnesium oxide, etc. crystals makes the anion–cation distances smaller than those observed. It is predicted that the fluorite structure is more stable than the rutile structure when the ratio of the cation radius to the anion radius exceeds 0·65, and *vice versa*. This has been verified experimentally. Similarly, the sodium chloride structure is more stable than the sphalerite structure when this ratio is greater than 0·33. This has been verified for certain beryllium compounds (*e.g.*, the oxide and sulphide), which are to be considered, therefore, as ionic crystals. The aptness of such tetrahedral crystals to show deformation is attributed to a tendency of the anion to share an electron pair with each cation. Complex ions are considered very briefly. S. K. TWEEDY.

Effective cross-section of the oriented hydrogen atom. R. G. J. FRASER (Proc. Roy. Soc., 1927, **A**, **114**, 212—221).—An apparatus is described for studying the normal hydrogen atom under conditions of space quantisation, and it is found that the effective collision area presented to the molecules of the resting gas (either hydrogen or argon) by the neutral hydrogen atoms in a beam of canal rays is unchanged by space quantisation. The hydrogen atom in the normal (1*s*) state is thus shown to be isotropic. This result is confirmed by Unsold's analysis of the helium arc spectrum (A., 1926, 550), and receives a satisfactory interpretation on the basis of Schrodinger's wave mechanics. L. L. BIRCUMSHAW.

Determination of the crystallite orientation [of metals] by the production of lines of slip. G. TAMMANN and H. H. MEYER (Z. anorg. Chem., 1927, **160**, 347—354).—The method of maximum reflexion (A., 1925, ii, 1132) admits of the differentiation of three chief groups of crystallites on the surface of a

metal, the cubic, octahedral, and dodecahedral. By examining the lines of slip produced when the metal is subsequently subjected to deformation, it is possible to determine the exact orientation of these surface planes to the crystal. For example, with copper or iron, where slip takes place along an octahedral plane, the surface, if a cube plane, will show two systems of slip lines intersecting at an angle of 90°; if an octahedral plane, three systems intersecting at 60°, and if a dodecahedral plane, three systems two of which intersect at 110° and the third bisects this angle. In any conglomerate of crystallites, all these three systems may develop together with a fourth, characteristic of cubic crystals, in which the lines are perpendicular to each other, but, owing to the orientation of the crystallites to the direction of rolling, no slip takes place along one or two of the slip planes in most of the crystals. The usual average is that 75% of the crystals show two systems of slip lines, 25% show three, and 0—0·2% show all four. Examples are given of the use of the method combined with the method of maximum reflexion in determining the orientation of the crystallites in cast copper ingots.

A. R. Powell.

Tetragonal structure of carbon steel. N. Seljakov, J. Kurdumov, and N. Goodtzov (Nature, 1927, **119**, 494).—Carbon steel quenching in water shows the body-centred, tetragonal structure. The numerical data indicate that the observed tetragonal structure of steel is a solid solution of carbon in the body-centred tetragonal lattice of metal atoms.

A. A. Eldridge.

Constitution of mixed crystals. G. Lunde (Bull. Soc. chim., 1927, [iv], **41**, 304—308).—From the results of the *X*-ray examination of certain mixtures (cf. Barth and Lunde, A., 1926, 114, 895), the general conclusion is reached that two compounds having different lattices of more or less compact formation can exhibit pronounced isodimorphism only if that compound formed from the smaller ions (atoms) crystallises in the more compact lattice. Exceptions to this rule are to be attributed to the reciprocal action of the electronic envelopes of the ions. A general consideration of the rule together with certain experimental results leads to the conclusion that in mixed crystals the constituents are perfectly mixed, but one of the constituents replaces the other in some arbitrary and irregular manner (cf. Vegard and Schjelderup, A., 1917, ii, 243).

S. K. Tweedy.

Spatial systems of rhombic and monoclinic heptahydrates of sulphates of bivalent metals, and the series of mixed crystals $Mg(Zn)SO_4,7H_2O$. H. G. K. Westenbrink (Rec. trav. chim., 1927, **46**, 105—123).—*X*-Ray investigation of $MgSO_4,7H_2O$ showed that the space-lattice is of the simple rhombic type V_4 in Wyckoff's notation, and the substitution of CrO_4 for SO_4, or of Ni or Zn for Mg, has negligible effect on the dimensions of the elementary cell. The monoclinic modification of $FeSO_4,7H_2O$ is of the type C_m^6, and again the substitution of Co for Fe has little effect on the lattice. Of the three views on the nature of mixed crystals, the one that they consist of conglomerations of pure crystals of the two constituents is contrary to *X*-ray and other evidence. Tammann's view that a mixed crystal is derived from a pure one by the replacement atom for atom of one type of atom by another, is also unlikely, for it necessitates the supposition that the value of n (*i.e.*, the number of identical atoms distributed about a given atom) and also the dimensions of the elementary cell vary with the composition of the mixture. The best view is that the two types of atoms are distributed irregularly throughout the crystal, so that, in a given region, only those of one type are present, arranged according to their appropriate space-lattice. Thus the crystal possesses quasi-homogeneity only, but its action on *X*-rays will be identical with that of a lattice the dimensions of which are the mean of those of the constituents. Mixed crystal formation and compound formation can occur between the same constituents; with the system $MgSO_4,7H_2O$–$ZnSO_4,7H_2O$, however, the compounds $Mg_2Zn(SO_4)_3,21H_2O$ and $MgZn(SO_4)_2,14H_2O$, as supposed by Hollmann (A., 1901, ii, 436), are not formed, for both the specific gravity and the refractive index of the mixed crystals vary continuously with composition, and, further, consideration of the lattices of the constituents and of the mixed crystals shows that such compounds are impossible. S. J. Gregg.

Effect of temperature on the crystal structure of calcite. C. Tsuboi (Proc. Imp. Acad. Tokyo, 1927, **3**, 17—18).—A preliminary account is given of the effect of temperature in altering the mean relative positions of the atoms in a crystal of calcite. The value of the parameter, ϕ, defining the positions of the oxygen atoms at the ordinary temperature is 0·25, and this value decreases as the temperature is raised.

W. E. Downey.

Crystal structure of hexamminecobaltic iodide $[Co(NH_3)_6]I_3$. R. W. G. Wyckoff and T. P. McCutcheon (Amer. J. Sci., 1927, [v], **13**, 223—233).—From powder and Laue photographs of crystals of $[Co(NH_3)_6]I_3$, it appears that the correct structure is Co at 4*b*, I at 4*c* and 8*e*, N at 24*a*, with u=about 0·20. The length of the edge of the unit cube containing these four molecules is 10·88 Å.

C. J. Smithells.

Crystal structure of selenides of beryllium, zinc, cadmium, and mercury, and determination of lattice constants. W. Zachariasen (Z. physikal. Chem., 1926, **124**, 436—448).—The crystals of beryllium, zinc, and mercuric selenides are of the zinc-blende type, and the lengths of the edges of the elementary cubes in Å. are 5·129±0·004, 5·661±0·003, and 6·068±0·004, respectively. Cadmium selenide crystals are of the wurtzite type, and the lattice dimensions are a=4·30±0·01 and c=7·01±0·02. A method of determining the limits of error in determinations of lattice constants by Wyckoff's method is worked out.

R. Cuthill.

Lattice-structure and electrical conductivity in the mixed-crystal series gold–copper, palladium–copper, and platinum–copper. C. H. Johansson and J. O. Linde (Ann. Physik, 1927, [iv], **82**, 449—478; cf. A., 1926, 112).—The correlation between maxima in the conductivity–composition curves in mixed-crystal series and the appearance of superimposed structure effects in the *X*-ray study of the

alloys have been fully confirmed. Alternate heating and cooling hasten the appearance of regular orientation in the gold–copper series. In the palladium–copper system, alloys richer in palladium than 50 at.-% exhibit poor conductivity together with a face-centred cubic lattice free from superimposed structure effects. Tempered alloys containing up to about 25 at.-% of palladium are good conductors and show evidence of structure superimposed on the face-centred cubic lattice. Within the range 38—50 at.-%, the conductivity is high and the body-centred cubic lattice shows the superimposed structure. On the other hand, alloys quickly cooled from the m. p. show poor conductivity and ill-defined crystal structure. The absence of the body-centred lattice at concentrations higher in palladium than 50 at.-% is said to be due to the inability of palladium atoms to replace copper atoms in this lattice. Højendahl's views on electrical conductivity in alloys indicate that a lattice lacking in continuous lines or planes of similar atoms will exhibit poor conductivity, and the present work provides support for the idea. The system copper–platinum exhibits a face-centred cubic lattice with superimposed structure accompanied by high conductivity in the neighbourhood of 25 at.-% of platinum. In the region 40—50 at.-%, a trigonal phase appears with a maximum in the conductivity–composition curve at 1Cu : 1Pt. From about 60 at.-%, the lattice is a face-centred cube with the conductivity decreasing as the proportion of platinum increases. The quickly-cooled alloys show no superimposed structure and the conductivity falls to a relatively low minimum in the region 50—70 at.-%. The trigonal phase is discussed in some detail.

R. A. Morton.

X-Ray patterns of mullite and sillimanite. J. F. Hyslop and H. P. Rooksby.—See B., 1927, 219.

X-Ray analysis of clays. L. B. Strutinski.—See B., 1927, 219.

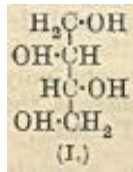
Analytical interpretation of the X-ray spectra of fatty acids and their mixtures. J. J. Trillat (Compt. rend., 1927, **184**, 812—814; cf. A., 1926, 890).—Variations previously recorded in the *X*-ray spectra of pure fatty acids are due to the method of preparation of the specimen rather than to the presence of impurities. Orientation by fusion or evaporation of alcoholic solutions gives consistent results. The spectra of mixtures of two fatty acids consist usually of faint rays, and depend on the method of preparation of the specimen and on the proportion and difference in m. p. of the constituents. Separate spectra of the constituents are not obtained if the acids contain almost the same number of carbon atoms, except when traces of an impurity lower the m. p. of the mixture and promote their simultaneous orientation. With triglycerides, this has been used for detection of margarine in butter. The positions of the rays cannot be determined from the proportions of the constituents, and the use of thin lead sheets is preferable to that of glass for mounting in their qualitative determination.

J. Grant.

X-Ray investigation of optically anomalous crystals of racemic potassium chlorosulphoacetate. W. G. Burgers (Proc. Roy. Soc., 1927, **A, 114**, 222—229).—Jaeger's view (A., 1925, ii, 948), that the apparently orthorhombic crystals of racemic potassium chlorosulphoacetate are really twins produced by almost perpendicular crossing of monoclinic lamellæ, has been tested by an *X*-ray investigation of the crystals. The crystals used were either the same as those employed by Jaeger or had been grown under similar conditions, *i.e.*, from aqueous solutions containing potassium bromide or chloride. A number of oscillation photographs about different crystallographic directions were taken, and the results indicated that the crystals are truly orthorhombic, and that the irregularities of their habit must be caused by a slight difference in orientation of successively crystallised layers. The dimensions of the unit cell, which contains eight groups $[CHCl(SO_3K)\cdot CO_2K,1{\cdot}5H_2O]$, are $a=8{\cdot}58$, $b=8{\cdot}60$, $c=23{\cdot}76$ Å. The halvings correspond with the space-group Q^{14}, the underlying lattice being the simple orthorhombic lattice Γ_0. It is probable that the optical anomalies of the investigated crystals can be explained by the presence of internal strains, and that the presence of alkali halides in the mother-liquor was, directly or indirectly, the cause of strained lamellar growth.

L. L. Bircumshaw.

Space-lattice of *i*-erythritol. N. Schonfeldt, K. Herrmann, and O. Hassel (Z. physikal. Chem., 1926, **124**, 305—317; cf. Burgers, A., 1926, 339).—The *X*-ray diagram of *i*-erythritol shows that the unit cell is space-centred, has a volume of $1116{\cdot}72\times10^{-24}$ cm.^{3}, and contains eight molecules. The molecules are symmetrical with respect to a centre of inversion. Thus both the active and the *meso* forms have the space formula (I), but in the active form the $-CH_2\cdot OH$ groups lie in front of the plane of the paper, whilst in the *meso* form the lower one lies behind it.



(I.)

R. Cuthill.

Structure of soil colloids. J. Duclaux (2me. Cons. Chim. Inst. Intern. Chim. Solvay, 1926, 91—123).—Both cellulose nitrate and cellulose films have the properties of a uniaxial crystal cut perpendicular to its axis; whatever be the conditions under which the film is formed, the birefringence remains constant. It is concluded that cellulose in a normal condition can be likened to a uniaxial crystal and that the biaxial varieties are oriented. Work on the birefringence and *X*-ray investigations of nematic soil colloids is discussed.

Chemical Abstracts.

Recrystallisation centres in metals. A. E. van Arkel and P. Koets (Z. Physik, 1927, **41**, 701—707).—It is shown that the number of crystals of γ-iron in mechanically deformed strips of steel is approximately proportional to the number of crystals of α-iron in the undeformed strips.

R. W. Lunt.

Matthiessen's rule. W. Geiss and J. A. M. van Liempt (Z. Physik, 1927, **41**, 867—871).—The temperature coefficients of resistance of cold-wrought pure tungsten, molydenum, nickel, and platinum have been compared with those of samples of the metals treated in various ways. Although the specific resistance of each group of samples varies considerably, Matthiessen's rule (Ann. Physik, 1864, **122**, 47) that

the product of the specific resistance and the mean temperature coefficient of resistance is a constant has been verified for these metals. R. W. LUNT.

Electrical properties of some metallic compounds. H. ANDRÉ (Compt. rend., 1927, **184**, 741—742).—Compounds of silver with sulphur or phosphorus will absorb a further quantity of these elements, in the fused state, at low temperatures. Their electrical resistances then decrease regularly with rise of temperature, particularly when sulphur is present, within limits which vary according to the sample. Direct current slowly displaces the silver, but alternating current at low temperatures has no apparent effect. J. GRANT.

Conduction of electricity by heavy metal sulphides. C. TUBANDT and M. HAEDICKE (Z. anorg. Chem., 1927, **160**, 297—317).—At temperatures between 200° and 300°, compressed cylinders of black antimony trisulphide, lead sulphide, stannic sulphide, and molybdenum disulphide behave as purely metallic conductors. Cadmium sulphide is a non-conductor up to 250°, above which temperature it becomes a metallic conductor, its conductivity increasing rapidly with rise of temperature. Red antimony sulphide and yellow arsenic sulphide remain non-conductors below their transformation and m. p., respectively. Silver sulphide and cuprous sulphide are therefore the only electrolytic and mixed conductors (in the β-modifications) among the heavy metal sulphides. The double sulphides of silver with arsenic and antimony sulphides behave, like α silver sulphide, as purely electrolytic conductors in which the arsenic and antimony sulphides are inert constituents, only the silver ion migrating under the influence of the current. A. R. POWELL.

Dependence of surface tension on electric charge. O. RUFF, G. NIESE, and F. THOMAS (Ann. Physik, 1927, [iv], **82**, 618—626).—The relation between the surface tension on a spherical droplet of a conducting material and the density of the electrical charge has been investigated. The equation $\sigma'=\sigma-\pi\rho\varepsilon^2-p/2\rho\pi$ (ε is the density of the charge in e.s.u., σ is the normal surface tension, σ that of the charged droplet, ρ the radius) is deduced and confirmed experimentally for mercury. R. A. MORTON.

Behaviour of drops and drop-electrodes in high electrical fields. O. RUFF, G. NIESE, and F. THOMAS (Ann. Physik, 1927, [iv], **82**, 631—638).—The behaviour of drops of a variety of organic and inorganic materials in electric fields of high intensity has been investigated with respect to atomisation, brush discharge, phosphorescence induced when the particles fall into liquid air, viscosity, and surface tension. Atomisation occurs with a field of 20,000 volts in all the liquids tested except fused metallic elements and alloys. Liquids exhibiting low values for viscosity and surface tension are readily converted into sprays. The charge has only a small effect on the surface tension. The brush discharge observed at the orifice of the capillary is especially marked for glycerol, wax, fatty oils, phenanthrene, phenyl salicylate, and dextrin solution. The phosphorescence excited when the charged particles fall into liquid air is very marked for diphenylamine, ethyl benzoate, gelatin solution, paraffin oil, and glycerol. The sodium and potassium eutectic exhibits a bright yellow glow as the droplets fall in an atmosphere of hydrogen at pressures below one atmosphere. R. A. MORTON.

Unipolarity of lead sulphide. H. LUKE (Physikal. Z., 1927, **28**, 213—221).—Thieme's observation (*ibid.*, 1916, **17**, 615) that etched or roughened metals and crystalline alloys show unipolarity is denied. The compressed powder of crystalline lead sulphide behaves similarly to the crystal. Heating does not affect the unipolarity of large crystals, but increases the unipolarity of the compressed powder. Chemically-prepared lead sulphide shows no unipolarity, but heating at 150° or outgassing in a vacuum confers unipolarity on the resulting material. Heating at 600° causes the unipolarity to be reversed. The removal of moisture and gas from the compressed powder increases the unipolarity. W. E. DOWNEY.

Transverse thermo-electric effect in metal crystals. P. W. BRIDGMAN (Proc. Nat. Acad. Sci., 1927, **13**, 46—50).

Magnetic properties of various substances. S. BERKMAN and H. ZOCHER (Z. physikal. Chem., 1926, **124**, 318—326).—The magnetic susceptibilities of a number of dyes and metallic oxides and salts have been determined by measuring the force exerted upon them in a non-uniform magnetic field. R. CUTHILL.

Calculation of magnetic susceptibility of sodium chloride from data on intensities of *X*-ray reflexions. E. S. BIELER (Trans. Roy. Soc. Canada, 1926, [iii], **20**, III, 489—495).—A method of calculating the susceptibility of a diamagnetic atom from the electron distribution curve is described. The values calculated from available data for sodium chloride are rather larger than the experimental values, but the agreement is such as to justify the calculation of electron distribution from *X*-ray reflexion data. R. CUTHILL.

Measurement of resolving power of photographic materials. O. SANDVIK (J. Opt. Soc. Amer., 1927, **14**, 169—177, and Z. wiss. Phot., 1927, **24**, 336—347).—Resolving power, as determined by the parallel line method, decreases linearly with the logarithm of the ratio width of line/width of space. L. F. GILBERT.

Extinction coefficient measurements with diverging light. D. S. VILLARS (J. Opt. Soc. Amer., 1927, **14**, 29—32).—The divergence of the light beam from a monochromator slit introduces less than 0·5% error in extinction coefficient measurements if the ratio of the total light transmitted rather than the ratio of the intensities is used in the calculations. The use, in photo-chemical work, of parallel light, produced at the expense of intensity, is therefore often unnecessary. L. F. GILBERT.

Preparation and optical properties of calcium hydroxide crystals. F. W. ASHTON and R. WILSON (Amer. J. Sci., 1927, [v], **13**, 209—218).—Calcium hydroxide crystals obtained by various methods, which are described, show the same crystal

form and refractive indices. The crystals belong to the hexagonal system and occur as short hexagonal prisms or plates with perfect cleavage parallel to the (0001) face. The refractive indices are $\omega = 1{\cdot}574 \pm 0{\cdot}003$, $\varepsilon = 1{\cdot}545 \pm 0{\cdot}003$ for sodium light. Birefraction is 0·029; d_4^{20} 2·230±0·005; interference figure is uniaxial negative. The lattice constants are $a_0 = 3{\cdot}579$, $e_0 = 5{\cdot}028$ Å.; the unit cell contains one molecule. C. J. SMITHELLS.

Specific heats of a highly-cooled non-condensed phase. J. E. VERSCHAFFELT (Compt. rend., 1927, **184**, 603—604).—The author disagrees with the assumptions of Perrakis (this vol., 101; de Kolosovski, *ibid.*, 301). J. GRANT.

Limiting value of latent heat of vaporisation at the absolute zero. J. J. VAN LAAR (J. Chim. phys., 1927, **24**, 115—119).—The latent heat of vaporisation does not tend to zero at the absolute zero of temperature, as stated by de Kolosovski (A., 1926, 1198). The internal latent heat comprises two terms, the thermal energy and the potential energy; according to Nernst's heat theorem, the thermal energy may become zero at 0° Abs., but the potential energy, which is represented by a term of the form a/v, could only do so if the volume v of the liquid were to vanish. Onnes has shown experimentally that the latent heat of helium reaches a minimum at 1·5° Abs. and then increases with falling temperature, which is explained by the variation (with temperature) of the constants a and b of the equation of state; b increases with falling temperature, but a reaches a maximum at a very low temperature and then decreases, reaching a limiting value at 0° Abs. Contrary to de Kolosovski's assertion, Kirchoff's law for the variation of latent heat with temperature holds at very low temperatures. S. J. GREGG.

Thermal decomposition of nitrosyl chloride. H. A. TAYLOR and R. R. DENSLOW (J. Physical Chem., 1927, **31**, 374—382; cf. Trautz and Gerwig, A., 1925, ii, 878).—The decomposition of nitrosyl chloride has been investigated between 700° and 900° by a dynamic method in which the rapidity of the reverse reaction was overcome by an increased rate of flow of the gas, by diluting with nitrogen. The effect of an increased surface (quartz) was negligible, and the temperature coefficient and energy of activation apparently have the values 1·025 and 6000 g.-cal., respectively. On the radiation theory, this energy of activation at the temperatures employed corresponds with a wave-length of 4·769 μ, which does not correspond with any known absorption band in the spectrum of nitrosyl chloride. L. S. THEOBALD.

Thermal conductivity of carbon dioxide. H. GREGORY and S. MARSHALL (Proc. Roy. Soc., 1927, **A, 114**, 354—366).—The discrepancies in the absolute values of the thermal conductivity of carbon dioxide, as determined by various observers either by the cooling-thermometer method or the hot-wire method, are probably due to the practice of attempting to eliminate convection losses by reducing the pressure. Such a procedure is justified only if the reduction of pressure is not carried beyond the point at which the mean free path of the molecules becomes comparable with the dimensions of the containing vessel. The apparatus used in the present investigation is a modification of that described by Gregory and Archer (A., 1926, 231), using a vertical instead of a horizontal system of tubes, and taking every precaution to eliminate convective losses. Six series of readings were taken, corresponding with six wire temperatures varying from 8·908 to 25·147°, the thermostat temperature being maintained at 0°. By plotting the values of the absolute thermal conductivity against the corresponding mean gas temperatures, it is found by extrapolation that the value at 0° is $3{\cdot}604 \times 10^{-5}$ g.-cal. cm.$^{-1}$ sec.$^{-1}$ deg.$^{-1}$ The temperature coefficient of thermal conductivity in this region, deduced from the slope of the curve, is 0·0027. L. L. BIRCUMSHAW.

Heat conductivity of gases. S. WEBER (Ann. Physik, 1927, [iv], **82**, 479—503).—Further refinements have been introduced into the improved Schleiermacher method. The new measurements result in a value of $573{\cdot}8$—$574{\cdot}2 \times 10^{-7}$ for the absolute heat conductivity of atmospheric air at 0°; the earlier value was $568{\cdot}0 \times 10^{-7}$. For neon, the new value is 1104×10^{-7}, the old was 1089×10^{-7}; for carbon dioxide, the corresponding values are $343{\cdot}1 \times 10^{-7}$ and $339{\cdot}3 \times 10^{-7}$. The source of this discrepancy of about 1% has not been traced. R. A. MORTON.

Uncondensed systems at low temperatures. N. PERRAKIS (J. Chim. phys., 1927, **24**, 169—172).—It is demonstrated thermodynamically that the molecular heat of any gas at a sufficiently low temperature becomes identical with that of a monatomic gas, thus confirming Eucken's data for the specific heat of hydrogen at low temperatures (A., 1912, ii, 232). H. F. GILLBE.

Density of water vapour. T. SHIRAI (Bull. Chem. Soc. Japan, 1927, **2**, 37—40).—A sealed bulb containing a weighed quantity of water was broken by electrical heating, thus releasing its contents into the enlarged top of a barometer tube, on which the pressure was read. The mol. wt. of water so obtained never deviated by more than 0·3% from the theoretical value for unassociated water molecules, over the range 80—140°. S. J. GREGG.

Simple proof of the failure of Dalton's law for real gases. M. JAKOB (Z. Physik, 1927, **41**, 737—738).—It is shown that Dalton's law of partial pressures does not apply to gases for which pv is not constant with increasing p. W. E. DOWNEY.

Pressure effect on mixing gases. M. JAKOB (Z. Physik, 1927, **41**, 739—742).—From the measurements of the isotherms of helium, neon, and helium–neon mixtures by Holborn and Otto (A., 1925, ii, 851), it is deducible that when helium and neon, both at the same pressure, are mixed, under constant volume and isothermal conditions, a comparatively large pressure alteration is to be expected. W. E. DOWNEY.

Vapour pressure of liquid oxygen and nitrogen. B. F. DODGE and H. N. DAVIS (J. Amer. Chem. Soc., 1927, **49**, 610—620).—The vapour pressure of oxygen is given by $\log_{10} p(\text{atm.}) = -372{\cdot}808/T + 4{\cdot}18939 - 0{\cdot}0006195T$, or, less accurately, $\log_{10}$ $-366{\cdot}523/T + 4{\cdot}06295$; that of nitrogen is given by $\log_{10} p = -316{\cdot}824/T + 4{\cdot}47582 - 0{\cdot}0071701T + 2{\cdot}940 \times 10^{-5}T^2$,

or $\log_{10} p = -304{\cdot}494/T + 3{\cdot}93352$. The simpler relations hold remarkably well over a very large pressure range up to the critical point. S. K. TWEEDY.

Vapour pressures of hydrogen cyanide. H. SINOZAKI, R. HARA, and S. MITSUKURI (Tech. Repts. Tohoku Imp. Univ., 1927, 6, 157—167).—An accurate method of determining the vapour pressures of liquid and solid hydrogen cyanide is described. Vapour-pressure equations derived from measurements made between 187·09° and 319·30° Abs. have been calculated and the following constants deduced: m. p. $-13° \pm 0{\cdot}1°$, heat of fusion 1942 g.-cal./mol., heat of sublimation at a number of temperatures including the value 8768 g.-cal./mol. at the m. p., heat of vaporisation at a number of temperatures including the value 6484 g.-cal./mol. at the b. p. 25·8°, the chemical constant 3·58. M. S. BURR.

Van der Waals' equation at the critical point. V. KIREJEV (Z. Elektrochem., 1927, 33, 91—94).—Theoretical. The ordinary solution of van der Waals' equation at the critical point leads to three values of the constant a in terms of the critical constants and, on substituting experimental critical data, these values are usually notably divergent. The value $a = 27R^2T_c^2/64p_c$ and the corresponding value $b = RT_c/8p_c$ give best agreement when substituted in van der Waals' equation at the critical point. Moreover, such values of a for various substances give values of $(p_c + k_c)v_c$, where $k_c = a/v_c^2$, which agree with the corresponding values of $T_c v_c (dp/dT)_c$ obtained from independent data for $(dp/dT)_c$ previously calculated (A., 1926, 1088). Hence, $k_c = 3\alpha^2 p_c$, where $\alpha = 3RT_c/8p_c v_c$; if α has its mean value, 1·42, for normal substances, $k_c = 6{\cdot}1 p_c$ instead of the usual relation $k_c = 3p_c$. The reduced equation of state then becomes: $[\pi + 3(\alpha/\phi)^2][3(\phi/\alpha) - 1] = 8\theta$, which is converted into the usual reduced van der Waals equation when $\alpha = 1$.

H. J. T. ELLINGHAM.

Compressibility isotherms of hydrogen, nitrogen, and mixtures of these gases at 0° and pressures to 1000 atm. E. P. BARTLETT (J. Amer. Chem. Soc., 1927, 49, 687—701).—The observed compressibilities of hydrogen and nitrogen agree with those found by Verschoyle (A., 1926, 894); they are slightly lower (0·5—0·7%) than Amagat's values at low pressures, but for nitrogen agree closely with his values at high pressures (800—1000 atm.). The compressibility of a mixture of the gases is not a linear function of the composition. Empirical relationships are deduced. The normal density of hydrogen is 0·08982 g. per litre. S. K. TWEEDY.

Molecular association in the liquid state. K. M. STAKHORSKY (J. Chim. phys., 1927, 24, 204—208).—The degree of association of a number of liquids at various temperatures has been calculated from existing surface tension data, and is shown to decrease with increase of temperature and with increase of mol. wt. If the degree of association of water be calculated by the same method, an abnormally high value is obtained at low temperatures, owing to the anomalous variation of density with temperature in the neighbourhood of 4°.

H. F. GILLBE.

Molecular states of liquids. E. GAPONE (Ukraine Chem. J., 1926, 2, 321—329).—Various formulæ for the calculation of the internal compression of liquids are given and it is concluded that the equation, $P(Mv)^{2/3}.T_s - 0{\cdot}113$, where P is the internal compression, represents the facts best. It is found that the internal compression (112·3) of chlorobenzene is approximately equal to that of dimethylaniline (115·2), whence the above constant is calculated. It is concluded that there is no evidence for supposing that there is greater internal pressure in liquids the molecules of which are associated than in those the molecules of which are not.

E. ROTHSTEIN.

Measurement of surface tension. N. E. DORSEY (U.S. Bur. Standards Sci. Paper 540, 1926, 21, 563—595).—Seventeen of the more important methods of measuring surface tension are described, the most frequent sources of error considered, and methods whereby they may be avoided described in detail. The working equations applicable to each method are given, and a number of inaccuracies in the literature are pointed out. H. F. GILLBE.

Surface tension of solids. N. K. ADAM (Phil. Mag., 1927, [vii], 3, 863—864).—It is shown that the assumption made by Antonov (A., 1926, 671), that the surface tension of a solid is the same as that of a liquid which neither rises nor falls in a capillary tube made of the solid, is incorrect and that *the* quantity responsible for the condition of equilibrium is the work of adhesion of the liquid to the solid. It is thought to be improbable that any relationship can exist between this quantity and the surface tension of a solid. A. E. MITCHELL.

Variation of logarithmic decrement with amplitude and viscosity of certain metals. IV. G. SUBRAHMANIAM (Phil. Mag., 1927, [vii], 3, 854—857; cf. *ibid.*, 1926, [vii], 1, 1074).—Determinations of the viscosities of a number of metals from measurements of the logarithmic decrements of the amplitudes of vibration when wires are vibrating in states of maximum torsional elasticity, indicate that the coefficient of most metals is of the order 10^8 poises. This value is in agreement with that obtained by Iokibe and Sakai (*ibid.*, 1921, [vi], 42, 397), but is very different from those obtained by other observers.

A. E. MITCHELL.

Viscosity of ether at low temperatures. E. H. ARCHIBALD and W. URE (J.C.S., 1927, 610—614; cf. A., 1924, i, 493).—Measurements have been made of the viscosity of ethyl ether over a temperature range of 0° to −110°. The temperature coefficient of the viscosity increases rapidly, as the temperature falls, from 0·99 between 0° and −10° to 3·24 between −100° and −110°. M. S. BURR.

Diffusion in solutions. E. ULLMANN (Z. Physik, 1927, 41, 301—317).—Furth's micro-method for the determination of the velocity of diffusion in solutions has been improved so that diffusion coefficients of coloured solution can be obtained within 6%. Measurements on solutions of neutral-red and trypanon-red show that the coefficient of diffusion varies with the concentration in agreement with Fick's law, the values given for infinite dilution being

$4{\cdot}2\times10^{-6}$ and $3{\cdot}5\times10^{-6}$. The size of the particles has been calculated from Einstein's equation (Ann. Physik, 1905, [iv], **17**, 549—560). For potassium permanganate solution, Fick's law has been found to hold for concentrations up to 1 or 2%. The coefficient of diffusion for infinite dilution is $15{\cdot}2\times10^{-6}$, in good agreement with the value $15{\cdot}9\times10^{-6}$ calculated from Nernst's diffusion equation. Data obtained for solutions of ferric saccharate are employed to derive an expression for diffusion in concentrated solutions, according to which it appears that the rate of diffusion is not proportional to the gradient of the concentration. The rate of diffusion is given within 10% by the first two terms of an exponential series in which the coefficients are themselves functions of the concentration. R. W. LUNT.

Pressure of gaseous mixtures. J. E. LENNARD-JONES (Nature, 1927, **119**, 459).—Published results show that the pressure of a gaseous mixture may be greater than that of either of its constituents, even when the molecular concentration and temperature are in all cases the same. Cohesive forces between molecules tend to diminish the pressure, whilst repulsive forces tend to increase it; the relationship of the effects depends on the temperature.
A. A. ELDRIDGE.

Properties of mixtures of acetone and *iso*propyl alcohol. G. S. PARKS and C. S. CHAFFEE (J. Physical Chem., 1927, **31**, 439—447).—The behaviour of this system departs markedly from the ideal. Mixing is accompanied by absorption of heat, amounting to 387 g.-cal./g.-mol. in the case of the equimolar mixture. The heats of mixing were determined at 20°, and densities and refractive indices at 25°. An increase in volume, on the average 0·3%, accompanies the mixing. The vapour pressures observed at 25° and the partial pressures of the components of the various mixtures are larger than the values calculated from Raoult's law. The viscosities at 25°, measured in an Ostwald viscosimeter, show an average negative deviation of 34% from the values given by the cube-root equation of Kendall (A., 1920, ii, 670). The results indicate that pure *iso*propyl alcohol is associated to some extent, and that the addition of acetone causes dissociation of the associated molecules. L. S. THEOBALD.

Significance of dielectric constant of a mixture. H. H. LOWRY (J. Franklin Inst., 1927, **203**, 413—439).—A review of the literature showing that the dielectric constant of a mixture cannot in general be calculated from the data for the components.
R. A. MORTON.

Systems formed by certain inorganic compounds with liquid sulphur dioxide. H. T. BEACH and P. A. BOND (Proc. Iowa Acad. Sci., 1925, **32**, 328—329).—An investigation of the solubility relationships of carbon, titanium, and tin tetrachlorides, tin tetrabromide, and tin tetraiodide with liquid sulphur dioxide. CHEMICAL ABSTRACTS.

Formulæ for the azeotropic constants for mixtures of alcohols and halogen compounds. M. LECAT (Compt. rend., 1927, **184**, 816—818).—Formulæ are given for the azeotropic lowering (A., 1926, 1199) in the case of mixtures of an alcohol (methyl alcohol, ethyl alcohol, propyl alcohol, *iso*butylcarbinol, or glycol) with one of a number of organic halides. In general, the observed and calculated values agree for the mono- but not for the di-halogen derivatives. Trihalogen compounds agree with the formula, except in the case of methane derivatives, which evolve heat when mixed with ethyl alcohol. Carbon tetrachloride appears to be normal.
J. GRANT.

Partial molal volumes of water and salt in solutions of the alkali halides. V. K. LAMER and T. H. GRONWALL (J. Physical Chem., 1927, **31**, 393—406).—A method for the calculation of the partial molal volumes of water, $\partial v/\partial n_0$, and of a salt, $\partial v/\partial n$, where n_0 and n are the number of mols. of water and salt, respectively, contained in a volume v of solution, from density determinations is described. Values for water and the alkali halides at 0°, 25°, and 50° have been calculated from the equations $\partial v/\partial n_0 = a_0+a_2m^2+a_3m^3+a_4m^4$ and $\partial v/\partial n = +b +b_2m^2+b_3m^3$, where m is the molality, and a_0, b_0, etc. are constants, which have been evaluated from the density data of Baxter and Wallace (A., 1916, ii, 219). These values are tabulated and discussed. The density data for potassium chloride at the above temperatures, and for rubidium chloride and cæsium iodide at 0°, may be sufficiently in error to account for certain irregularities, but the values for the remaining chlorides are mutually consistent. The results, and especially the effect of temperature, are discussed in relation to the theory of Webb (A., 1926, 1208).
L. S. THEOBALD.

***X*-Ray study of alloys of lead and thallium.** E. MCMILLAN and L. PAULING (J. Amer. Chem. Soc., 1927, **49**, 666—669).—*X*-Ray powder photographs of a series of lead–thallium alloys at the ordinary temperature show the presence of two solid solutions, one having the structure of lead and the other the low-temperature structure of thallium. There are no indications of the existence of the compound $PbTl_2$ (Lewkonja, A., 1907, ii, 261). S. K. TWEEDY.

Solubilities and densities of saturated solutions of sodium and potassium halides at 25°. A. F. SCOTT and W. R. FRAZIER (J. Physical Chem., 1927, **31**, 459—463; cf. Baxter and Wallace, A., 1916, ii, 220).—The densities at 25° and solubilities (g. salt/100 g. water) recorded are: sodium chloride, 1·19796, 26·406; bromide, 1·54181, 48·61; and iodide, 1·91901, 64·76; potassium chloride, 1·17786, 26·38; bromide, 1·37937, 40·57; and iodide, 1·72111 and 59·75.
L. S. THEOBALD.

Solubility. X. Solubility relations of stannic iodide. M. E. DORFMAN and J. H. HILDEBRAND (J. Amer. Chem. Soc., 1927, **49**, 729—737).—The solubility of stannic iodide between 10° and 40° in nine organic solvents and in sulphur at 104° and 130° is recorded. The specific volume of liquid stannic iodide between 145° and 275° is given by $v=0{\cdot}2368(1+0{\cdot}00079t)$. The solubilities in these solvents and in iodine and methylene iodide agree well with the relative internal pressures of the substances, although there is no strict proportionality. Ideal solutions are obtained with sulphur and with iodine; the heat of fusion of stannic iodide is calculated to be 4000 g.-cal./mol. S. K. TWEEDY.

Solubilities of metallic derivatives of nitrosophenylhydroxylamine. A. PINKUS and F. MARTIN (J. Chim. phys., 1927, **24**, 83—102).—The application of potentiometric and conductivity methods is complicated by the tendency of the compounds to polymerise. An "indirect" colorimetric method is suggested as an alternative. Results obtained by the conductivity method for the ammonium and potassium salts are recorded. The values derived for λ_0 are 93·0 and 86·0, respectively. The mobility of the nitrosophenylhydroxylamine ion deduced from the potassium salt is 21·3 and from the ammonium salt 27·8, the divergence being explained by the instability of the ammonium salt. S. J. GREGG.

Solubilities of metallic derivatives of nitrosophenylhydroxylamine. II. A. PINKUS and F. MARTIN (J. Chim. phys., 1927, **24**, 137—168).—The solubilities of the nitrosophenylhydroxylamine salts of the following metals have been determined at 18° by potentiometric, colorimetric, and conductivity methods (cf. preceding abstract); the results are in g.-mol./litre, and are the mean values of all the determinations made: silver, $1{\cdot}4\times10^{-3}$; mercurous, $<6{\cdot}6\times10^{-7}$; lead, $1{\cdot}2\times10^{-4}$; copper, $1{\cdot}1\times10^{-5}$; cadmium, $3{\cdot}7\times10^{-4}$; bismuth 4×10^{-5}; antimonious, $4{\cdot}5\times10^{-5}$; stannous, $3{\cdot}5\times10^{-5}$; stannic, 2×10^{-5}; iron, 3×10^{-7}; aluminium, $3{\cdot}4\times10^{-5}$; nickel, $8{\cdot}9\times10^{-4}$; cobalt, $1{\cdot}3\times10^{-3}$; zinc, $4{\cdot}9\times10^{-4}$. Arsenious, arsenic, and antimonic salts are not precipitated by cupferron. A scheme has been drawn up for a systematic examination of the employment of cupferron in gravimetric analysis. The electrochemical method of determining the solubilities of sparingly soluble substances has been modified so that it may be employed for compounds of unknown composition; comparison of the results obtained by this method and by the classical method indicates that whereas the precipitates formed by silver, copper, cadmium, and zinc are ionised normally in saturated aqueous solution, giving a cation of the metal and an anion of nitrosophenylhydroxylamine, the compounds of lead, nickel, and cobalt exist in solution largely as complexes.

The equivalent conductivities of aqueous solutions of cupferron and of its potassium derivative have been measured at 18°. The degree of ionisation of the salt and the mobility of the anion have been calculated at a number of concentrations between 0 and 0·1 g.-mol./litre. H. F. GILLBE.

Solubility. (Ternary systems of two salts in a volatile solvent.) C. TOURNEUX and (MLLE.) M. PERNOT (Bull. Soc. chim., 1927, [iv], **41**, 397—400).—Experimental technique is described, including a rapid and accurate method for the removal of the solid phase by means of a centrifuge.

S. K. TWEEDY.

Adsorption of gases by glass walls. IV. Methyl chloride and oxygen. M. CRESPI (Anal. Fís. Quím., 1927, **25**, 25—41; cf. Crespi and Moles, A., 1926, 1200).—The adsorption of methyl chloride by glass walls is given by $A=0{\cdot}25\times10^{-8}p^{3/5}$ or $0{\cdot}38\times10^{-8}p^{3\cdot5}$ per sq. cm. of surface, according as the glass is drawn into tubes or blown into bulbs. The corresponding values for oxygen are $0{\cdot}043\times10^{-8}p^{-3}$ and $0{\cdot}065\times10^{-8}p^{2/3}$. G. W. ROBINSON.

Adsorption of water vapour by charcoal. A. S. COOLIDGE (J. Amer. Chem. Soc., 1927, **49**, 708—721).—The adsorption isotherms of non-polar substances on charcoal are concave towards the log p axis, whereas those of polar substances are mostly convex. The explanation may lie in molecular association of the polar substance. Pure charcoal adsorbs only very small quantities of water, traces of inorganic impurities increasing the amount to a large extent. Similar results hold for ammonia. The hydrophobic nature of charcoal is offered as an explanation. For relative pressures (*i.e.*, absorption pressure/vapour pressure of liquid) below 0·1, the adsorption of water vapour obeys Henry's law over a range −30° to 218°. Above this, the pressure increases less rapidly than the concentration until a constant relative pressure of 0·5 is attained. The adsorption reaches a maximum at the triple point. The heat of adsorption at the ordinary temperature is approximately equal to the latent heat of evaporation of liquid water; it increases slightly as the concentration increases. At higher temperatures, it is smaller at low concentrations and increases more rapidly with rising concentration. The partial molal heat capacity of adsorbed water at low concentration is 38 g.-cal./mol.

S. K. TWEEDY.

Absorption of hydrogen and carbon dioxide by pyrophoric iron, nickel, and cobalt. I. N. I. NIKITIN (J. Russ. Phys. Chem. Soc., 1926, **58**, 1081—1094).—The absorption of hydrogen and carbon dioxide by finely-divided iron, cobalt, and nickel was investigated at various pressures and temperatures. The pyrophoric metals were obtained by the reduction of their carbonates with hydrogen at 520° for iron, and 350° for nickel and cobalt. At higher temperatures, the metal powders rapidly became crystalline, and lost much of their absorptive power. The addition of aluminium oxide raised the crystallisation temperature. Iron, which adsorbed hydrogen strongly at the temperature of liquid air, was inert between −80° and +16°, and at higher temperatures absorbed the gas in increasing quantities. The low-temperature surface absorption obeyed Freundlich's expression, $a=kp^{1/n}$. Carbon dioxide was strongly absorbed, even at the ordinary temperature. On heating at 500°, absorption of the gas by the metal and interaction took place. Nickel (which contained 9% of occluded gas impossible to remove) adsorbed hydrogen at low temperatures. A film of hydride is formed at the ordinary temperature, which begins to dissociate at 100°. The absorption of carbon dioxide was very slight at all temperatures. Cobalt and hydrogen gave variable results, whilst values with carbon dioxide were intermediate between those of iron and nickel. M. ZVEGINTZOV.

Absorption of gases by finely-divided metals. II. N. I. NIKITIN and W. I. SHARKOV (J. Russ. Phys. Chem. Soc., 1926, **58**, 1095—1100; cf. preceding abstract).—The preparation and absorptive properties of finely-divided lead, copper, and silver were investigated. No results could be obtained with pyrophoric lead, prepared by the reduction of the carbonate, as it became crystalline below 300°. Copper did not absorb hydrogen at all, and carbon

dioxide only in small quantities at −80°. Silver, prepared by coagulation of Bredig's colloidal solution, absorbed hydrogen and large quantities of carbon dioxide at low temperatures, but rapidly became crystalline at 150—200°.

Iron absorbed gaseous ammonia readily between −18° and 100° according to Freundlich's expression, but not at all at 500°. The absorptive power of cobalt is about one tenth that of iron, but persists up to 330°. Pyrophoric nickel could not be easily obtained, as it crystallised rapidly. Addition of precipitated aluminium oxide greatly increased its absorptive power, due, probably, to the specific adsorptive properties of the alumina.

M. Zvegintzov.

Chemical reactions and sorption phenomena. II. S. Liepatov (J. Russ. Phys. Chem. Soc., 1926, 58, 983—993; cf. A., 1926, 571).—The application of the law of mass action to sorption phenomena is investigated. The selective sorption of acid radicals by basic gels, and *vice versa*, from neutral salt solutions is considered as a heterogeneous chemical reaction, which takes place inside the solid phase, after an initial surface adsorption. The active mass of the solid sorbent does not remain constant. Various expressions for the kinetics of sorption processes are compared, and the bimolecular formula : $dx/dt = k(a-\gamma x)^2$, where γ is a constant due to secondary processes, is investigated experimentally for the systems : alcoholic starch–alcoholic potassium hydroxide, wool–nitric acid, and wool–hydrochloric acid. The agreement is satisfactory. Regarding the phenomenon as a balanced reaction salt, RA + acid HA′ RA′ + HA, an expression for the amounts of free RA′ and HA produced is deduced and tested for the systems nitroalizarin–copper acetate; manganese dioxide gel–copper acetate, manganese dioxide–cupric chloride. The agreement is very close. The effect of temperature is also studied. The theoretical significance of these results is pointed out, and the necessity of considering absorption and adsorption as fundamentally different phenomena is emphasised.

M. Zvegintzov.

Adsorption in salt solutions by manganese dioxide and general deductions from this phenomenon. I, II, and III. M. Geloso (Ann. Chim., 1926, [x], 6, 352—424; 7, 113—115).—The adsorption of salts from solution, more particularly by precipitated manganese dioxide, has been examined (cf. A., 1920, ii, 334; 1922, ii, 589; 1923, ii, 540; 1924, ii, 413). The variation in the properties of manganese dioxide precipitated under varying conditions was also studied. The main conclusions are summarised below. The composition of the manganese dioxide varies slightly but definitely with the conditions of precipitation. The precipitate is colloidal in nature, and is represented in general by the formula $80MnO_2,MnO$, the bivalent manganese oxide representing the "impurity" present in the colloid. This is more or less completely replaced by the adsorbed substance, the composition approaching more and more closely to the simple formula MnO_2 as the quantity of adsorbed substance is increased. A relatively smaller amount is displaced by iron than by nickel, but the total adsorption of the latter is less. This variation in the composition of the adsorbent is, however, negligible in the study of the adsorption phenomenon itself. The latter is specific and characteristic of the salt solution employed, being relatively the more marked the more dilute the solution. In no case was evidence of a definite compound between the adsorbed substance and the adsorbent obtained, the adsorption increasing with increasing concentration of the soluble salt towards a maximum value, which corresponds with saturation of the solid phase. The same results are obtained with a previously precipitated specimen of manganese dioxide, but the total adsorption is less (about 0·6 in the case of iron). This is presumably due to the smaller surface area of the adsorbent owing to the presence of larger grains. The effect of concentration, temperature, and acidity on the adsorption is similar to the corresponding effects on the hydrolysis of salt solutions. It would therefore seem that the adsorption involves a preliminary hydrolysis, and the subsequent substitution of the "impurity" in the adsorbent by one of the products of hydrolysis. Thus increase of temperature increases the amount of adsorption, whilst an increase in the acidity of the medium decreases it, but the decrease is less when a strong acid, such as sulphuric acid, is replaced by a weak acid, such as acetic or formic acid. For the same adsorbent, the same increase in the molecular concentration of the solution corresponds with the same increase in the number of molecules adsorbed, independently of the nature of the substance adsorbed. This increase in adsorption with concentration decreases with rise of temperature, but at no temperature is the adsorption independent of the concentration of the soluble salt. Previous digestion of the adsorbent decreases its surface area, and hence its adsorptive power, the decrease at any particular temperature being greater the longer the period of pre-digestion (but never vanishing), whilst for equal periods of digestion the decrease is greater the higher the temperature employed. After adsorption, however, the surface is no longer modified by contact with the solution, whatever the temperature. In some cases, adsorption proceeds with a definite velocity, and probably obeys the general law for velocity of reactions in heterogeneous systems. The adsorption is probably reversible, tending to attain a dynamic equilibrium, which, however, is established too slowly for satisfactory experimental investigation.

The green solution obtained by the reduction, in acid solution, of potassium permanganate by arsenious acid (Geloso, A., 1921, ii, 115) is a colloidal solution of manganese dioxide of composition $nMnO_2,MnO$, where n is much greater than 2. On keeping or warming, an oxide of manganese is precipitated; the composition of this varies continuously according to the conditions of its formation. In neutral solution, precipitation occurs during titration; with insufficient acid a yellow solution (Mn_6O_{11}) instead of a green (Mn_3O_5) is obtained, and with a large excess of acid the solution becomes rose-coloured (Mn_2O_3). The precipitates are not regarded as definite chemical compounds, since a very slight alteration in the conditions alters their composition. Addition of increasing quantities of silver ions or manganous

sulphate increases the proportion of oxygen present in the precipitate, which, in the latter case, approximates very closely to the composition MnO_2. Arsenic acid has a similar, but very much less marked effect, whilst potassium and nitrate ions are without action. A similar green solution is also obtained when concentrated sulphuric acid is added to a solution of potassium permanganate and an alkali arsenite (oxygen being evolved), but in this case both the liquid and the precipitated solid phases contain the same oxide, MnO_2. In this colloidal state, the manganese dioxide possesses a large adsorptive power, the "impurity" being displaced by adsorbed salts in the same manner as previously observed for precipitated manganese dioxide (cf. above), but to a much greater extent. On the assumption that the adsorption is reversible, the heat of adsorption is calculated with the aid of the laws of displacement of equilibrium with temperature variation, and (except at the b. p.) the calculated value of K in the equation $\gamma=KC^{\frac{1}{n}}$ (Geloso, A., 1923, ii, 540) agrees closely with those obtained experimentally. An exact determination of manganese by a modification of Knorre's method is given (cf. A., 1922, ii, 398). J. W. Baker.

Adsorption of ions by glass. H. Devaux and E. Aubel (Compt. rend., 1927, 184, 601—603).—The adsorption of ions by glass was determined by washing a column of glass-wool with a solution containing the ion concerned, and afterwards washing with distilled water. Glass adsorbs cations (*e.g.*, calcium, hydrogen, potassium, and quinine) reversibly, one ion being replaceable by another. Glass weakly decalcified by acids or by alkali metal salts will adsorb a single layer of calcium ions instantaneously. If the glass is strongly decalcified, penetration takes place into the glass corresponding with several layers of ions, and is a function of the time. Thus the glass behaves as a gel. J. Grant.

Simultaneous adsorption of ions from solution. I. Adsorption of metal ions by hydrated manganese dioxide. M. Mehrotra and K. C. Sen (J. Indian Chem. Soc., 1926, 3, 297—306).—The simultaneous adsorption of metallic ion pairs by hydrated manganese dioxide has been investigated for mixtures of barium and copper chlorides, barium and silver nitrates, barium and potassium nitrates, barium and aluminium nitrates, and silver and potassium nitrates. With the exception of silver, the adsorption of any metallic ion is decreased in presence of another adsorbable ion, but the sum of the adsorption of the two ions from a mixture is always greater than the adsorption of either of them alone. Adsorbed silver ion cannot be replaced by either potassium or barium ions, although the latter can be replaced by each other, and in general the greater the concentration of the replacing ion in solution the greater is the amount of adsorbed ion displaced. The cation is adsorbed to a greater extent from a salt which contains a highly adsorbable anion, the adsorption of barium from a mixture of its chloride and aluminium nitrate being greater than from pure barium chloride, and that of copper from a solution of copper chloride being increased in presence of sulphate. J. W. Baker.

Adsorption by metallic hydroxides. I. Adsorption of arsenious acid by precipitated ferric hydroxide. K. C. Sen (J. Physical Chem., 1927, 31, 419—429; cf. Boswell and Dickson, A., 1919, ii, 49).—The ferric hydroxide used was precipitated at approximately 25° from 2*N*-ferric chloride by excess of dilute ammonia, washed by decantation, and dialysed until free from chloride. Potassium chloride, which, in common with ammonium chloride, was found to have no effect on the adsorption by ferric hydroxide, was added to prevent peptisation. The adsorption of arsenious acid in varying concentrations by a fixed quantity of hydroxide was then measured. Ageing of the latter for 4 months resulted in a 50% decrease in adsorption (cf. Boswell and Dickson, *loc. cit.*). Equilibrium is reached in 3 hrs., and increased contact of the solute with adsorbent has no effect on the adsorption. The generalisation of Mecklenburg (A., 1913, ii, 676) has also been studied. Sodium arsenite is strongly adsorbed by ferric hydroxide, and the adsorption of sodium hydroxide is appreciable. When the total amount of solute remains constant, adsorption increases with the concentration of the solution, and when the concentration remains constant, it is proportional to the quantity of solute present.

L. S. Theobald.

Adsorption. XX. Adsorption of ions from mixtures of electrolytes by sols of ferric hydroxide and stannic acid, and ion-antagonism. S. Ghosh and N. R. Dhar (Kolloid-Z., 1927, 41, 223—229).—Quantitative experiments were carried out on the adsorption of anions by ferric hydroxide sols from mixtures of potassium sulphate with each of the following salts of potassium: bromate, iodate, oxalate, ferrocyanide, and chloride. Similar experiments were made with stannic acid sol in mixtures of potassium chloride and barium chloride, copper chloride and barium chloride, silver nitrate and copper sulphate. In general, the adsorption of a given electrolyte is repressed by the presence of another electrolyte, the degree depending on the relative adsorbability of the two ions and also on the adsorbent power of the colloid. The effect of the second electrolyte is most marked when the adsorbent power of the colloid is low. The adsorption of the sulphate ion by ferric hydroxide is increased in presence of hydrochloric acid or ferric chloride.

E. S. Hedges.

Hydrolytic adsorption. II. Adsorption of electrolytes by barium sulphate and liberation of acids and alkalis in presence of neutral salts. J. N. Mukherjee and J. K. Basu (J. Indian Chem. Soc., 1926, 3, 371—388).—Detailed results of experiments previously summarised (Mukherjee, A., 1925, ii, 1149) are given. The amount of acidity developed in a neutral solution of potassium chloride in presence of well-washed barium sulphate depends both on the concentration and nature of the acid present during the precipitation of the sulphate. If the precipitation is carried out in absence of acid, the well-washed precipitate kept in contact with acid for 48 hrs., and again well washed, it is possible by sufficient washing to remove the adsorbed acid, so that no acidity develops on treatment with potassium chloride solu-

tion. The acidity developed is therefore due to the liberation of hydrogen ions by interaction between the adsorbed acid and the neutral salt. The development of alkalinity or acidity when, in the precipitation of barium sulphate, one of the solutions is in excess (*loc. cit.*) is confirmed by *E.M.F.* measurements, and the variation of p_H with time is investigated. By electro-osmotic measurements, it is shown that the barium sulphate precipitated in presence of excess of barium chloride is positively charged, whilst it is negatively charged when potassium sulphate solution is in excess during the precipitation. This negative charge is reversed in the presence of 0·0004*N*-barium chloride solution. The washed precipitate obtained by mixing equal volumes of *N*-solutions of potassium sulphate and barium chloride has a slight negative charge, but when the potassium sulphate is replaced by *N*-sulphuric acid the precipitate carries a definite positive charge. The theoretical bearing of the results is discussed.

J. W. Baker.

Adsorption by a polar precipitate. III. Electro-osmotic experiments with silver iodide. J. Mukherjee and P. Kundu (J. Indian Chem. Soc., 1926, 3, 335—341).—The adsorption of ions from solutions of silver, potassium, barium, calcium, and aluminium nitrates, and of potassium chloride, sulphate, bromide, and iodide by carefully purified silver iodide (cf. Taylor and Beckley, A., 1925, ii, 855) has been studied by electro-osmotic measurements. The silver iodide carries a negative charge in contact with water. The order of adsorption of the cations is Ag>Al>(Ba,Ca)>K, silver reversing the charge on the precipitate. Unexpectedly, the iodide ion is only weakly adsorbed. The order of adsorption of the other anions is $Br'>NO_3'>Cl'>SO_4''$.

J. W. Baker.

Adsorption. I. Explanation of adaptability phenomenon. V. N. Krestinskaia (J. Russ. Phys. Chem. Soc., 1926, 58, 998—1017).—An investigation of the observations of Bayliss and Freundlich on the phenomenon of adaptability. Both reversible and irreversible adsorption reactions were investigated. In the reversible systems, charcoal–aqueous bromine and charcoal–acetic acid, the total adsorption was independent of whether the charcoal was added at once or in successive small quantities separated by time intervals. In the irreversible systems: charcoal–crystal-violet solution, benzoic acid–charcoal, many days were required for the attainment of equilibrium, and consequently the parallel experiments were not strictly comparable. A new method was devised, based on the principle of "action impulse," *i.e.*, the product of the active mass of the reactants into the time of action, which gave sets of results which could be compared. The phenomenon of adaptability was not observed in these circumstances, and must be ascribed to the fact that the systems in which it appeared were not in equilibrium.

M. Zvegintzov.

Surface tensions of water–alcohol mixtures. P. Brun (Compt. rend., 1927, 184, 685—687).—Comparative studies of the surface tensions of mixtures of water, ethyl alcohol, and an alcohol completely, partly, or non-miscible (propyl, *iso*butyl, and *iso*amyl alcohols, respectively) have been made. Triangular diagrams, analogous to those for the densities and refractive indices (A., 1926, 683), have been constructed, from which the composition of the mixtures may be determined. In no case does the simple mixture law hold for the surface tensions.

J. Grant.

Surface tension and viscosity of solutions of the hydroxides of potassium, sodium, lithium, thallium, and barium, and of sodium carbonate solution. O. Faust (Z. anorg. Chem., 1927, 160, 373—376).—The surface tension, viscosity, and specific gravity of solutions of the hydroxides of the alkali metals, barium and thallium, and of sodium carbonate have been determined at 20° for concentrations varying from 0·1 to 6*N*. In all cases, except thallous hydroxide, the viscosity increases rapidly and the surface tension slowly with the concentration; this effect is most marked with sodium hydroxide and least noticeable with potassium hydroxide. The viscosity of solutions of thallium hydroxide decreases with rise in concentration, probably owing to the lower state of hydration of the ions.

A. R. Powell.

Cell mitosis. W. D. Bancroft and C. Gurchot (J. Physical Chem., 1927, 31, 430—438).—When the surface tension of a drop of liquid is lowered locally at two opposite points, the drop tends to divide equatorially, along the line of the relatively highest surface tension.

L. S. Theobald.

Dielectric constants of dilute solutions of electrolytes. H. Sack (Physikal. Z., 1927, 28, 199—210; cf. A., 1926, 456).—The dielectric constants of certain aqueous solutions of electrolytes have been determined by the Nernst "bridge" method for concentrations of the order 0·00017—0·0013*M*. The expression $D_1=D_0(1-\alpha c)$ reproduces the experimental values (D_1 and D_0 are the dielectric constants of solution and solvent, respectively, c is the molar concentration, and α is a constant depending on the solute). The following values for α were obtained: sodium chloride, $7\cdot1\pm1\cdot2$; potassium chloride, $6\cdot9\pm1\cdot0$; lithium chloride, $7\cdot4\pm1\cdot4$; barium chloride, $16\cdot5\pm2\cdot8$; magnesium sulphate, $17\cdot3\pm2\cdot7$; copper sulphate, $19\cdot0\pm2\cdot3$; lanthanum nitrate, $24\cdot2\pm3\cdot4$; lanthanum chloride, $26\cdot5\pm3\cdot3$.

On the basis of the dipole theory of the dielectric constant of aqueous solutions, the author's expression $D=D_0(1-3\cdot0c)$, which is applicable only to uni-univalent salts, has been extended to multivalent ions. If d_1 is the drop in the dielectric constant of water due to the presence of a univalent ion, and d_z is that due to an ion of valency z, $d_z=d_1\sqrt{z^3}$. This expression gives, in conjunction with a value of 3·3 for d_1, a complete account of the experimental data, within the limits of error. The mathematical basis for the views expressed is discussed.

R. A. Morton.

Rotatory dispersion, in the ultra-violet, of aqueous solutions of tartaric acid containing boric acid. R. Descamps (Compt. rend., 1927, 184, 876—878).—Earlier experiments (this vol., 307) have been continued using widely different molecular pro-

portions of boric and tartaric acids. Where definite conclusions can be reached, the rotatory dispersion curves all belong to the anomalous complex type. The results are explained by the presence of at least two constituents of opposite optical activities and different dispersions. J. GRANT.

Anomalies of Raoult's cryoscopic law. A. JOUNIAUX (Bull. Soc. chim., 1927, [iv], 41, 308—313).—The abnormal mol. wt. obtained for metals in metallic solvents by cryoscopic methods (A., 1926, 116), as compared with those obtained by other methods, are shown to give the correct values when multiplied by the "coefficient of equivalence" of the solute with respect to the solvent (Guillet, A., 1906, ii, 357). If, from the point of view of structure and mechanical properties, 1% of tin in an alloy is equivalent to 2% of zinc, then the coefficient of equivalence of tin with respect to zinc is 2. The correction is inapplicable when allotropic changes occur (*e.g.*, in the thallium–tin system).
S. K. TWEEDY.

Preparation of sols by reduction with tobacco liquor. A. JANEK (Kolloid-Z., 1927, 41, 242—243).—A filtered, aqueous extract of a cigar produces colloidal gold on boiling with a dilute solution of gold chloride, the product being red, violet, or blue, according to the amount of tobacco liquor used. A similar experiment, using silver nitrate, gives a brown colloidal solution of silver. E. S. HEDGES.

Colloidal zinc. W. ENGELHARDT (Kolloid-Z., 1927, 41, 234—242).—An apparatus is described for the preparation of colloidal zinc in hot water by an electro-dispersion method, the influence of temperature, applied voltage, and duration of experiment on the stability of the product being investigated. Attempts to stabilise the product by previous addition of protective colloids were unsuccessful. The colloidal zinc, especially in hot solutions, is rapidly transformed into zinc oxide. The total zinc content of the sol was measured by adding 0·1*N*-sulphuric acid and titrating the excess with sodium hydroxide, and the content of free zinc by adding 0·1*N*-iodine and titrating the excess with sodium thiosulphate, or by analysis of the gaseous products of dispersion, or by measurement of the hydrogen produced on addition of acid to the colloid. The properties of colloidal zinc are described as regards colour, coagulation, viscosity, addition of electrolytes, and protection by other colloids. The system may be regarded as colloidal zinc in which the particles are protected by a sheath of zinc oxide. E. S. HEDGES.

Preparation and properties of colloidal and monoclinic sulphur in organic liquids. I. D. GARARD and (MISS) F. M. COLT (J. Amer. Chem. Soc., 1927, 49, 630—636).—Sulphur sols were prepared by passing hydrogen sulphide and sulphur dioxide into organic liquids, the dense precipitate being removed by filtration. The sulphur concentration obtained in benzene (taken as a typical liquid) is practically independent of the purity of the latter, the order of introduction of the gases, and the method of stirring. The deep yellow benzene sols contain 1·4—1·8% of sulphur and are almost unaffected by electrolytes; their high stability is probably not due to the protective action of acids or water. The sulphur dialyses through animal and cellulose acetate membranes more slowly than dissolved sulphur. Evaporation and freezing of the sol yield amorphous sulphur (? Sμ), and the solubility of crystalline sulphur in the sol is the same as in pure benzene. The sols in ethyl alcohol and glycerol are very unstable, the filtrate in the former case depositing all the sulphur as monoclinic crystals within 2 days. These crystals, some of which were remarkably stable, were also obtained from alcoholic ammonium polysulphide solutions.
S. K. TWEEDY.

Electrolytic preparation of colloidal silver halides. T. WEREIDE (Z. Physik, 1927, 41, 864—866).—Colloidal silver halides are produced when dilute solutions of hydrochloric, hydrobromic, and hydriodic acids are electrolysed between silver electrodes by alternating current of frequency 50 cycles per sec. The freshly-produced micelles have an abnormal mobility of 450×10^{-5} cm. sec.$^{-1}$/volt cm.$^{-1}$, which is reduced to the normal value for colloid particles by the addition of agar-agar.
R. W. LUNT.

Modification of the electric sign of colloids at will. A. BOUTARIC and (MLLE.) G. PERREAU (Compt. rend., 1927, 184, 814—816).—Two zones exist in the flocculation of colloidal solutions by multivalent electrolytes (this vol., 309). The *signs* of positive and negative colloids are reversed by the action of electrolytes with multivalent anions and cations, respectively, when the concentrations are such that flocculation does not occur. J. GRANT.

Non-existence of the amorphous state. P. P. VON WEIMARN and T. HAGIWARA (Koll.-Chem. Beih., 1927, 23, 400—427; cf. A., 1926, 338).—It is shown how von Weimarn's theory has led to the view that not only crystals, but all forms of matter possess a vectorial structure. The influence of the degree of dispersion of the structural elements of a substance on the vectorial character and the dependence of the degree of stability on the dimensions of the individual structural elements which occur in aggregates in the practically unoriented condition are considered. A summary is given of the conclusions reached from von Weimarn's theory which have been confirmed by the investigation of disperse systems in polarised light, and by *X*-ray examination. The views of Haber (A., 1922, ii, 553), relative to the conditions which give rise to crystalline or amorphous precipitates or sols, are criticised. L. L. BIRCUMSHAW.

Mechanical methods for dispersion of cellulose. P. P. VON WEIMARN (Kolloid-Z., 1927, 41, 258—260).—The author's method for the production of cellulose sols by means of the "dispersoid mill" is described. Nordlund's method for the dispersion of liquids (A., 1920, ii, 376) was applied to cellulose, using a concentration of 0·02—0·08 millimol. of sodium citrate per litre as the dispersion agent. Ultramicroscopic particles of cellulose were also observed in distilled water which had been vigorously shaken with filter-paper and kept, but the yield of colloid obtained by this method is too low to make it of practical use. E. S. HEDGES.

Influence of polymerisation on the Röntgen diagram. I. Polymerisation and amorphous Röntgen spectra. J. R. KATZ (Z. physikal. Chem., 1927, 125, 321—330).—The types of Röntgen spectra given by polymerised substances such as caoutchouc, proteins, and polysaccharides are discussed. From Keesom's work on liquids composed of small molecules (Proc. K. Akad. Wetensch. Amsterdam, 1922, 31, 87), it would be expected that the diameter of the chief amorphous ring would decrease sharply when the molecules aggregate to form a polymerised molecule. The Röntgen diagrams have been determined for styrene and *m*-styrene, isoprene and caoutchouc, acrylic acid and polymerised acrylic acid, di*cyclo*pentadiene and di*cyclo*pentadiene-caoutchouc, and tung oil. The results show that in no case is there any appreciable difference between the diameters of the chief rings given by the polymerised and unpolymerised molecules. H. F. GILLBE.

Colloidal phenomena in dye solutions. W. C. HOLMES (J. Amer. Chem. Soc., 1927, 49, 790—791).—Sparingly soluble rosaniline phenoxide, $C_{20}H_{20}N_3 \cdot OPh$, prepared by the fusion of rosaniline base with phenol, readily forms aqueous colloidal solutions. Dilution of such solutions is accompanied by a deepening of the colour, owing to the dissociation of the solute molecules; after a time, association occurs and the colour fades. Dilute alcoholic solutions are fairly stable. Spectrophotometric measurements are recorded. S. K. TWEEDY.

Spontaneous structure formation in vanadium pentoxide sols. H. ZOCHER and K. JACOBSOHN (Kolloid-Z., 1927, 41, 220—222).—An introductory paper to experiments which show that some sols separate spontaneously into two phases, one isotropic and dilute and the other anisotropic and concentrated. E. S. HEDGES.

Spontaneous structure formation and thixotropy in fresh vanadium pentoxide sols. J. JOCHIMS (Kolloid-Z., 1927, 41, 215—220).—A drop of 1—2% vanadium pentoxide sol was examined under the ultramicroscope during strong illumination, and the formation of radially disposed, angular, rod-like particles was observed, the process being accompanied by increase in viscosity. This change is due to heat radiation rather than to light, since the effect is not observed when the heat rays are filtered out. The same change is brought about by the addition of small quantities of sodium chloride, calcium chloride, or potassium sulphate, whilst higher concentrations of the electrolyte cause the formation of a thixotropic gel. E. S. HEDGES.

Formation of hailstones and cause of the polymorphic behaviour of ice. K. C. BERZ (Kolloid-Z., 1927, 41, 196—200).—Attention is directed to the similarity in structure between hailstones and gallstones, oolites, etc., particularly in regard to their formation in concentric shells, and it is suggested that the water passes into a colloidal state during the formation of hail. The known physical properties of solid water under different conditions of temperature and pressure are considered in the light of molecular association, and it is thought likely that a colloidal solution of polymerised molecules is produced in unassociated water molecules acting as the dispersion medium. E. S. HEDGES.

Continuity of electrical structure of colloid particles, ions, electrons, and sub-electrons. S. N. RAY (Kolloid-Z., 1927, 41, 193—195).—Theoretical. The ratio e/a, where e is the maximum charge on a particle irradiated by ultra-violet light and a the diameter of the particle, is a constant for a given colloidal substance. Consideration of the increase in charge of a particle resulting from the increase of the diameter by an element of length leads to a new "atomic" view of electricity differing from the electronic view. The cataphoretic motion of the particles is considered in this light. E. S. HEDGES.

Theory of the colloid reactions of the cerebrospinal fluid in reference to clinical practice. W. SCHMITT (Kolloid-Z., 1927, 41, 261—271).—A review of the colloid reactions of the cerebrospinal fluid. E. S. HEDGES.

Cerebrospinal fluid. A. STEIGMANN (Kolloid-Z., 1927, 41, 276—277).—In connexion with the work of Epstein and Rubinstein (this vol., 274) on the part of the cerebrospinal fluid precipitable by gold, the author points out that, in the inhibitive action of physiologically important substances on the reduction of silver sodium thiosulphate by hyposulphite, only cystine has an appreciable effect. It also appears to be necessary for the nitrogen to remain tervalent through the absence of acids. E. S. HEDGES.

Protected silver hydrosols. J. VOIGT (Kolloid-Z., 1927, 41, 271—275).—Addition of water to "collargol" causes partial precipitation of the colloidal silver, whilst with the silver sol "dispargen," complete precipitation occurs. The precipitated silver is peptised by the addition of small quantities of sodium chloride, and it is considered that small quantities of electrolytes are necessary for the stability of these sols. The minimal quantity of sodium chloride required to peptise completely the precipitate from diluted "dispargen" was determined. E. S. HEDGES.

Colour and sensitiveness to light of silver sols. E. WIEGEL (Z. wiss. Phot., 1927, 24, 316—325).—The slow change of colour of dextrin silver sols through orange, purple-red, and violet to blue is due to the presence of the sodium hydroxide used in their preparation. The time necessary for the coagulation to attain a given stage is greater the smaller the concentration of the sodium hydroxide originally present. Coagulation is also accelerated by the action of light, especially that of small wave-length. Spectrometric measurements in which the extinction coefficient is plotted against wave-length show well-defined maxima for the purple-red, violet, and blue sols, and the sols obtained by rapid coagulation show several absorption maxima, due to the irregularity of flocculation. Sols having an identical colour by transmitted light may be different with reflected light, according to the method of preparation; if produced by slow coagulation, they show only a turbidity, since the colloidal particles consist of smaller particles not in complete optical contact, whereas if obtained

by rapid coagulation they exhibit a metallic lustre, the particles being of a compact structure.

S. J. GREGG.

Constitution of arsenious sulphide sol in presence or absence of arsenious acid. S. G. CHAUDHURY and P. KUNDU (J. Indian Chem. Soc., 1926, **3**, 345—348).—The atomic ratio of arsenic to sulphur in an arsenious sulphide sol in which arsenious acid is in excess is 1 : 1·46, whilst in another sol prepared by the action of an excess of hydrogen sulphide on arsenious acid, but in which both free arsenious acid and hydrogen sulphide are absent, the ratio is 1 : 2. The constitution of the former sol therefore corresponds with arsenic trisulphide and the latter either with As_2S_3,As_2S_5 or As_2S_3,H_2S, the latter being the more probable. J. W. BAKER.

Complexity and micelles. Ferric hydroxide sol as a typical example of the colloidal state. G. MALFITANO and M. SIGAUD (J. Chim. phys., 1927, **24**, 173—203).—An extensive investigation has been made of the properties of ferric hydroxide sol. The physico-chemical properties, studied chiefly from conductivity and osmotic pressure measurements, are shown to be those of electrolytic couples, with, however, a much greater tendency to association. Three types of flocculation are recognised: (1) When the solution is slightly opalescent, of a reddish-yellow colour, and does not show visible particles in the ultramicroscope, ultrafiltration effects no separation; (2) when the liquid is opaque, yellow-ochre in colour, but homogeneous to the eye, and shows distinct points of light in the ultramicroscope, ultrafiltration separates part of the colloid, which is said to be in the second stage of flocculation; the ultrafiltrate contains the colloid in the first stage of flocculation; (3) when the liquid commences to separate visibly into layers, ultrafiltration removes the whole of the colloid from solution, in what is termed the third stage of flocculation. The properties of the three forms of precipitate are: yellowish-red, and not sensibly reversible; dark red, and easily reversible; brick-red, and very resistant to the dissolving action of acids. Each precipitate is formed between certain limits of the ratio iron : chlorine, but is not necessarily of constant composition.

It is suggested that the precipitates are of the same type as Werner's co-ordination compounds; three forms are therefore theoretically possible: $\{[Fe(OH)_3]_6\cdot Fe\}^{+++}Cl_3^-$; $\{[Fe(OH)_3]_3\cdot FeCl\}^{++}Cl_2^-$; $\{[Fe(OH)_3]\cdot FeCl_2\}^{+}Cl^-$

A theory of micellary structure is built up from this point of view, and is adequately supported by a large amount of experimental evidence.

H. F. GILLBE.

Plant colloids. XVII. Peptisation of starch by ultra-violet light. M. SAMEC (Koll.-Chem. Beih., 1927, **23**, 377—399).—On exposing thin layers of potato starch in presence of air to the rays of a quartz lamp, the starch becomes yellow and the odour of acraldehyde is observed. The properties of solutions obtained by heating such starch with water under pressure indicate that considerable peptisation has occurred, together with a certain amount of oxidation and hydrolysis. The behaviour on electrodialysis depends on the length of exposure to ultra-violet light, the amount of "gel" being smaller the longer the time of exposure. The phosphorus remains largely in organic combination, and a simple organo-phosphoric acid can be isolated in the anode cell on electrodialysis. The cleavage products separated by ultrafiltration, although possessing a lower optical rotation, show the typical iodine colorations of the amylo-compound. The mean molecular magnitudes of such compounds have been determined. Observations have also been made at 50° on starch which has been previously dried, or washed with hydrochloric acid and dried and exposed to ultra-violet light in a stream of dry nitrogen and in closed vessels in an atmosphere of nitrogen, whereby oxidation and hydrolysis are prevented. The solutions prepared under pressure from the exposed starch are sometimes cloudy and deposit a precipitate on centrifuging. Wheat starch is also peptised by ultra-violet light, and in this case the behaviour of the solution on electrodialysis is the reverse of that of the unexposed starch. An explanation is offered for this. As with potato starch, a relatively simple organic acid containing phosphorus is found in the anode cell on electrodialysis. L. L. BIRCUMSHAW.

Complexity and micelles. G. MALFITANO and M. SIGAUD (J. Chim. phys., 1927, **24**, 103—109).—Colloidal particles are formed by the union of complexes, which in turn are micellar, produced by the grouping of x mols. of a non-electrolyte M about one or more ions, so that the charge is concentrated at the centre of the particle; these complexes may capture more ions, in which case the newly-acquired charge will be resident in the periphery. A primary complex would thus be represented as $(M_xa)^{\pm}b_r^{\mp}$, and a secondary as $[(M_xab_r)(M_xa)]^{\pm}b_r^{\mp}$. In flocculation, which consists in the union of complexes, growth proceeds mainly in geometrical progression, whilst in crystallisation, where atoms or molecules are added to much larger particles, it proceeds in arithmetical progression. The theory explains the three modifications of colloidal solution obtained by hydrolysing ferric chloride, since they are readily represented by $[Fe(FeO_3H_3)_m]^{+++}Cl_3$, $[Fe(FeO_3H_3)_mCl]^{++}Cl_2$, and $[Fe(FeO_3H_3)_mCl_2]^{+}Cl$. Moreover, the marked effect of the addition of anions of high valency in stabilising ferric chloride sol, contrasted with the negligible effect of cations, is also readily explained. S. J. GREGG.

Apparent viscosity of colloidal solutions. E. HATSCHEK (J. Physical Chem., 1927, **31**, 383—392).—McBain's hypothesis of ramifying micellar aggregates (A., 1926, 351) is adversely criticised. There is no direct evidence of the existence of these aggregates in viscous sols. The ultramicroscope gives little information on the structure of these sols, but there is direct evidence that high viscosity and even gelation may be exhibited by a sol without aggregation or even mutual approach of the particles. Furthermore, sorption experiments can give no information on the degree of hydration in true or in colloidal solution and its variation with concentration. The amounts of liquid taken up by gelatin or rubber during swelling show that the volumes of the disperse phase postulated by Hatschek's formula are not impossible

or improbable. An examination of the behaviour of rubber in benzene, carbon tetrachloride, and in tetrachloroethane shows that rubber swells more in the chlorine-substituted derivatives, *i.e.*, in those solvents in which it exhibits higher viscosities. This is in strict accordance with the assumptions and formula of Hatschek. Finally, if the viscosity of a sol varies with the shear gradient, then single measurements at arbitrary and unknown shear gradients have no theoretical value. L. S. THEOBALD.

Elasticity and some structural features of soap solutions. W. SEIFRIZ (Third Colloid Symposium Monograph, 1925, 285—295).—Elastic sodium stearate solution has rod-shaped particles, and curd masses crystallise from it; inelastic sodium stearate solution has spherical particles, and no curd crystallises. Sodium oleate is inelastic, and shows ultramicroscopic spherites. Ammonium oleate forms a highly elastic dilute solution, but concentrated solutions may be inelastic as sol, although elastic as gel. CHEMICAL ABSTRACTS.

Viscosity and flow-elasticity of starch paste. H. FREUNDLICH and H. NITZE (Kolloid-Z., 1927, **41**, 206—215).—The viscosity and flow-elasticity of starch paste rise rapidly with increasing concentration, and the high values are due mainly to the amylopectin in the outer sheath of the starch grain. As long as this retains its original membranous structure, the elastic properties do not appear, for a solution of the amylopectin prepared by warming is viscous, but inelastic. Addition of potassium thiocyanate to starch solutions produces a marked decrease in viscosity, and particularly in elasticity, which disappears altogether in a 2*N*-solution. Potassium chloride and potassium sulphate exert a similar effect, except that at higher concentrations the viscosity and elasticity rise once more. Ultramicroscopical observation shows that in solutions of potassium thiocyanate the membranes of the starch grains rapidly disappear. It is believed that amylopectin and amylose are peptised and subsequently broken down, with decrease in viscosity and elasticity. E. S. HEDGES.

Viscosity and hydration. II. Ageing and synæresis. S. LIEPATOV (Kolloid-Z., 1927, **41**, 200—206).—A sol of geranin-*G* exhibits "structure viscosity, and thus the particles cannot be regarded as independent spheres. Application of Hatschek's formula leads to a value for the density of the substance which is not in keeping with its true density, indicating that the particles are heavily hydrated. Measurements of the increase in viscosity and the change in volume of sols kept for 4 hrs. indicates that continuous hydration of the particles occurs, and this is believed to be the cause of the increased stability of emulsoid colloids with age. On the other hand, the decrease in stability and in viscosity of suspensoid sols with age is attributed to aggregation of the primary particles. With emulsoid colloids, the particles increase in size until the force of attraction between them is sufficient to give the rigidity of a gel. The liquid still separating the particles may then withdraw, accounting for the phenomenon of synæresis. Synæresis was not observed in gels of geranin-*G* more concentrated than 3%. E. S. HEDGES.

Velocity of coagulation of colloids by salts in the presence of a peptiser. K. JABŁCZYNSKI, G. KAWENOKI, and J. KAWENOKI (Rocz. Chem., 1926, **6**, 861—868).—The relative rates of coagulation of ferric hydroxide sols, peptised by ferric chloride, are, for equivalent quantities of potassium iodide, bromide, nitrate, and chloride, in the ratio 1 : 7·92 : 72·9 : 169, whilst potassium thiocyanate and acetate coagulate immediately, although, according to Schulze (A., 1883, 295) and Hardy (A., 1900, ii, 396), the effects produced by these univalent anions should be equal. The differences are attributed to chemical reaction between the ferric chloride and the added salt. This effect is well marked with the chlorides, and much less so with the iodide. In the case of thiocyanate and acetate, double decomposition occurs and iron is removed from solution. It is thus evident that the precipitating power of these anions is closely connected with their ability to combine with ferric chloride.

For chlorides of the alkali and alkaline-earth metals, the rates of coagulation give the following series: $Li > Na > K, NH_4 < Rb < Cs$; and $Mg > Ca > Sr > Ba$. Whereas the adsorption of cations increases with increasing atomic weight, this stabilising factor is opposed by the tendency towards the formation of double salts. R. TRUSZKOWSKI.

Volume changes in the formation of rubber sols. I. W. A. GIBBONS and E. HAZELL (J. Amer. Chem. Soc., 1927, **49**, 620—630).—The formation of rubber sols in xylene is accompanied by a small volume change, usually (above 30°) a contraction, which is greatest at high temperatures and low concentrations. This is in agreement with the known density change of rubber near 30°. The condition of the rubber (milling etc.) has no great influence on the volume change. S. K. TWEEDY.

Electrolytic coagulation of colloids. IV. Electrometric and conductimetric titration of mastic sols. A. J. RABINOWITSCH and R. BURSTEIN (Biochem. Z., 1927, **182**, 110—120).—The preparation of *a* and *b* mastic sols is described. The former is obtained by pouring water into an alcoholic solution of gum mastic, the latter by pouring the alcoholic solution into water. *a*-Sols when titrated with alkali give a conductivity curve with a sharp minimum, whilst *b*-sols show a continuous increase in conductivity with no minimum or break. The hydrogen-ion concentration of *a*-sols, but not of *b*-sols, determined by conductimetric and electrometric methods is the same. *b*-Sols filter very slowly. *a*-Sols are more acid than *b*-sols, and consist of smaller particles. Mastic sols, when coagulated by salt solutions, undergo no increase in acidity. Mastic sols are much weaker acids than arsenic trisulphide sols. Various cations replace the hydrogen ions of mastic sols in equivalent proportions. The Hardy–Schulze law is inapplicable to the process. J. PRYDE.

Influence of dielectric constant of medium on rate of coagulation of an arsenious sulphide sol by electrolytes. J. MUKHERJEE, S. G. CHAUDHURY, and S. MUKHERJEE (J. Indian Chem. Soc., 1926, **3**, 349—357).—The coagulating concentrations of hydrochloric and sulphuric acids, and of potassium, lithium,

barium, and aluminium chlorides on an arsenious sulphide sol in presence of varying concentrations of ethyl and methyl alcohols, acetic, propionic, oxalic, and formic acids have been determined. In most cases, the addition of ethyl alcohol stabilises the sol. With aluminium chloride, the coagulating concentration diminishes with increasing concentration of the added substance, but when oxalic acid is added, it first increases and then diminishes. With barium chloride, the coagulating concentration is unchanged with formic acid, decreases with increasing concentration of methyl alcohol, and increases in all other cases. The authors believe that the main effect of the added substance is to lower the dielectric constant of the medium, and, in agreement with the results of Kruyt and van Duin (A., 1914, ii, 182), find that the behaviour of the coagulating ion cannot be predicted from its valency. Weiser's explanation (A., 1925, ii, 108) is shown to be insufficient. J. W. Baker.

Charge reversal by hydrogen and hydroxyl ions with insoluble organic acids and amines, and reversal of the charge of hydrated silica and copper oxide by solutions of salts. J. N. Mukherjee and M. P. V. Iyer (J. Indian Chem. Soc., 1926, **3**, 307—322; cf. Mukherjee, A., 1922, ii, 689).—The effect of hydrogen and hydroxyl ions and of neutral salts on various insoluble organic acids, amides, and esters, and on hydrated silica and copper oxide has been determined by electro-osmotic measurements. Benzoic and *m*-aminobenzoic acids are positively charged in contact with their solutions in pure water, cinnamic, salicylic, boric, and phenylglycine-*o*-carboxylic acids are negatively charged. Hydrochloric acid causes a marked increase in the positive charge or decrease in the negative charge, and in the case of boric and the amino-acids, actually causes a reversal in sign. With the exception of amino-acids, which show a preferential adsorption of hydrogen ions, addition of alkali causes an increase in the negative charge, whilst neutral salts have very little effect. The insoluble organic acids, therefore, show a strong, and generally preferential adsorption of the constituent ions, and also adsorb hydrogen and hydroxyl ions in the dehydrated state, their effect being in all probability to neutralise the hydroxyl and hydrogen ions, formed by the dissociation of the fixed water molecules, in the primary layer. Both salol and *p*-nitroaniline are negatively charged in contact with pure water and show a preferential adsorption of hydroxyl ions. Both aniline hydrochloride and aluminium chloride cause reversal of the charge in hydrated silica. With the latter salt, there is an increase in the negative charge at low concentration, then a decrease, and finally reversal as the concentration is increased. Sulphate ions reverse the charge on hydrated copper oxide, but no reversal is observed with chlorides and nitrates. Neutral electrolytes increase the positive charge on copper hydroxide, the effect being independent of the nature of the cation. J. W. Baker.

Peptisation of metathoria. G. R. Levi and A. Reina (Atti R. Accad. Lincei, 1927, [vi], **5**, 174—180).—From *X*-ray observations made according to a modified form of the Debye–Scherrer method it would seem that the space-lattice of metathoria is unchanged after peptisation. R. W. Lunt.

Sensitisation of sols by small amounts of other colloids. S. Ghosh and N. R. Dhar (Kolloid-Z., 1927, **41**, 229—234).—The sensitisation of positively-charged colloids, such as ferric hydroxide, chromic hydroxide, aluminium hydroxide, and certain colouring matters by the negatively-charged colloids gelatin, albumin, and tannin is due to a neutralisation of the charge. On the other hand, the sensitisation of the negatively-charged colloids, arsenious sulphide, antimony sulphide, molybdenum pentoxide, silicic acid, silver, gold, and gum arabic by the same agents is due to repression of hydrolysis of the sols through the presence of small amounts of hydrogen ions in the gelatin, albumin, etc. E. S. Hedges.

Sensitising of hydrophobe colloids by proteins. N. N. Andrejew (Biochem. Z., 1927, **182**, 65—71).—Native proteins contain protein anions only, which at certain concentrations produce a coagulation of positively-charged sols. At lower concentrations, the protein anions sensitise the colloids to the action of neutral salts, whilst at higher concentrations the protein anions confer protection on the colloids. Native proteins produce no flocculation or sensitisation of negatively-charged colloids, but may exercise a protective action, as in the case of positive sols. Acidified protein solutions do, however, in certain concentrations, cause flocculation of negative sols. J. Pryde.

Decomposition of salt solutions by "galvano-colloidal" metal hydroxides. K. Ruegg (Kolloid-Z., 1927, **41**, 275—276).—When a paste of aluminium hydroxide, or similar colloid, is placed in a solution of certain metallic salts, adsorption of either acid or base occurs, leaving the solution with excess of alkali or acid. This effect is considered in relation to the softening of water and the corrosion of metals in neutral salt solutions. In the latter case, it is supposed that the colloidal skin of hydroxide first formed adsorbs the basic constituent of the salt, leaving the acid to attack the metal further. E. S. Hedges.

Imbibition of gelatin dried as a gel and as a sol. R. A. Gortner and W. F. Hoffman (J. Physical Chem., 1927, **31**, 464—466; cf. A., 1923, i, 965; Sheppard and Elliott, A., 1922, i, 387).—The imbibition of water by gelatin dried as a gel and as a sol has been studied. The initial rate of imbibition is generally greater in the gelatins prepared from the sols, but the amount imbibed is always greater in those prepared from the gels. The behaviour of the latter reflects, to a considerable degree, their previous history, and the differences in behaviour between the sol and the gel preparations are attributed partly to the persistence of a gel structure. L. S. Theobald.

Differences in the heat of reaction between artificial and soil gels of silica, alumina, and iron with hydroxides. G. J. Bouyoucos (Soil Sci., 1927, **23**, 243—247).—When soils, soil colloids, or artificial gels of silica, or the hydrated oxides of iron and aluminium are treated with potassium hydroxide or sodium hydroxide, heat of reaction apart from heat of wetting is developed. More heat is developed

with artificial gels than with soils or soil colloids. It is probable that the soil gels are not in the same condition as those prepared artificially.

G. W. ROBINSON.

Diffusion of aqueous sodium silicate solutions across semipermeable membranes. P. B. GANGULY (J. Physical Chem., 1927, **31**, 407—416).—The diffusion of aqueous solutions of sodium silicate across membranes of parchment and of collodion has been studied. After equilibrium is reached, the concentration of silica in the original silicate compartment is usually greater than that in the water compartment. The distribution depends largely on the original ratio $SiO_2 : Na_2O$ of the solutions. Solutions up to the ratio 3 : 1 show but small variations in concentration during diffusion, indicating that the non-diffusible matter is small in these cases. Beyond this ratio, the amount of non-diffusible matter increases rapidly. The amount of sodium left in the silicate compartments also increases, and is greater than the quantity of sodium in the water compartment. This is taken to indicate that the colloidal matter at the higher ratios is present as molecular aggregates or ionic complexes containing sodium and silica. Measurements of osmotic pressure after equilibrium has been reached show that the colloidal matter increases with an increase in the ratio of SiO_2 to Na_2O (cf. Harman, this vol., 415), and p_H measurements show that hydrolysis plays no great part in the distribution processes.

L. S. THEOBALD.

Cation and anion exchange at the surface of permutite. H. JENNY (Koll.-Chem. Beih., 1927, **23**, 428—472).—The ionic exchange between lithium, sodium, potassium, ammonium, magnesium, calcium, barium, and aluminium permutites and solutions of a number of chlorides of uni- and bi-valent metals has been investigated. The constants $1/p$ and K in Wiegner's modification of Freundlich's adsorption isotherm, $y=K[c/(a-c)]^{1/p}$ (where y=the exchanged quantity on 1 g. of permutite, a=the concentration of the added solution, and c=the concentration at equilibrium) have been calculated. The equivalence of the exchange was confirmed by experiments with potassium permutite and sodium chloride. The power of exchange of an ion increases with increasing atomic weight, and the exchange constants are directly proportional to the ionic volumes. The connexion with the hydration effect is discussed. In the case of univalent ions, the course of exchange from liquid to solid phase and from solid to liquid phase proceeds normally. With increasing hydration, the exchange from liquid to solid decreases, whilst that from solid to liquid increases. Hydrogen occupies an anomalous position. At low concentrations, bivalent ions have a greater power of exchange than the corresponding hydrated univalent ions, but at higher concentrations the power of exchange is less. The bivalent ions are more strongly adsorbed by the permutite than the univalent. The lyotropic series is not reversed with bivalent ions, as is the case with univalent. The anomalies shown by bivalent ions are ascribed to insoluble hydroxide formation with the hydroxyl ions of the Helmholtz inner layer.

L. L. BIRCUMSHAW.

Thermal dissociation of iodine and bromine. T. DEVRIES and W. H. RODEBUSH (J. Amer. Chem. Soc., 1927, **49**, 656—666).—The thermal dissociation of iodine and bromine has been measured between 300° and 1300° Abs. (approx.) by an adaptation of Knudsen's vapour-pressure method (A., 1909, ii, 385). The equilibrium constant for $I_2 \longrightarrow 2I$ is $\log_{10} p_I^2/p_{I_2} = -6840/T+\log_{10}T+1{\cdot}121$. The entropy of monatomic iodine at 298° Abs. and 1 atm. is 40·5; this is in agreement with the value predicted by the Tetrode equation (40·4), but is considered to be too low. The heat of dissociation of iodine is 31,600 g.-cal. (calc.). The results for bromine are less satisfactory. The equilibrium constant is $\log p^2_{Br}/p_{Br_2} = -9000/T+3{\cdot}695$, the calculated heat of dissociation being 41,200 g.-cal. The entropy of monatomic bromine at 298° Abs. and 1 atm. is 38·2, the Tetrode equation predicting 39·0.

S. K. TWEEDY.

Theory of concentrated solutions. III. E. WILKE and W. MARTIN (Z. physikal. Chem., 1927, **125**, 420—430).—Measurements have been made of the *E.M.F.* of cells of the type $Br_2|0{\cdot}1N\text{-HBr}\ 3N\text{-KCl}|N\text{-HBr}|Br_2$, with the object of testing the authors' theory of highly concentrated solutions (cf. A., 1926, 906).

H. F. GILLBE.

Dilution law for strong electrolytes. B. SZYSZKOWSKI (Bull. Acad. Polonaise, 1926, **A**, 325—346).—Molecular conductivity can be expressed as a function of concentration by $1-\alpha = 1-\lambda/\lambda_0 = 0{\cdot}5(\nu-1)[\beta c^{1/2}-2\gamma c+3\delta c^{3/2}\ldots$ in which α is the conductivity coefficient ($\alpha=\lambda/\lambda_0$), ν the number of ions into which the electrolyte dissociates, c the concentration in moles per litre, and β, γ, and δ are constants. By using a sufficient number of terms in the serial expansion, a dilution law for strong electrolytes at any concentration can be obtained. For uni-univalent salts over the range 0·1—0·0001M, $1-\lambda/\lambda_0 = 1/2\,.\,\beta c^{1/2}-\gamma c+3/2\,.\,\delta c^{3/2}$ is in agreement with experiment. Kohlrausch's data for 16 suitable salts were used for the calculation of the constants λ_0, β, γ, and δ. The relationships found provide independent support for the Debye–Hückel theory, and require that λ_0, β, γ, and δ should be considered as characteristic chemical constants of salt solutions. The ionic mobilities of a number of univalent ions are computed, and the values compared with those of Kohlrausch and of Debye. By an application of the Debye–Hückel theory, the mean ionic radii have been calculated for the 16 salts considered.

R. A. MORTON.

Formation of complexes between cadmium and alkali halides. F. BOURION and E. ROUYER (Compt. rend., 1927, **184**, 598—600).—Ebullioscopic determination of the equilibrium constants has shown that in the formation of salts of the type $K_2[CdI_4]$, $K_2[CdCl_4]$, and $Na_2[CdCl_4]$, the constants decrease with the atomic weights of the halogens and of the alkali metals (cf. A., 1923, ii, 534; 1926, 796).

J. GRANT.

Aqueous solutions of sodium silicates. V. Osmotic activity, lowering of vapour pressures and f. p. R. W. HARMAN (J. Physical Chem., 1927, **31**, 355—373; cf. A., 1925, ii, 1065; 1926, 478, 796, 907).—Measurements have been made at 25° by a

dynamic method of the lowering of the vapour pressure of sodium silicate solutions of the ratio $Na_2O : SiO_2$ = 1 : 1 and 1 : 2 over the concentration range 0·1—2·5N_w, and the lowering of the f. p. by the ordinary Beckmann method has been found for the ratios 2 : 1, 1 : 1, 1 : 2, 1 : 3, and 1 : 4 over concentrations ranging from 0·01 to 2·0N_w. The results from the two sets of measurements are in fair agreement, and are expressed, in both cases, in terms of the ionic and activity theories. The osmotic activity in the case of the ratios 2 : 1 and 1 : 1, and to a lesser extent 1 : 2, is high, especially in dilute solutions, but in concentrated solutions the ratios 1 : 3 and 1 : 4 show an abnormally low osmotic activity, which, however, is unexpectedly high in dilute solutions. It is suggested that the ratio 1 : 1 represents the metasilicate, Na_2SiO_3, which hydrolyses and ionises, giving rise to sodium, hydroxyl, and SiO_3'' ions and crystalloidal silicic acid. The ratio 1 : 2 represents the salt $NaHSiO_3$, behaving in a manner similar to the metasilicate, and giving, in addition, the ion $HSiO_3'$. The ratios 1 : 3 and 1 : 4 suggest the existence of complex aggregates in concentrated solution and of ionic micelles of the composition $[m SiO_3, n SiO_2 aq]^m$, where $(m+n)/m$ equals the ratio $Na_2O : SiO_2$ (cf. Ganguly, this vol., 415). L. S. THEOBALD.

Influence of an "indifferent" gas on the concentration and activity of a vapour in equilibrium with a condensed phase or phases. II. I. R. MCHAFFIE (Phil. Mag., 1927, [vii], **3**, 497—510; cf. A., 1926, 355).—The concentration of water vapour, in equilibrium with liquid water in presence of air up to a pressure of 100 atm., has been measured at 25°. The presence of filters in the high-pressure portion of the apparatus has been found to influence the results to a marked extent. The probable influence of such filters is discussed. The calculated activity coefficients are in good agreement with those derived from the results of Pollitzer and Strebel (A., 1925, ii, 104). The results are compared with those obtained previously for the system sodium sulphate–water (A., 1926, 355). A. E. MITCHELL.

Dissociation pressures of calcium, strontium, and barium carbonates. W. DUTOIT (J. Chim. phys., 1927, **24**, 110—114).—The pressure was measured by a dynamic method, the carbonate being placed in a tube heated in a long furnace, and the carbon dioxide swept out by a slow stream of nitrogen and weighed in an absorption vessel. The results for calcium carbonate, covering the range 707—885°, agree closely with those of previous workers obtained by the static method using a manometer. Measurements were also made on strontium carbonate at temperatures between 950° and 1175°, and on barium carbonate over a small range. S. J. GREGG.

Influence of salts on the solubility of water in phenol. R. CERNATESCU and E. PAPAFIL (Z. physikal. Chem., 1927, **125**, 331—340, and Ann. Sci. Univ. Jassy, 1927, **14**, 285—301).—The solubility was determined by measuring the temperature at which a solution of water in phenol, saturated at 18°, became turbid as the solution was cooled, after the addition of a known quantity of the salt in question. The solubilities of the alkali halides in phenol, saturated with water at 18°, are found to be in the same order as that of the metals in the periodic table, as is also their power of reducing the solubility of water in phenol. For a constant ratio of phenol to water, the Rothmund equation $(\eta-\eta_0)/\eta = K$ (A., ii, 1900, 467) is found to hold for the alkali halides over a wide range of concentrations. For the alkali iodides, K is proportional to the true radius of the positive ion, as calculated by Born. H. F. GILLBE.

Solubility influences. IV. Salting-out of aniline from aqueous solutions. S. GLASSTONE, (MISS) J. BRIDGMAN, and W. R. P. HODGSON (J.C.S., 1927, 635—640).—A continuation of previous work (cf. A., 1926, 18; this vol., 14). The solubility of aniline has been determined at 25° and 50° in aqueous solutions of various salts. From the data for salts insoluble in aniline, "hydration numbers" for both cations and anions have been determined on the assumption that the number for the iodide ion is zero. The hydration numbers of the anions are very similar to those previously obtained (*loc. cit.*) by the salting-out of ethyl acetate, but the results for some of the cations are abnormal. This may be due to hydrolysis of the salts, or may be connected in some way with the basic nature of the aniline. Experiments on the salting-out power of mixtures confirm the previous conclusion, that this is equal to the sum of the salting-out powers of the constituents, provided allowance be made for the electrical interaction of the ions. M. S. BURR.

Solubility of calcium salts. I. Solubility of calcium carbonate in salt solutions and biological fluids. II. Solubility of tricalcium phosphate in salt solutions and biological fluids. III. Solubility of calcium carbonate and tricalcium phosphate under various conditions. J. SENDROY, jun., and A. B. HASTINGS (J. Biol. Chem., 1927, **71**, 723—781, 783—796, 797—846).—I. A formula for the solubility of calcium carbonate in solutions of known hydrogen-ion concentration and carbon dioxide tension has been derived. The influence of the hydrogen-ion concentration and of the presence of other salts on the solubility product has been studied. In the presence of dissolved phosphate, there is a tendency to form supersaturated solutions. The solubility of calcium carbonate in solutions of sodium citrate varies with the concentration of citrate and with the hydrogen-ion concentration. It is concluded that a slightly dissociated calcium citrate compound is formed. When solutions of citrate saturated with calcium carbonate are shaken with solid calcium phosphate, the calcium content decreases. From analyses of serum, it would appear that the solubility product for calcium carbonate is $10^{-6\cdot40}$, compared with $10^{-7\cdot40}$ in salt solutions of similar ionic strength. Calcium carbonate does not dissolve in serum from which much of the calcium has been removed by oxalate, nor does it precipitate from serum the calcium concentration of which has been augmented by the addition of calcium chloride even in presence of solid calcium carbonate, but after inorganic phosphate has been removed the equilibrium appears to be reversible with respect to

calcium salts. The solubility of calcium carbonate in serum of various concentrations and in exudates has been studied. Although it was not possible to demonstrate that the serum of parathyroidectomised dogs was less able than normal serum to retain calcium in solution, it was found that the parathyroid hormone, when added to solutions of inorganic salts, did actually tend to prevent the precipitation of calcium carbonate.

II. The following equations are derived for the dissociation constants of phosphoric acid: $pK_1' = 2{\cdot}11 - 0{\cdot}5\sqrt{\mu}$, $pK_2' = 7{\cdot}15 - 1{\cdot}25\sqrt{\mu}$, and $pK_3' = 12{\cdot}66 - 2{\cdot}25\sqrt{\mu}$, where μ is the ionic concentration. Values are obtained for the solubility product of calcium phosphate. When serum is shaken with calcium phosphate, the calcium content decreases without a corresponding diminution in the phosphate ions, and it is suggested that calcium carbonate is precipitated, although no precipitation of calcium takes place when the serum is shaken with calcium carbonate.

III. From the solubilities of calcium carbonate and of calcium phosphate in salt solutions of various hydrogen-ion concentrations, expressions have been obtained for the solubility products in terms of the total ionic concentration and also for the activity coefficients of these two salts as well as of the calcium ion. The results have been compared with similar data obtained from experiments in which the calcium content of serum was determined under various conditions, and in particular the rate at which calcium is lost when the serum is shaken with calcium phosphate and calcium carbonate has been ascertained. The effect of alteration of the serum concentration and of the presence of red blood cells on the solubility of these salts has been determined. These results are best explained by the assumption of the existence of some slightly dissociated calcium complex.

W. O. KERMACK.

Co-existing liquid and vapour phases of solutions of oxygen and nitrogen. B. F. DODGE and A. K. DUNBAR (J. Amer. Chem. Soc., 1927, **49**, 591—610).—The liquid–vapour phase equilibria for binary mixtures of oxygen and nitrogen have been examined, the pressure and the composition of the phases being tabulated from 90° to 125° Abs. The interpolated results for 1 atm. differ considerably from those obtained by Baly (A., 1900, ii, 589). S. K. TWEEDY.

Application of phase rule to calculation of liquid and vapour compositions in binary systems. Deviations from Raoult's law for hydrocarbon mixtures. G. CALINGAERT and L. B. HITCHCOCK (J. Amer. Chem. Soc., 1927, **49**, 750—765).—The isothermal p–v graph for the vapour in equilibrium with a homogeneous binary liquid mixture yields a family of curves, each curve corresponding with a given composition of the liquid. Such systems are completely defined by two independent variables, *e.g.*, p and T. If two systems are known for which p and T are the same, x and y, the molar fractions of constituent A in the liquid and vapour phases, respectively, will also be the same, and for each system $L_A x + V_A y = C_A$, where L_A and V_A represent the molar quantity of A in the two phases, and C_A the total quantity of A in the system. V_A is obtained with the aid of the appropriate p–v curves, p and T being the same for each system; L is calculated from $C_A + C_B - L + V$, and so x and y may be determined without involving analysis of the phases present. Vapour pressure–composition data for 25° are tabulated for systems of butane with pentane, heptane, benzene, and "straw-oil," and also for the pentane–heptane system. The respective deviations of the total pressure at 20 mol.-% of the lighter constituent are 4, 0, 64, −2·6, and 7. Except for the butane–heptane system, which obeys Raoult's law even although the relative internal pressures are not the same, the results agree very well with Hildebrand's views. A critical review of previously published relevant data is given. S. K. TWEEDY.

Freezing points. III. The syncrystallisation rule of Bruni. J. TIMMERMANS (Bull. Soc. chim. Belg., 1927, **36**, 179—190; cf. Viseur, this vol., 312).—Using methyl alcohol as solvent, the solubility curves at 20° for various salt-pairs have been investigated in an attempt to determine the miscibilities of *cis*- and *trans*-isomerides with one another and with the corresponding saturated compounds, and the following results obtained: sodium maleate and fumarate, immiscible; sodium succinate and maleate, systems rich in succinate form mixed crystals; sodium succinate and fumarate, apparently immiscible; potassium maleate and fumarate, possibly limited miscibility; potassium succinate and maleate, mixed crystals with gap from 0 to 30% maleate; potassium succinate and fumarate, unbroken series of mixed crystals. Measurements of the f. p. gave the following results: *cis*- and *trans*-acetylene dichloride, ethylene chloride and *cis*-acetylene dichloride, ethylene bromide and *cis*-acetylene dichloride, acetylene tetrachloride and *cis*-acetylene dichloride, acetylene tetrachloride and *trans*-acetylene dichloride, no mixed crystals; ethylene chloride and *trans*-acetylene dichloride, ethylene bromide and *trans*-acetylene dichloride, mixed crystals. Summarising the present data and those of Viseur (*loc. cit.*), it may be said that, in general, the *trans*-compound has a more marked tendency to form mixed crystals with the corresponding saturated compound than has the *cis* isomeride. It would hence appear that in the solid state similar atom groups in the saturated compounds are placed at antipodes, the molecule having a structure approximating to that of the corresponding *trans* unsaturated compound.

Ethylene dibromide and dichloride form an unbroken series of mixed crystals, a fact in harmony with their behaviour towards the two isomeric acetylene dichlorides. J. S. CARTER.

Double salts in the series of isomorphous mixed crystals of magnesium and zinc sulphate, and the occurrence of chemical compounds in the solid state. H. G. K. WESTENBRINK (Proc. K. Akad. Wetensch. Amsterdam, 1926, **29**, 1374—1384).—X-Ray examination shows that $MgSO_4,7H_2O$ and $ZnSO_4,7H_2O$ form a continuous series of mixed crystals. Compounds such as those described by Hollmann (A., 1901, ii, 436) are not formed.

M. S. BURR.

Solid solutions of calcium and sodium disilicates. A. GINSBERG and C. NIKOYCSIEN (Nachr. geochem. Sekt. Ver. Metall. Chem., 1926, 35—38).—The system Na_2SiO_3–$CaSiO_3$ yields the compound $2Na_2SiO_3,3CaSiO_3$, m. p. 1255°; minimal m. p. occur at 1042° and 1230°. CHEMICAL ABSTRACTS.

Equilibrium between molten metals and salts. C. TUBANDT and E. MUNZING (Z. anorg. Chem., 1927, **160**, 323—332).—The equilibria $Pb+2AgCl \rightleftharpoons 2Ag+PbCl_2$ have been investigated between 500° and 1000°, and found to be in agreement with Lorenz' modification of the mass action law (A., 1924, ii, 484, 761). The silver content of the metal phase decreases linearly with rise in temperature, but is only slightly influenced by the addition of sodium or potassium chlorides, thus indicating that, in the molten state, silver chloride exists as Ag_2Cl_2. Similar results were obtained in studying the equilibria $Cu+AgCl \rightleftharpoons Ag+CuCl$. A. R. POWELL.

Binary alloys of lead with up to 2·2% of lithium. J. CZOCHRALSKI and E. RASSOW (Z. Metallk., 1927, **19**, 111—112).—The saturated solid solution of lithium in lead contains from 0·04 to 0·09% Li, according to the temperature. With more lithium, a eutectic of lead and the compound Pb_3Li_2 is formed, which contains 0·65% Li and melts at 230°. The compound melts at 470° and contains 2·15% Li. All alloys containing less lithium than this are stable in the air, but those containing more lithium rapidly disintegrate. On allowing the alloy containing 5% Li to cool, liquid drops with a glistening metallic lustre are expressed from the interior of the ingot at 200°. A. R. POWELL.

Binary system cobalt–tungsten. W. GEISS and J. A. M. VAN LIEMPT (Z. Metallk., 1927, **19**, 113—114).—The temperature coefficient of electrical resistance of bars of cobalt–tungsten alloys, made by sintering intimate mixtures of the powdered metals with a current equal to 95% of that required to melt the alloy, have been measured and the results plotted against the composition. The figures obtained show that the two metals do not form a continuous series of mixed crystals. The curve falls abruptly with the addition of a very small quantity of cobalt to tungsten to a minimum at 5% Co, rises slightly to a maximum with 10% Co, falls again to a second, flat minimum at 30—55% Co, then rises sharply again to the value for pure cobalt. A. R. POWELL.

Ternary systems. IV. Potassium carbonate, sodium carbonate, and water. A. E. HILL and F. W. MILLER, jun. (J. Amer. Chem. Soc., 1927, **49**, 669—686).—No hydrated double carbonate is formed in the above system between 20° and 50°, but a continuous series of hydrated solid solutions exists, $(K_2,Na_2)CO_3,6H_2O$, in which the atomic ratio of potassium to sodium varies from 1 : 0·88 to 1 : 2·07. Above 25·12° and within limited concentrations, a stable anhydrous double carbonate K_2CO_3,Na_2CO_3, is formed. Four quintuple points exist, each involving three solid phases. The lowest hydrate of potassium carbonate is $K_2CO_3,1{\cdot}5H_2O$, stable at the ordinary temperature; below −6·2°, the stable hydrate is $K_2CO_3,6H_2O$. S. K. TWEEDY.

System copper–tin–antimony. W. BONSACK (Z. Metallk., 1927, **19**, 107—110).—The ternary system copper–tin–antimony at 20° may be divided into eight regions, characterised by three constituents crystallising in the following order: (i) Cu_3Sn+CuSn, SbSn, ternary eutectic or pure tin; (ii) Cu_3Sn, CuSn, SbSn; (iii) Cu_3Sn, Sb_3Sn_2, SbSn; (iv) Cu_3Sn, Cu_2Sb, Sb_3Sn_2; (v) Cu_3Sn, Cu_4Sn, Cu_2Sb; (vi) Cu_2Sb, antimony, Sb_3Sn_2; (vii) copper, Cu_4Sn, Cu_3Sb; (viii) Cu_4Sn, Cu_3Sb, Cu_2Sb. Thus in bearing metals which contain a large proportion of tin, no antimony–copper compound is stable at the ordinary temperature. All the above quasi-ternary systems exhibit peritectic reactions at higher temperatures, with corresponding instability and sensitivity to change on repeated melting. For the recovery of tin from old bearing metal by the liquation process, a temperature of 229° gives the most satisfactory results, the runnings then consisting of the ternary eutectic, which contains only relatively small quantities of copper and antimony. A. R. POWELL.

Equilibria in systems in which the phases are separated by a semipermeable membrane. XVIII. F. A. H. SCHREINEMAKERS (Proc. K. Akad. Wetensch. Amsterdam, 1926, **29**, 1292—1302).—Theoretical. The influence of pressure on osmotic systems is considered. M. S. BURR.

Kinetic theory of Eotvos' law. M. SATÔ (Sci. Rep. Tohoku Imp. Univ., 1926, **15**, 805—817).—The physical meaning of surface tension is examined from the point of view of the kinetic theory. If λ is the surface energy per unit area and σ the surface tension, the relation between them is $\lambda=\sigma-T.d\sigma/dT$. If a thin liquid film is stretched on a wire frame with forces holding the wires balanced against surface tension, the physical meaning of the above equation is that σ is the force on the wire, $-T.d\sigma/dT$ the force due to the molecular impacts on the wire, and λ the cohesive force among the molecules in the film. Since the molecular impacts increase with temperature, the surface tension diminishes, but λ is independent of temperature. Since the thinnest film obtained by stretching is bimolecular, the surface layer is probably unimolecular, and the molecules in the surface are regularly oriented. If two molecules are in the first and second layers of the surface, respectively, and Z_0 is the mean distance between their centres, the physical meaning of Eotvos' law is that ε_0/Z_0 is constant for most liquids, ε_0 being the mean gap between the circumferences of the two molecules. The values of the molecular cohesion calculated on the above assumption are in fair agreement with those given by van der Waals' equation. W. HUME-ROTHERY.

Change in activity of molten lead chloride on dilution with potassium chloride. J. H. HILDEBRAND and G. C. RUHLE (J. Amer. Chem. Soc., 1927, **49**, 722—729).—Activity coefficients have been calculated from *E.M.F.* measurements at 500—600 of cells of the type Pb|fused $PbCl_2+KCl(c)|Cl_2$, where c, the molar fraction of potassium chloride, is 0·0—0·4. The results are interpreted on the assumption that certain complexes which separate as solids (Lorenz and Ruckstuhl, A., 1907, ii, 152) also exist in a

partly ionised state in the lead chloride solution. The free energy change corresponding with the decomposition potential of fused lead chloride is −58,700 g.-cal. at 498°, in agreement with Gerke's value at 25° (A., 1922, ii, 682). S. K. TWEEDY.

F. p. and activity coefficients of aqueous barium nitrate, sodium sulphate, and sulphuric acid. M. RANDALL and G. N. SCOTT (J. Amer. Chem. Soc., 1927, 49, 647—656).—With an improved form of the Randall and Vanselow apparatus (A., 1925, ii, 33), the f. p. of the above dilute solutions were determined. The calculated activity coefficients suggest that sodium sulphate is a strong electrolyte, barium nitrate distinctly weaker, and sulphuric acid moderately strong. S. K. TWEEDY.

Activity of chlorine at various partial pressures. N. KAMEYAMA, H. YAMAMOTO, and S. OKA (Proc. Imp. Acad. Tokyo, 1927, 3, 41—43).—The *E.M.F.* at 25° of the cell $Hg|Hg_2Cl_2$, saturated $KCl|PtCl_2$, with chlorine at various concentrations has been measured. The cell behaves normally with respect to the change of partial pressure of chlorine above a partial pressure of 0·240 atm. W. E. DOWNEY.

Thermodynamics of non-isothermal systems. W. H. RODEBUSH (J. Amer. Chem. Soc., 1927, 49, 792—794).—The equilibrium condition assumed by Eastman (A., 1926, 797) is incomplete. Gibbs' equilibrium criteria are applied to the case of an ideal gas in a temperature gradient. Contrary to Eastman's statement, the reversible Soret effect is not necessarily zero. The difficulty in defining osmotic temperature might be surmounted by considering equilibrium to be established through the vapour phase (cf. following abstract). S. K. TWEEDY.

Thermodynamics of non-isothermal systems. E. D. EASTMAN (J. Amer. Chem. Soc., 1927, 49, 794—795).—The equilibrium condition previously used is considered to be sufficient, and when applied to an ideal gas yields the same result as that obtained by Rodebush (preceding abstract). The reversible Soret effect is not necessarily zero, although it is considered to be so in perfect solutions. Rodebush's suggestion regarding the definition of osmotic temperature is criticised. S. K. TWEEDY.

Calculation of affinity from entropy considerations. G. BOZZA and G. DEVOTO (Atti R. Accad. Lincei, 1927, [vi], 5, 180—186).—A mathematical note, preliminary to experimental work shortly to be published in which expressions for affinity and fugacity are derived from the Planck form of Nernst's hypothesis without making use of the Clausius–Clapeyron equation. R. W. LUNT.

Physico-chemical processes as the effects of the sum total of elementary adiabatic reactions. W. TANTZOV (J. Russ. Phys. Chem. Soc., 1926, 58, 947 956).—Theoretical. The thermodynamic nature of physico-chemical processes is considered from the point of view of chemical kinetics. The motion of molecules in systems not in equilibrium results in momentary adiabatic expansions and contractions of the elementary molecular volume. Changes of phase are considered from such a point of view. The formation and persistence of nuclei during crystallisation from supercooled liquids occur more readily if the heat of the resulting contraction is small and the temperature of dissociation of the nucleus large, *i.e.*, dQ/T or the change in entropy is small. Only those molecules coalesce, to form stable nuclei, and may be termed "active" molecules, which possess energy between certain limits. In metastable systems, where several phases may be formed, the nature of the nuclei which are formed is determined by the above energy considerations, and not by the law of chance. For crystallisation an optimum temperature exists, when the average kinetic energy of the molecules is equal to that of the "active" molecules which form the nuclei. The considerations are extended to chemical reactions. In consecutive reactions, the first, which is the easiest, must have the smallest entropy change. The Marcelin–Rice conception of the "critical increment" $d \log K/dT = \epsilon/RT^2$ in a decomposition reaction is shown to follow necessarily from the adiabatic nature of the individual molecular reactions. M. ZVEGINTZOV.

Heat of dissolution of sparingly soluble electrolytes. I. Heat of precipitation as a function of the concentration. [Silver chloride.] E. LANGE and R. M. FUOSS (Z. physikal. Chem., 1927, **125**, 431—441; **126**, 304).—Previous methods of determining the heat of dissolution of sparingly soluble electrolytes have assumed that it is of equal magnitude and of opposite sign to the heat of precipitation. It is shown that this is not strictly true, but that the heats of dilution of the solutions employed should be taken into account; the error involved by the omission may amount to several hundred g.-cal. A calorimetric method is described for determining the heat of precipitation of silver chloride from a solution of silver nitrate by potassium chloride solution, together with an account of tests made to ensure that the heat value is not subject to errors owing to adsorption from the solution by the precipitate or to variations in the crystal form of the silver chloride. The heat of precipitation of silver chloride at three concentrations is given, and by extrapolation of the heat–concentration curve to zero concentration, the true heat of dissolution is found to be −15·98 kg.-cal./mol. H. F. GILLBE.

Twenty-five years of theoretical electrochemistry. W. D. BANCROFT (Trans. Amer. Electrochem. Soc., 1927, 51, 63—78).

Conductance in liquid hydrogen sulphide solutions. G. N. GUAM and J. A. WILKINSON (Proc. Iowa Acad. Sci., 1925, 32, 324—325).—Solutions of the halides of phosphorus, arsenic, and antimony in liquid hydrogen sulphide are electrical conductors, the conductivity largely increasing with the atomic weight of the element. Replacement of the hydroxyl group of acetic acid by the thiol or amido-group or by chlorine largely increases the conductivity, whereas replacement of the hydrogen of the radical by chlorine or the amido-group abolishes the conductivity. Ammonium chloride in hydrogen sulphide is a non-conductor, but replacement of hydrogen by a methyl or an ethyl group greatly increases the conductivity. CHEMICAL ABSTRACTS.

Molecular conductivity of cadmium iodide in acetonitrile. F. K. V. Koch (J.C.S., 1927, 647—650).—The conductivity was determined at 0° and 25° for the range $v=10$—8000. The temperature coefficients change from positive to negative and back to positive again as the solutions become more dilute. This suggests the existence of at least three molecular species in solution. Since λ_v for the most dilute solution is only 49·98, whilst the conductivity of the iodine ion is 96, cadmium iodide cannot be regarded as completely dissociated even at high dilutions. The temperature coefficient tends, with increasing dilution, towards the value of the temperature coefficient of fluidity of acetonitrile. M. S. Burr.

Influence of iodine on the conductivities of sodium, potassium, cadmium, and mercuric iodides in alcoholic and in acetone solutions. E. Thonnessen (Z. Physik, 1927, **41**, 810—827).—Using Kohlrausch's method, the change in conductivity on the addition of iodine has been measured in the temperature range 5—40° for the following solutions: cadmium iodide, potassium iodide, and mercuric iodide in methyl alcohol, potassium iodide and sodium iodide in acetone, and sodium iodide in amyl alcohol. The observed increase is more marked in dilute solutions of these salts, and is greatest for the iodides of cadmium and mercury. These results are discussed with reference to viscosity and complex-ion formation; it is concluded, in contradiction to the results of recent work on strong electrolytes, that none of these salts is completely dissociated in aqueous solution. R. W. Lunt.

Thermodynamic theory of reversible electrodes. B. Szyszkowski (Bull. Acad. Polonaise, 1926, **A**, 313—323).—Using the Debye–Hückel equations, the equilibrium between an electrode and an electrolytic solution has been treated by general thermodynamic methods. The treatment is illustrated by the calculation of the equilibrium constant for the reaction in the Daniell cell.

R. A. Morton.

Effect of intermediate solutions on diffusion potentials. C. Drucker (Z. physikal. Chem., 1927, **125**, 394—400).—The efficacy of various liquids when used as intermediate solutions to eliminate the potential at a liquid–liquid junction has been determined by *E.M.F.* measurements against the calomel electrode. Potassium nitrate and mixtures of potassium and sodium nitrates eliminate the liquid–liquid potential incompletely in strongly acid solutions. In addition to the concentrated solutions of potassium chloride and ammonium nitrate which are in common use for this purpose, saturated solutions of sodium nitrate and of lithium acetate may be employed. It is suggested that the acid and acetate form a layer of neutral salt on the two sides of the acetate bridge and that the resulting *E.M.F.* is zero. The measurements made confirm this view.

H. F. Gillbe.

Electrokinetic potential of metals. A. Coehn and O. Schafmeister (Z. physikal. Chem., 1927, **125**, 401—419).—The applicability of Stern's theory of electrokinetic potential (Z. Elektrochem., 1924, **30**, 508) to the case of metals in contact with liquids has been tested. A method is described for measuring the electrokinetic potential, independently of the thermodynamic; its validity has been demonstrated by measuring the potentials of a number of dielectrics for which the potential–concentration curves are known. Results are given for platinum, gold, silver, molybdenum, and tungsten, which all have a negative charge in pure water. In solutions of potassium, calcium, and aluminium chlorides, the charge decreases with increasing concentration of electrolyte, and changes sign at a concentration which is lower the higher the valency of the positive ion. The maxima and minima in the concentration–potential curve required by Stern's theory are apparent only for molybdenum and tungsten in aluminium chloride solution; in other cases, the concentrations at which the maxima and minima occur are probably below the range investigated. Analogous results are found for lead and zinc, which have a positive charge when in contact with pure water, in solutions of potassium chloride and ferricyanide. Copper and cadmium, which have an indefinite charge in water, are positively charged when in contact with potassium ferricyanide solution of low concentration, and negatively charged at higher concentrations.

The influence of the valency of the active ion is demonstrated clearly by the nature of the concentration–potential curves, and the results are in good agreement with the theory of Stern.

The electrokinetic potential is independent of the thermodynamic. Measurements of the latter for metals in contact with various liquids show that it is usually of opposite sign to the electrokinetic potential, that it is influenced by valency and concentration in a totally different manner, that there is no change of sign with increasing concentration, and no maxima or minima occur in the concentration curve. A brief discussion is given on the nature of the difference between the two types of potential, together with its bearing on colloid chemistry. H. F. Gillbe.

***P.D.* between two liquid phases.** S. W. Vosnessinski (J. Russ. Phys. Chem. Soc., **57**, 475—486).—The *E.M.F.* of concentration cells containing electrolytes distributed between two liquid phases was investigated, in order to test the thermodynamic equation. Two types of cell were used: *N*-calome electrode|aqueous solution of A|non-aqueous A|aqueous B|non-aqueous B|*N*-calomel electrode; and *N*-calomel electrode|aqueous A|non-aqueous A (C_1)|non-aqueous A (C_2)|aqueous A|*N*-calomel electrode. The electrolyte A was always potassium chloride, whilst B was potassium bromide, potassium iodide, potassium thiocyanate, lithium chloride, or hydrochloric acid. The non-aqueous phases were amyl alcohol and phenol. Assuming Nernst's formula, the liquid/liquid *P.D.* is given by: $\pi=RT/F \cdot \log_e \sqrt{\alpha k/\alpha a}$ for cells containing one electrolyte, for which αk, αa are the partition coefficients of the cation and anion. If the simple partition law holds, the *E.M.F.* of such cells is zero. For cells containing two electrolytes with a common ion, the *E.M.F.* is given by $E=RT/F \cdot \log_e C_{\mathrm{i}}C_{\mathrm{iii}}/C_{\mathrm{ii}}C_{\mathrm{iv}}$, where C_{i}, C_{ii}, C_{iii}, C_{iv} are the concentrations of that ion.

Potassium chloride in water and phenol gave no

E.M.F., whilst the same salt in water and amyl alcohol gave an *E.M.F.* which decreased with rise of concentration. A theoretical expression for the *E.M.F.* of this cell was deduced which agrees with the observations.

In cells with pairs of electrolytes, that electrolyte which had the greater solubility in a given phase charged that phase to the higher potential.

M. ZVEGINTZOV.

Standard calomel electrodes and their preparation. A. BRODSKI (Ukraine Chem. J., 1926, **2**, 277—288).—The author finds that calomel electrodes prepared by the method of Ostwald and Luther are not constant and cannot be reproduced. When purified calomel is introduced in constant proportion into the cell solutions, calomel and mercurous bromide electrodes can be obtained which have a constant reproducible potential within 0·0001—0·0002 volt, whether in alcoholic or aqueous-alcoholic solutions.

E. ROTHSTEIN.

Production of ions from solutions of mercury salts in water. A. BRODSKI and G. CHERCHEVER (Ukraine Chem. J., 1926, **2**, 289—310).—The *E.M.F.* of $Hg|Hg_2(NO_3)_2$, $Hg|Hg_2Cl_2$,KCl, and $Hg|Hg_2Br_2$,KBr electrodes have been determined between 11° and 27° by a new method free from errors associated with previous determinations. The solubility products of mercurous chloride and mercurous bromide derived therefrom are satisfactorily constant. The solubility products of other mercurous salts have also been determined. E. ROTHSTEIN.

Temperature coefficient of contact *E.M.F.* J. J. McHENRY (Phil. Mag., 1927, [vii], **3**, 857—863).—The contact *E.M.F.* between clean copper and zinc has been found to be a linear function of the temperature, and may be expressed in the form $E=q+T.dE/dt$, where dE/dt is 0·002 volt per degree, and q is very small and may be either positive or negative, depending on the relative cleanliness of the metals. It is suggested that for absolutely clean metals the contact *E.M.F.* is proportional to the absolute temperature, *i.e.*, that q should vanish. Measurements made with copper–aluminium and copper–tin cells confirm this. A. E. MITCHELL.

Platini-platino-chloride electrode. New type of chlorine electrode. V. F. MILLER and H. TERREY (J.C.S., 1927, 605—610).—Measurements have been made of the *E.M.F.* of the following cell: $Hg|Hg_2Cl_2$,NaCl|NaCl+Na_2PtCl_6+$Na_2PtCl_4|\overset{+}{Pt}$, the reaction at the positive electrode being $\overline{PtCl}_6+2e\longrightarrow PtCl_4+2Cl$. With a constant sodium chloride concentration, the *E.M.F.* of this electrode is given by $E=E_0+(RT/2F)\log[a_i]/[a_o]\times[a_{Cl}]_2$, where a_i, a_o, and a_{Cl} are the activities of the chloroplatinate, the chloroplatinite, and the sodium chloride, respectively. E_0, however, changes slightly with change in concentration of sodium chloride, and the complete relationship may be expressed by the empirical equation $E-(E_0+C)+(RT/2F)(\beta-2)\log a_{Cl}+(RT/2F)\log i/o$, where C and β are constants. From the temperature coefficient of the cell, the heat of formation of sodium chloroplatinate from the chloroplatinite and chlorine, calculated by means of the Gibbs–Helmholtz equation, is 40,880 g.-cal., as compared with 42,000 g.-cal. found by Thomsen by direct measurement. M. S. BURR.

Potential of the quinhydrone electrode in reference to the hydrogen electrode. E. BILLMANN and A. L. JENSEN (Bull. Soc. chim., 1927, [iv], **41**, 151—166).—The mode of preparation and the age of the quinhydrone have no essential influence on the electrode potential. Slight impurities in the quinhydrone have only a very small influence on the *E.M.F.* The best method of purification is to wash the specimen with the electrolyte to be used immediately before making up the electrode. Reproducible values for the *E.M.F.* of the cell composed of quinhydrone and hydrogen electrodes are obtained when the quinhydrone is 0·00016*M* and above. At 18°, the *E.M.F.* is 0·70439 volt when the electrolyte is 0·1*N*-hydrochloric acid and 0·70479 volt when it is 0·01*N*-acid, whilst its value is 0·70416 volt when the electrolyte is 0·01*N*-hydrochloric acid and 0·09*N*-potassium chloride. The variations in *E.M.F.* produced by the presence of small quantities (3%) of oxygen in the hydrogen are within the experimental error.

S. K. TWEEDY.

Variation of cell constant with concentration and molal conductivity of aqueous barium nitrate, sodium sulphate, and sulphuric acid. at 0°. M. RANDALL and G. N. SCOTT (J. Amer. Chem. Soc., 1927, **49**, 636—647).—The ratios of the constants of two cells, made of "pyrex" glass and having platinised electrodes, varies with the concentration of the three electrolytes used, as observed by Parker (A., 1923, ii, 530, 722). The variation is smaller in the cell with the more widely-spaced electrodes, in agreement with Parker's adsorption theory. It is predicted that sodium sulphate is more suitable than potassium chloride for the standardisation of cells. Adsorption of electrolyte by the glass walls also has a perceptible influence. The accurate determination of conductivity entails the careful standardisation of procedure and the use of the same cell for measuring both the unknown and standard solutions. The conductivities of the above electrolytes (0·001—0·2*M*) are tabulated for 0°; a graphical–analytical method for extrapolating and interpolating conductivity curves is described. S. K. TWEEDY.

Electrode potential of aluminium. P. DROSSBACH (Z. Elektrochem., 1927, **33**, 114—117).—Theoretical. From the heat of the reaction $4Al+3O_2=2Al_2O_3$, and the specific heats of the participants at various temperatures, the decrease of thermodynamic potential accompanying the process is calculated to be 706,700 g.-cal. at 20°, whence the *E.M.F.* of the cell, $Al|Al_2O_3|O_2$ is 2·565 volts. Taking the potential of the oxygen electrode as +1·231, the potential of the aluminium electrode is $\varepsilon_h=-1\cdot33\pm0\cdot01$ volt at 20°. The value obtained by Neumann and Richter (A., 1925, ii, 797) is criticised. H. J. T. ELLINGHAM.

Decomposition potentials in non-aqueous solvents. S. C. BISWAS and S. BOSE (Z. physikal. Chem., 1927, **125**, 442—451).—Current–voltage curves have been obtained for solutions of potassium iodide and bromide, lithium chloride, and hydrogen chloride

in pure methyl alcohol. The decomposition potentials are compared with those for aqueous solutions. The presence of water in a methyl alcohol solution of hydrogen chloride has a marked effect on the decomposition potential, which in pure methyl alcohol is at 0·41 volt; in the presence of 10% of water there is another break in the current–voltage curve at 1·0 volt, and with 30% of water a third at 1·3 volts. The second break is ascribed to the formation of a complex between the hydrogen chloride and the solvent, whilst the third corresponds with the decomposition potential of hydrogen chloride in aqueous solution. The presence of water in the solutions of potassium iodide and bromide has very little influence on the current–voltage curves, since the ions show little tendency to combine with the strongly associated molecules of methyl alcohol; neither are the conductivities altered appreciably. On the other hand, traces of water in the solutions of lithium chloride alter the form of the decomposition curve very considerably, probably because of the formation of lithium hydroxide and of complexes with the solvent. The decomposition potentials in pure methyl alcohol are: potassium iodide, 0·32 volt; potassium bromide, 0·68—0·71 volt; lithium chloride, 1·2 volts; and hydrogen chloride, 0·41 volt. These values lie below the corresponding figures for aqueous solutions, but follow the same sequence. H. F. Gillbe.

Electrolytic polarisation. VI. Electrodeposition potentials of alloys of zinc with iron, cobalt, and nickel. S. Glasstone (J.C.S., 1927, 641—647).—In the electrolysis of a solution containing a mixture of zinc and nickel or iron sulphates the cathodic potential at low current density has a value which corresponds with the separation of the pure iron group metal; as the current density increases, the potential rises rapidly at a certain point, and an alloy consisting mainly of zinc is formed. Solutions of cobalt and zinc exhibit the same phenomenon. The critical current density is in general smaller the lower the temperature, the greater the proportion of zinc in solution, and the lower the hydrogen-ion concentration. On diminishing the current density, the corresponding fall in potential takes place only at very low current densities. The deposition potential of the alloy rich in zinc decreases with increasing temperature, but is independent of the hydrogen-ion concentration. The results do not appear to be in accordance with the theories of previous investigators. The sudden increase of potential may be attributed to a decrease in the concentration of the iron group ion in the neighbourhood of the cathode, resulting in the deposition of an alloy richer in zinc to maintain the flow of current, and hence an increase in the hydrogen overvoltage causing still more zinc to be deposited. The persistence of the higher potential on reducing the current density is probably due to the retardation, by the presence of large amounts of zinc, of the change from the metastable to the stable form of the iron group metal.
M. S. Burr.

Electro-endosmosis and electrolytic water transport. H. C. Hepburn (Proc. Physical Soc., 1927, 39, 99—107).—Liquid transport produced by passing an electric current through aqueous solutions of copper sulphate divided perpendicular to the flow of electricity by a diaphragm of powdered glass is determined. With constant applied potential, it decreases regularly with the concentration up to 0·005N, but is not thereafter appreciably changed up to 0·5N. The charge on the diaphragm decreases to a negligible value with concentrations above 0·005N. With solutions above this concentration, the liquid transport per faraday is related to the dilution by a linear law, and decreases to zero at 1·0N. Above 0·005N, the current flowing through the diaphragm is due entirely to the motion of ions in the electrolyte. C. J. Smithells.

"Anode effect." V. Schischkin (Z. Elektrochem., 1927, 33, 83—91).—The anode effect at carbon electrodes in molten sodium, barium, and calcium chlorides, cryolite, and solutions of alumina in molten cryolite has been examined with reference to the appearance of the anode and the voltage–current relations. With increasing current, the voltage rises very sharply to about 20—25 volts: the "sparking" visible at the anode is attributed to the glowing of particles of carbon on the unwetted anode surface. With further increase of current, the voltage–current curve is slightly less steep: the continued sparking is now attributed to tiny arcs at the points of contact of the carbon particles with the underlying conducting surface of the anode. At a certain voltage, varying from 40 to 60 with different electrolytes, the curve becomes very much less steep, and sparking ceases. Under these conditions, the current passes by continuous discharge of ions and electrons across the gas film on the electrode surface. Finally, with further increase of voltage and current, this silent discharge changes to an arc discharge and the voltage–current curve becomes irregular. It is considered that the occurrence of the anode effect, when not due to a layer of some insoluble substance, is due to the production of chlorine (or fluorine) over the whole anode surface, which causes a change in the physical condition of this surface. This change may be produced either by superficial disintegration of the electrode by the halogen or by the formation of carbon halides and their subsequent decomposition with deposition of finely-divided carbon. The molten salt remains isolated from the anode surface by a gas film on the porous layer of carbon. Oxides dissolved in the molten salt oppose the onset of the anode effect, since the oxygen produced from them causes combustion of this porous carbon layer. For solutions of alumina (p%) in cryolite, the critical current density, D_K, for the onset of the anode effect is given by $D_K = ap^{2\cdot3}$, where a is a constant. This relation also applies to data for solutions of barium and strontium oxides in the corresponding molten chlorides obtained by Arndt and Probst (Z. Elektrochem., 1923, 29, 323).
H. J. T. Ellingham.

Dependence of current efficiency on anodic current density in the preparation of ammonium persulphate. O. Essin and E. Krylow (Z. Elektrochem., 1927, 33, 107—111).—In the electrolysis of saturated solutions of ammonium sulphate at temperatures between 10° and 30°, the current effi-

ciency, η, of persulphate formation at the anode at any moment is given by: $\eta=100[\{(c_0-2c)/(c_0-c)\}-K]\%$, where c_0 is the number of g.-equivalents of ammonium sulphate per litre originally present, and c is the equivalent concentration of persulphate at the given moment. For current densities between 2 and 16 amp./cm.^{2} $K=0$ (cf. A., 1926, 804); at lower current densities, K has a value which represents the fraction of the discharged sulphate ions which give sulphuric acid and oxygen instead of persulphuric acid. At 1 amp./cm.^{2} K is constant (0·064), but at lower current densities it has a higher initial value and increases during electrolysis. If, however, the anolyte is kept neutral by continued additions of ammonia, K remains constant at a given current density, and its dependence on current density can be deduced from the probability theory, assuming that sulphate ions must be discharged within a certain distance of each other in order that persulphate may be formed. When the anolyte is not kept neutral, K increases during electrolysis at low current densities owing to increasing concentration of sulphuric acid producing free persulphuric acid which hydrolyses into monopersulphuric acid (H_2SO_5) and sulphuric acid, the former being converted into sulphuric acid and oxygen at the anode. H. J. T. Ellingham.

Electrochemical behaviour of chromium. III. Equilibrium potential Cr|Cr$^{\cdot\cdot}$ in sulphate solutions. G. Grube and G. Breitinger (Z. Elektrochem., 1927, 33, 112—114).—From measurements of the *E.M.F.* of cells of the type Cr|$CrSO_4$ solutions (various concentrations)|saturated KCl solution|normal calomel electrode, the potential of the electrode Cr|Cr$^{\cdot\cdot}$ was obtained for concentrations of chromous sulphate from 0·033 to 1·142*N*, assuming liquid junction potentials to be negligible and the calomel *P.D.* to be +0·286. The potentials remained constant for 15—20 min., but eventually became more positive. Assuming the degree of dissociation of chromous sulphate to be equal to that of copper sulphate in a solution of the same concentration, several concordant values were obtained for the normal electrode potential Cr|Cr$^{\cdot\cdot}$; the mean is ${}_0\varepsilon_h=-0{\cdot}557\pm0{\cdot}007$ volt. Since for the equilibrium Cr$^{\cdot\cdot}$|Cr$^{\cdot\cdot\cdot}$, ${}_0\varepsilon_h=-0{\cdot}412\pm0{\cdot}002$ volt (A., 1926, 687), Luther's rule gives for Cr|Cr$^{\cdot\cdot\cdot}$, ${}_0\varepsilon_h=-0{\cdot}509$ volt.

H. J. T. Ellingham.

Passivity. H. Eggert (Z. Elektrochem., 1927, 33, 94—102).—If in one state (active) a metal dissolves spontaneously or anodically with a low valency in a particular solution, but in another state does not dissolve, or dissolves with a higher valency, the latter is a passive state. Electrode potential is not regarded as a true criterion for distinguishing active and passive states (cf. Schmidt, A., 1923, ii, 732). In a special apparatus a metal can be scraped in an atmosphere of any desired gas, and without removal from this atmosphere can be dipped into an electrolyte and its potential measured against a standard mercurous sulphate electrode. If iron, nickel, or chromium is scraped in nitrogen or hydrogen and then dipped into an aqueous electrolyte, it exhibits an active potential which gradually becomes somewhat more negative. If, however, oxygen is introduced, the potentials become rapidly more positive. Scraping in oxygen reduces the potential slightly, but it soon recovers its noble value. Similar results are obtained when using non-aqueous electrolytes, *e.g.*, methyl alcohol or even pyridine. Again, in solutions of lithium chloride in methyl alcohol, nickel and iron dissolve anodically according to Faraday's law; chromium dissolves as chromate. In methyl alcohol solutions of silver nitrate, iron and nickel do not dissolve anodically, but chromium dissolves slightly. The behaviour in pyridine solutions is complicated by the impossibility of removing the last traces of water from the pyridine. Part of the current is carried by the ions of water, and anodes of iron or nickel become oxidised. Moreover, in pyridine solutions of lithium chloride, the cathode becomes coated with a badly-conducting film (probably lithium hydroxide derived from the trace of water present). Nevertheless, it is shown that in pyridine solutions of lithium chloride, iron and nickel are active, whilst in solutions of silver nitrate, they are passive. Chromium dissolves in these solutions probably as chromate. Thus the anodic behaviour of iron, nickel, and chromium in non-aqueous electrolytes is similar to that in aqueous electrolytes. Experiments were also made to discover whether chromium which has been activated by scratching or by heating in perfectly dry hydrogen or nitrogen would retain its activity indefinitely when kept in these gases. This was found to be the case when using electrolytic chromium and gases quite free from oxygen (cf. Schmidt, *loc. cit.*). On exposure to air, however, the metal soon became passive. It was also shown that passive chromium is not activated by exposure to hydrogen or nitrogen unless it is scratched or heated. H. J. T. Ellingham.

Becquerel effect. I. Lifschitz (Chem. Weekblad, 1927, 24, 143—147).—The changes in potential of an electrode immersed in an electrolyte on exposure to specific radiations are reviewed and discussed. The results of Svensson have been examined and confirmed. The data so far available are insufficient for any comprehensive hypothesis. S. I. Levy.

Electrodialysis in biochemistry. C. Dhéré (Kolloid-Z., 1927, 41, 243—258).—The literature relevant to the application of electrodialysis to biochemical problems is reviewed and an account (with photographic illustrations of apparatus) given of the author's practical methods of electrodialysis. In reference to the purification of colloids, the author's experiments show not only that electrolyte impurities are removed more rapidly by application of an electric field, but also that the last traces of electrolyte can be readily eliminated, although these are retained strongly by the colloid when subjected to ordinary dialysis. The conductivity of such highly purified gelatin has been measured, and is shown to be higher than that of equally purified serum-albumin; the gelatin has an acid reaction towards litmus and the particles carry a negative charge, although the rate of migration towards the anode is less than that of less highly purified gelatin. Electrodialysed gelatin exhibits strong opalescence at a concentration of 2—2·5% and is completely coagulated by heating at 100°. Electrodialysed calf-serum coagulates when

heated at 39°, but is not coagulated by immersion in liquid air. E. S. HEDGES.

Velocity of physico-chemical reactions. G. VAN LERBERGHE (Bull. Acad. roy. Belg., 1926, [v], **12**, 520—526).—Mathematical. Equations for the velocity of physico-chemical reactions are given in a generalised form accessible to experimental verification. S. J. GREGG.

Initial stages of gaseous explosions. I. Flame speeds during the initial "uniform movement." II. Supposed law of flame speeds. W. A. BONE, R. P. FRASER, and D. A. WINTER. **III. Behaviour of an equimolecular methane–oxygen mixture when fired with sparks of varying intensities.** W. A. BONE, R. P. FRASER, and F. WITT (Proc. Roy. Soc., 1927, **A**, **114**, 402—419, 420—441, 442—449).—I. The speed of initial uniform flame movement through stagnant mixtures of oxygen with hydrogen, ethylene, and acetylene, respectively, when ignited at 15—18° and atmospheric pressure at the open end of a tube of diameter 2·5 cm. (closed at the other end) has been determined, using either a photographic or an electrical method. The photographic method is described in detail, and is applicable to all the hydrocarbon–oxygen (or air) mixtures with initial flame speeds exceeding 1000 cm./sec. The probable experimental error is less than 2·5%. The electrical method may be used for measuring flame speeds up to 300 cm./sec., and in some cases up to 600 cm./sec., with fair accuracy. When used with the same mixture, the two methods give results agreeing within the limits of experimental error. With hydrogen–oxygen mixtures, the "range of inflammability" lay between 10 and 94% hydrogen content appromixately. With any given mixture containing either between 10 and 55%, or between 75 and 94% of hydrogen, a fairly constant initial uniform flame speed was observed; but between 55 and 75% the initial uniform speed was found to differ in successive experiments. With ethylene–oxygen or acetylene–oxygen mixtures, initially propagating flame at speeds exceeding 4000 cm./sec., no initial uniform movement was observable, but the flame was in each case continuously accelerated from the first until detonation was set up. The range of inflammability of the acetylene–oxygen mixtures lay between 3·5 and 88% of acetylene, and of the ethylene–oxygen mixtures between 4·5 and 60% of ethylene. It was found possible under suitable conditions to have a slow "uniform flame movement" developed in an explosive medium after a period of continuous acceleration, showing that such "uniformity" is not necessarily restricted to the initial phase of flame movement.

II. The validity of Payman and Wheeler's "law of flame speeds" (cf. A., 1926, 689), claimed to be applicable to all conditions of flame propagation, has been tested experimentally from the point of view of the behaviour of complex mixtures of certain hydrocarbons, hydrogen, and oxygen containing an excess of combustible gases. The fact that on the explosion of the mixture $C_2H_4+H_2+O_2$ or the mixture $C_2H_2+2H_2+O_2$ no carbon separates and no steam condenses on cooling (Bone and Drugman, J.C.S., 1906, 89, 669) is held to be incompatible with the supposed law. Moreover, according to the law, whenever either of these mixtures is exploded, the oxygen must be divided between the two combustible gases concerned in such proportion as would give rise to two primary mixtures propagating flame with the same speed as the original complex mixture. This is not confirmed by experiment. A number of "blending tests" have been applied to complex oxygen mixtures (both fast and slow) and to one complex air mixture; one of the two primary mixtures was always a hydrogen–oxygen (air) mixture, and the other a hydrocarbon–oxygen (air) mixture, the hydrocarbon being acetylene, ethylene, or methane. In no case have the requirements of the "speed law" been fulfilled. Moreover, with each complex ethylene– or methane–hydrogen–oxygen (or air) mixture examined, it has been found that the effect of progressively increasing the proportion of the primary hydrogen–oxygen (air) mixture in the various blendings in any given series is to lower the observed flame speed progressively, until a point is reached when the resulting complex mixture no longer propagates flame. This result is in direct contradiction to the "law."

III. A photographic study has been made of the behaviour of an equimolecular methane–oxygen mixture when ignited by sparks of varying character and intensity passed between electrodes fixed halfway along a horizontal glass tube, both ends being closed in one series of experiments, open in another. A series of observations was also made in which the same gaseous mixture was ignited at, or near, the open end of a horizontal glass tube of which the other end was closed. The phenomena observed are described, and a number of photographs reproduced. The photographs obtained in the first two series of observations suggest the possibility of (*a*) the occurrence, under ordinary sparking conditions, of a definite "induction period" of non-luminosity and no flame movement as a preliminary to the actual combustion; (*b*) an initial propagation through the medium of a feebly actinic "ghost-like flame" condition, involving only a very partial combination of the gases, and (*c*) the main combustion following later as the result of the superposing of a compression wave on a system which, during phase (*b*), has already become highly sensitive to chemical changes.

L. L. BIRCUMSHAW.

Ignition of gases. VI. Ignition by flames. Mixtures of the paraffins with air. N. S. WALLS and R. V. WHEELER.—See B., 1927, 243.

Gaseous explosions. Effect of fuel constitution on rate of rise of pressure. G. G. BROWN and G. B. WATKINS.—See B., 1927, 243.

Velocity of hydration of carbon dioxide in aqueous solution. A. EUCKEN and H. G. GRUTZNER (Z. physikal. Chem., 1927, **125**, 363—393).—The change with time of the conductivity of an aqueous solution of carbon dioxide immediately after dilution has been measured. The time–conductivity curve affords evidence of the change in the conductivity which may be ascribed to a slow hydration of the carbon dioxide. It is only possible by this method to assign an upper limiting value to the velocity co-

efficient. A more exact method in which the current flow through the solution is measured for different applied voltages gives for the velocity coefficient at 18°, 0·09; at 0°, 0·032.

The time change observed when an aqueous solution of carbon dioxide is neutralised with alkali is due to the instantaneous formation of carbonate, followed by a gradual combination with the excess of carbon dioxide to form hydrogen carbonate. By employing the velocity coefficient found for the hydration process, the rate of neutralisation may be calculated. The agreement between the observed and calculated values is good, but since the reaction is complete within about 1 min., inefficient stirring is liable to introduce large errors into the determinations.

H. F. GILLBE.

Decomposition of azomethane. A homogeneous, unimolecular reaction. H. C. RAMSPERGER (J. Amer. Chem. Soc., 1927, **49**, 912—916).—The isothermal decomposition at constant volume of azomethane at temperatures between 278·6° and 327·4° was studied in an apparatus similar to that used by Smith (A., 1925, ii, 876), the initial pressure being varied as much as 12-fold (3·62—43·46 cm.) and the glass surface 6·5-fold. The decomposition is homogeneous and unimolecular, although slight deviations occur at the lowest and highest initial pressures. The heat of activation is 51,200 g.-cal./mol. Photochemical decomposition proceeds in ultra-violet light, the rate being two thirds as great in a pyrex as in a quartz vessel, and the pressure becoming double on complete decomposition.

S. K. TWEEDY.

Hydrogen peroxide as an oxidising agent in acid solution. IV. W. H. HATCHER and G. W. HOLDEN. **V.** W. H. HATCHER, G. W. HOLDEN, and F. J. TOOLE. **VI.** W. H. HATCHER and G. W. HOLDEN. **VII.** W. H. HATCHER and F. J. TOOLE (Trans. Roy. Soc. Canada, 1926, [iii], **20**, III, 395—398, 399—405, 407—413, 415—421; cf. A., 1926, 270).—IV. The reaction between hydrogen peroxide and formaldehyde in the molecular proportions of 1 : 1·1 has been followed at 25°, and is found to occur in accordance with the equation $2H{\cdot}CHO+H_2O_2=2H{\cdot}CO_2H+H_2$, a complex compound of the reactants probably being formed as an intermediate product. The unimolecular velocity coefficient diminishes continuously from the start in the manner characteristic of those oxidations with hydrogen peroxide in which the latter is decomposed catalytically.

V. The oxidation of glyoxal by hydrogen peroxide in aqueous solution at 25° is a unimolecular reaction, the mechanism probably being $2CHO{\cdot}CHO+H_2O_2=2CHO{\cdot}CHO,H_2O_2$; $2CHO{\cdot}CHO,H_2O_2=2H{\cdot}CO_2H+2H{\cdot}CHO,H_2O_2$; $2H{\cdot}CHO,H_2O_2=2H{\cdot}CO_2H+H_2$. The process is accelerated by alkali and retarded by mineral acids. Glyoxal can conveniently be determined by titration with acid permanganate, or by treatment with hydrogen peroxide and titration with standard potassium hydroxide.

VI. The oxidation of acetic acid or glycollic acid by pure hydrogen peroxide at 100° occurs according to the unimolecular law, and probably involves the formation of per-acids as intermediate products according to the scheme: (*a*) $CH_3{\cdot}CO_2H+H_2O_2=CH_3{\cdot}CO_3H+H_2O$; (*b*) $CH_3{\cdot}CO_3H=CH_2(OH){\cdot}CO_2H$; (*c*) $CH_2(OH){\cdot}CO_2H+H_2O_2=CH_2(OH){\cdot}CO_3H+H_2O$; (*d*) $CH_2(OH){\cdot}CO_3H=CHO{\cdot}CO_2H+H_2O$; (*e*) $CHO{\cdot}CO_2H+H_2O_2=CO_2+H{\cdot}CO_2H+H_2O$; (*f*) $H{\cdot}CO_2H+H_2O_2=H{\cdot}CO_3H+H_2O$; (*g*) $H{\cdot}CO_3H=H_2O+CO_2$. Of these reactions, (*b*) and (*d*) are slow, and (*e*) and (*g*) are rapid. In no instance has formaldehyde been detected in the products of reaction, so that the formaldehyde reported by Dakin (A., 1908, i, 75) must have been due to a difference in the method of oxidation. Mineral acids retard the oxidation, whilst the sodium ion, and still more the potassium ion, decompose the hydrogen peroxide. Glycollic acid is much more resistant to oxidation than are formic, glyoxylic, and oxalic acids.

VII. The reaction between hydrogen peroxide and acetaldehyde at 61·5° to form acetic acid is slow, and the unimolecular velocity coefficient rises continuously from the commencement of the reaction, an effect which is ascribed to the formation of peracetic acid according to the equations $CH_3{\cdot}CHO+H_2O_2=CH_3{\cdot}CHO,H_2O_2$; $CH_3{\cdot}CHO,H_2O_2=CH_3{\cdot}CO_2H+H_2O$; $CH_3{\cdot}CO_2H+H_2O_2 \quad CH_3{\cdot}CO_3H+H_2O$. Lactic acid at 100° is also oxidised to carbon dioxide very slowly, perlactic acid probably being an intermediate product.

R. CUTHILL.

Decomposition and oxidation of dithionic acid. D. M. YOST and R. POMEROY (J. Amer. Chem. Soc., 1927, **49**, 703—707).—The rate of decomposition of dithionic acid in presence of hydrochloric and of perchloric acids at 50° and 80°: $S_2O_6''+H_2O=SO_4''+H_2SO_3$, is proportional to the dithionate concentration and the total acid concentration, provided the latter does not exceed 0·6*N*. The rate increases more rapidly at higher concentrations, showing that the catalytic effect is due to hydrolysis. The rate of oxidation of dithionic acid is independent of the concentration and nature of the oxidising agents (iodate, bromate, and dichromate), and is the same as the rate of decomposition into sulphate and sulphite, showing that the first stage in oxidation is hydrolysis (Muller, A., 1911, ii, 266).

S. K. TWEEDY.

Effect of alkali on the oxidation of ferrous hydroxide by air. S. MIYAMOTO (Bull. Chem. Soc. Japan, 1927, **2**, 40—44).—A standard stream of air was drawn through known mixtures of ferrous hydroxide and sodium hydroxide and the quantity of ferrous compound remaining after a given interval determined by treating with sulphuric acid and titrating with permanganate. If v c.c. of the latter are required at time t and v_0 at zero time, then $v-v_0=kt$; k is a constant for a given concentration of alkali, but decreases as the latter increases. Hence the addition of alkali reduces the velocity of oxidation.

S. J. GREGG.

Transformations of iron in nature. I. Theoretical. H. O. HALVORSON and R. L. STARKEY (J. Physical Chem., 1927, **31**, 626—631).—Equations indicating the relationships between the activities of ferrous, ferric, and hydrogen ions and oxygen concentration are derived. Measurements of the amounts of ferrous and ferric ions in solution at various p_H values indicate that at $p_H>5$ very small amounts of

ferrous iron will occur in solution under atmospheric conditions and that even smaller amounts of ferric iron are soluble. L. S. THEOBALD.

Mutarotation and alkalinity of the medium. H. COLIN and (MLLE.) A. CHAUDUN (Compt. rend., 1927, **184**, 749—751).—The rate of mutarotation of dextrose has been investigated in presence of ammonia and sodium hydroxide of concentrations ranging from $N/550$ to $N/6800$. Their effects become similar at concentrations below $N/5500$. In the case of lævulose, solutions of ammonia more dilute than $N/40{,}000$ have no effect. J. GRANT.

Influence of stirring on velocity of reaction in heterogeneous systems. E. BEKIER and K. RODZIEWICZ (Rocz. Chem., 1926, **6**, 869—880).—The velocity of dissolution of copper plates in solutions of iron alum is expressed by $K=(v/O\Delta t)\log_e c_1/c_2$, where O is the area of the plate, n the number of revolutions of the stirrer per min., and c_1 and c_2 are the initial and final concentrations of ferric salt over an interval of time Δt. K is a linear function of n and may be expressed by $K=a+bn$, where a is the value of K at which the y axis is cut by the curves obtained for the relation K/n, varying the volume of solution, the surface area of the plate, and the position and shape of the stirrer, and corresponds with the velocity constant of an unstirred solution. The value of a depends on conditions of stirring, and is not constant (cf. Klein, A., 1924, ii, 745).
R. TRUSZKOWSKI.

Velocity of reaction and energy of activation of halogen compounds. D. H. PEACOCK (J. Physical Chem., 1927, **31**, 535—542).—A theoretical paper in which the alternating effect of substituents on the energy of activation is discussed. The effect of energy of activation in altering the ratios of velocities, and hence that of the products formed, at different temperatures is pointed out, and it is suggested that the alteration in this energy is a more fundamental expression than is velocity of reaction of the effect of substituents on reactivity. The effects of substituting one halogen for another on the velocity constant and on the energy of activation are compared in a number of reactions. Velocities of reaction are affected, not only by alterations in activation energy, but also by variations in the sensibility of the molecule and the stability of the activated state. The reactions discussed are examined with reference to the velocity equation of Dushman (A., 1921, ii, 315). L. S. THEOBALD.

Complex homogeneous catalysis of hydrogen peroxide by sodium molybdate. E. SPITALSKY and A. FUNCK (Z. physikal. Chem., 1927, **126**, 1—23).—A study of the catalytic decomposition of hydrogen peroxide by sodium molybdate in aqueous solution. The catalyst exists in an unstable and in a relatively stable catalytic state. The stable condition is attained when the unstable form is subjected to repeated treatment with hydrogen peroxide. In this case, the catalysis is quite regular and the shape of the reaction curve is independent of the initial concentration of hydrogen peroxide. In neutral solution, the reaction velocity rises gradually to a well-defined maximum, and ultimately becomes very small as completion is approached. In dilute acid or alkali, the maximum disappears and the reaction velocity becomes sensibly constant over a wide range. The catalytic activity, with which the brown colour of the solution may be associated qualitatively, is greatest in dilute alkaline solutions. In strong acid or alkali, the catalysis ceases completely and the solution becomes colourless or nearly so. The results are discussed in terms of Spitalsky's theory of homogeneous catalysis (A., 1926, 1011), assuming the simultaneous formation of several catalytically active intermediate products with varying affinity constants and stabilities. G. A. ELLIOTT.

Theory of the catalytic combustion of ammonia. M. BODENSTEIN.—See B., 1927, 217.

Catalytic oxidation of ammonia. III. L. ANDRUSSOV.—See B., 1927, 217.

Thermal decomposition of ammonia on the surface of a molybdenum wire. R. E. BURK (Proc. Nat. Acad. Sci., 1927, **13**, 67—74).—The decomposition of ammonia on the surface of a heated molybdenum wire is apparently of zero order. The presence of hydrogen produces a slight accelerating effect, whilst that of nitrogen produces a marked retardation, the velocity after first decreasing with increasing concentration of nitrogen attaining a final limiting value. The film of nitrogen on the surface of the wire is very persistent and is not removed by pumping off in a vacuum. Wires, however, return to normal activity after performing one or more experiments with ammonia. Activated molecules only of nitrogen condense to form the poisoning film, which may consist of atomic nitrogen. Since the rate of reaction is not zero at nitrogen pressures which are so great that the surface is almost completely covered, the reaction must still proceed on parts of the surface which are not poisoned or, at a reduced rate, on a film of nitrogen. It is impossible to distinguish between the two possible mechanisms, since both yield theoretical kinetic expressions of the same type. At a given temperature and pressure of ammonia, the rate of reaction is represented by the equation reciprocal of half-life$=(k_3k_2/k_2+k_1p)+k_4$, where k_1, k_2, k_3, and k_4 are constants and p is the pressure of nitrogen. Experiments at various temperatures between 1097° and 1228° Abs. show that the logarithm of the half-life varies linearly with the reciprocal of the absolute temperature, the slope of the line corresponding with a heat of activation of 53,200 g.-cal. This is shown to be a true heat of activation. The present data are compared with those obtained with other catalysts (Hinshelwood and Burk, A., 1925, ii, 691). J. S. CARTER.

Contact catalysis and the activation of gases by adsorption. H. S. TAYLOR and G. KISTIAKOVSKI (Z. physikal. Chem., 1927, **125**, 341—362).—The activation of part of the adsorbed gas in hydrogenation reactions is ascribed to the action of the unsatisfied valencies of the outlying atoms on the solid surface. Earlier work on the ionisation potentials of adsorbed films of hydrogen and nitrogen on metallic surfaces is discussed and results are given which prove that the ionisations occurring at 11 and 13 volts are

due to nitrogen and hydrogen, respectively. A calorimetric method is described whereby measurements may be made of the heats of adsorption of small quantities of gas on catalytic surfaces. The curves showing the relation of the heat of adsorption to the degree of saturation of the surface are of different types for hydrogen adsorbed on active copper and on a copper surface poisoned with oxygen and for carbon monoxide adsorbed on active copper. The theory of catalytic surfaces, employed in conjunction with Langmuir's theory of adsorption, is capable of explaining these three types of curve, if it is assumed that only part of the surface atoms can activate the adsorbed gas molecules and that the activation is endothermic. The work of Schmidt and of Schwab and Pietsch is criticised, and it is suggested that the activation of hydrogen is due to atomic dissociation.

H. F. GILLBE.

Influence of the adsorptive power of the carrier on the catalytic activity of metal-carrier catalysts. T. SABALITSCHKA and W. MOSES (Ber., 1927, **60**, [*B*], 786—804).—The catalytic hydrogenation of maleic and fumaric acids and sodium cinnamate has been examined in the presence of palladium deposited on blood, beech, fungus, bone, and sugar charcoal and on barium sulphate and kieselguhr. The adsorptive power of the catalysts towards hydrogen cannot be definitely determined. The sequence of adsorptive powers towards fumaric and maleic acids and sodium cinnamate is: blood > beech > fungus > bone > sugar charcoals > barium sulphate = kieselguhr. The activity of the catalysts obtained by loading different carriers with an equal amount of palladium depends to a greater or less extent on the carrier. With freshly-prepared materials, the activity towards all three unsaturated substances diminishes in the sequence blood > fungus > beech > bone > sugar charcoals > barium sulphate = kieselguhr = palladium without carrier. The activity is also dependent on the manner in which any given carrier is charged with a definite amount of metal; for example, sugar charcoal, barium sulphate, and kieselguhr catalysts, prepared from the hydroxide and subsequently preserved, have a greater activity than fresh catalysts prepared from the chloride. Ignition in a high vacuum and saturation with hydrogen diminishes the activity of all catalysts to an extent which increases with the number of such treatments; the catalyst is not re-activated by oxygen. The adsorptive power of the catalysts towards hydrogen depends on the type of carrier and is scarcely affected by the mode of charging with palladium; palladium-free carriers do not adsorb hydrogen measurably.

The activity of the palladised carriers depends greatly on the extent to which the palladium compound is adsorbed by the carrier previous to reduction. With carriers of low adsorptive power, more efficient catalysts are obtained by use of the readily adsorbable palladium hydroxide in place of the chloride, whereas with good adsorbents little difference is observed in the various products. The activity of palladised barium sulphate is dependent on the degree of division of the palladium. The catalytic activity is influenced in varying degree by the volume of the liquid in which it is distributed during hydrogenation.

Separate determinations of the adsorptive powers of palladised catalysts toward hydrogen and the substances undergoing hydrogenation and of the catalytic activity of these catalysts under similar conditions indicate a proportionality between the three properties, but show that the catalytic activity does not depend directly on the magnitude of the adsorption. The important function of the carrier is the provision of a larger surface and favourable disposition of the catalysing metal by adsorption of the compound from which it is formed by reduction; it also secures a better distribution of the metal in the reaction mixture and preserves the fine division of the metal by hindering aggregation, which otherwise takes place readily.

H. WREN.

Products formed during the working of lead accumulators. II. L. MAZZA.—See B., 1927, 257.

Applications of passivity in electrolysis. O. DONY-HENAULT (Bull. Soc. chim. Belg., 1927, **36**, 261—270).—Certain iron alloys, notably steels of the "stainless" type, become passive in contact with solutions containing chlorates, and to a less extent in contact with perchlorate solutions. Such alloys may be substituted for platinum for use as anodes in electrolytic processes involving high current densities and considerable local acidities (*e.g.*, the decomposition of barium carbonate in the anode chamber of an electrolytic system containing chlorates). An iron–cobalt–copper alloy is rapidly attacked under these conditions. The passivity of lead is discussed and the importance of including overvoltage effects when considering the processes involved in the mechanism of the lead accumulator is emphasised.

J. S. CARTER.

Electrolysis of aqueous solutions of pure oxalic acid. E. DOUMER (Compt. rend., 1927, **184**, 747—749).—The anodic products of the electrolysis of oxalic acid and its salts vary with the reaction. Electrolyses with various concentrations of pure oxalic acid and various current densities have shown that oxygen and carbon dioxide are produced at the anode, the former usually in the largest quantities and in amounts depending on the current density, but falling within certain limits (0·25 and 0·5 of the corresponding volume of voltametric hydrogen liberated). The results may be explained by the ionisation of 2 mols. of water for 1 mol. of oxalic acid. The oxalate ions partly decompose into carbon dioxide and partly react with the hydroxyl ions to produce oxygen.

J. GRANT.

Photo-decomposition of chlorine water and of aqueous hypochlorous acid solutions. II. A. J. ALLMAND, P. W. CUNLIFFE, and R. E. W. MADDISON (J.C.S., 1927, 655—669).—Measurements of the extinction coefficients are described for the range 365—436 μμ for hypochlorous acid and chlorine water, both alone and also in presence of certain added strong electrolytes; the values of the extinction coefficient for chlorine in solution are very close to those for gaseous chlorine. From the amount of decomposition and the quantity of energy absorbed, the quantum efficiency at 365 μμ for chlorine water is

calculated, and lies between 1·6 and 2·0; it varies very little with wave-length over the range 313—436 μμ, but is greatly reduced by the addition of certain strong electrolytes, notably hydrochloric acid. A consideration of these results together with previous data (A., 1925, ii, 572) on the yield of chloric acid during decomposition, the volatility of chlorine in the different solutions, and the present extinction coefficient measurements leads to a theory of the mechanism of the reaction. This theory is found to be consistent with thermochemical data and with the observed order of reaction, and appears to permit of the separate determination of the efficiency of the primary and secondary photo-reactions.

S. J. Gregg.

Photochemical decomposition of hydrogen iodide. B. Lewis (Nature, 1927, **119**, 493).—On working at a pressure of hydrogen iodide of the order of 0·1 mm. of mercury, the quantum efficiency of the reaction is about two; Warburg's mechanism (Sitzungsber. Preuss. Akad. Wiss. Berlin, 1918, 300) is thus experimentally substantiated. Hence a polar molecule may dissociate in a single elementary act.

A. A. Eldridge.

Photochemistry of the alkali and alkaline-earth iodides. H. Stobbe and F. K. Steinberger (Z. anorg. Chem., 1927, **161**, 21—45).—If alkaline solutions of potassium iodide in vessels of quartz or "uviol" glass are exposed to sunlight or the light from a mercury-vapour lamp, the alkalinity diminishes somewhat, probably due to the action of carbon dioxide from the air, and solutions which were originally only slightly alkaline contain after exposure hypoiodite and free iodine, whilst if the alkalinity is increased, iodate is formed as well, and in strongly alkaline solutions is the only product. It is therefore concluded that the photolysis involves the reactions: $2KI+O+H_2O=2KOH+I_2$; $KI+I_2=KI_3$; $2KOH+I_2 \rightleftharpoons KIO+KI+H_2O$; $3KIO=KIO_3+2KI$. With neutral iodide solutions, no free iodine is formed in absence of oxygen, and even when oxygen is present, no iodate, and only small amounts of hypoiodite, are formed in addition to free iodine. In presence of oxygen only, there is very little reaction, but if increasing amounts of carbon dioxide are introduced, the photolysis increases up to a maximum, beyond which it diminishes. Since other weak acids such as boric acid and *p*-nitrophenol also promote the reaction, it seems that carbon dioxide acts by increasing the hydrogen-ion concentration of the solution. In ordinary air, the formation of free iodine from neutral iodide solutions apparently is due mainly to the photolysis of hydrogen iodide, the above reactions occurring only to a small extent. When preserved in the dark, some solutions become yellow but remain neutral, whilst others remain colourless but become slightly alkaline. In the decomposed solutions, hydrogen ions, from carbonic acid, have brought about the reaction $2HI+O=H_2O+I_2$, whereas in the other solutions the alkali, presumably from the containing vessel, has removed the hydrogen ions, so the reaction $2KI+O+H_2O=2KOH+I_2$ must be able to occur only in the light. The rate of decomposition of iodide solutions in the light increases with increase in the iodide concentration, but is not directly related to it. If nuclei of iodine are already present at the outset, the velocity of reaction is greater at first than it is later, whilst if the nuclei are absent, the reverse is the case. In either case, the velocity after the initial stage becomes approximately constant for a considerable time. The photolysis of neutral iodide solutions to which the oxygen of the air has free access is a bimolecular reaction, but the velocity coefficient is dependent on the intensity and wave-length of the light and on the proportion of effective radiation absorbed, and increases with the time until so much tri-iodide is formed that all the active radiation is absorbed. Thus the behaviour of these solutions closely resembles that of hydrogen iodide solution (cf. Winther, A., 1920, ii, 427), as might be expected from the above. The wave-lengths most active in bringing about decomposition are in the ultra-violet, but the blue of the visible spectrum has also a slight effect.

R. Cuthill.

Photochemical decomposition of potassium persulphate. III. Effect of added electrolytes. J. L. R. Morgan and R. H. Crist (J. Amer. Chem. Soc., 1927, **49**, 960—966).—There is no evidence of the existence of intermediate equilibria in the photochemical decomposition of potassium persulphate, such as occur in the thermal decomposition (Palme, A., 1920, ii, 685). The rate of decomposition is retarded by sulphuric acid, potassium sulphate, and potassium hydroxide; in no case can this retardation be due to an inner filter action. In each case, the velocity is a hyperbolic function of the amount of electrolyte added. The phenomena are discussed from the points of view of de-activation and of a kinetic salt effect.

S. K. Tweedy.

Alleged retardation of certain reactions by light. A. J. Allmand and R. E. W. Maddison (J.C.S., 1927, 650—655).—Experiments were carried out on the oxidation of solutions of sodium sulphite when exposed to light of various wave-lengths and also in the dark. Curves correlating time of exposure and amount of oxidation showed no discontinuity even although successive portions of the curves applied to alternate dark and light periods, except in the case of ultra-violet light of very short wave-length. Thus light of ordinary wave-length has no effect on the rate of oxidation of sodium sulphite in solution.

S. J. Gregg.

Oxygen transmission by chlorophyll and the photochemical equivalent law. H. Gaffron (Ber., 1927, **60**, [*B*], 755—766; cf. Warburg and Negelein, A., 1922, i, 1097; 1923, ii, 718).—Under the influence of light, a solution of chlorophyll in acetone absorbs oxygen with gradual oxidation of the dye. In presence of a suitable acceptor, the absorption is accelerated and the chlorophyll suffers much less change. For this purpose, allylthiocarbamide is selected, which, in addition to complex compounds, yields sulphur dioxide and thence sulphur trioxide. The relationship between the volume of oxygen absorbed and the amount of light used shows that in this case Einstein's photochemical equivalent law is obeyed for a large range of the spectrum. There is no relationship between strength of absorption for light of differing wave-lengths and photochemical action,

provided that the absorption is complete. Confirmation is afforded to the observation of Warburg and Negelein (*loc. cit.*) that every quantum absorbed by the chlorophyll, independent of its energy, causes the same chemical action in the living plant. Variations in the concentration of dye and acceptor show that each is free in the solution; excess of dye hinders the photochemical change, which is promoted by the acceptor. The solvent is indifferent. The observations may be expressed quantitatively by the formula $\phi/\phi_0 = (C_A/C_F)\alpha K+1$, where ϕ and ϕ_0 are the observed and calculated photochemical activities, C_A and C_F the concentrations of acceptor and dye, and K is an empirical constant.

Similar behaviour is exhibited by hæmatoporphyrin and allylthiocarbamide dissolved in acetone.

H. WREN.

Special action of radiations from a mercury arc. E. ROUSSEAU (Compt. rend., 1927, **184**, 683—685; cf. Lecarme, *ibid.*, 1925, **181**, 1079).—The photolytic effects of the mercury arc have been tested on a solution containing calcium monophosphate (10 g.), phosphoric acid (1 c.c.), and cherry-laurel water (Codex) (100 c.c.), the hydrogen cyanide remaining after various intervals of time being determined. The liquid was covered with a protecting layer of oil impermeable to ultra-violet rays. The effect must therefore be due to visible radiations in the green, red, or infra-red regions, or to an unknown photochemical radiation from the mercury arc analogous to that observed by Lecarme in ultra-violet solar radiations (*loc. cit.*). J. GRANT.

Determination of the energies of reaction from a knowledge of the active radiations. R. AUDUBERT (Compt. rend., 1927, **184**, 881—883).—The Perrin–Lewis radiochemical theory has been verified by the determination of the initial frequencies (ν_0' and ν_0) of the light required to produce and reverse the reaction in the equation $Q=hN(\nu_0'-\nu_0)$, Q being the energy of reaction, h Planck's constant, and N Avogadro's number. The reaction studied was the oxidation and reduction, respectively, of ferrous and ferric salts ($\nu_0=3{\cdot}5\times10^{14}$ and $\nu_0'=2{\cdot}0\times10^{14}$, respectively) by the same radiations, but with different intensities. The frequencies were determined electrometrically from the *E.M.F.* produced when a platinum electrode placed in an electrolyte is illuminated (A., 1923, ii, 827), the potential increasing with the frequency for a particular intensity of radiation. The result has been confirmed by measurements of the affinity, and the oxidation of ferrous to ferric iron has been shown to be an endothermic reaction. J. GRANT.

Existence of triatomic hydrogen. F. PANETH, E. KLEVER, and K. PETERS (Z. Elektrochem., 1927, **33**, 102—107).—Processes stated to yield triatomic hydrogen (cf. Wendt, A., 1920, ii, 425; 1922, ii, 369; Grubb, A., 1923, ii, 403; Venkataramaiah, A., 1923, ii, 235; 1924, ii, 34) have been examined, but it is concluded that no evidence for the existence of this substance has been obtained. Hydrogen which has been passed through hot palladium or submitted to a silent discharge in an ozoniser does indeed blacken lead acetate paper after passage through a tube of sulphur, but the effect is just the same if this sulphur tube is omitted. Hydrogen sulphide arises from traces of sulphur in the palladium or the glass, respectively. The phenomenon disappears if the palladium or the ozoniser is kept in use for some time and is not obtained if a quartz ozoniser is employed. Again, the supposed formation of ammonia by the action of pure nitrogen on hydrogen obtained by the action of acids on magnesium is disproved. Ammonia is obtained when pure hydrogen is substituted for nitrogen and arises from traces of nitride in the magnesium. The statement that when oxygen is exploded with excess of hydrogen the residual gas reduces permanganate or indigo could not be confirmed, in spite of wide variation of the experimental conditions. Hydrogen which had been subjected to α-rays from a mixture of thorium-*B* and thorium-*C* did not reduce sulphur, but using α-rays from polonium, a trace of hydrogen sulphide was detected. This is attributed, however, not to activation of the hydrogen, but to traces of finely-divided polonium being carried over on to the sulphur; sulphur and hydrogen are known to react under the direct influence of α-rays. H. J. T. ELLINGHAM.

Conversion of hydrogen into helium. F. PANETH, K. PETERS, and P. GUNTHER (Ber., 1927, **60**, [*B*], 808—809; cf. A., 1926, 1077).—Possible sources of error in the previous experiments are indicated by the observations that asbestos evolves its helium content at a much lower temperature in hydrogen than in oxygen and that the arrangement of the apparatus may not exclude the penetration of helium from the atmosphere. H. WREN.

Direct oxidation of lithium iodide. J. P. SIMMONS and C. F. PICKETT (J. Amer. Chem. Soc., 1927, **49**, 701—703).—Anhydrous lithium iodide decomposes at high temperatures in a stream of oxygen according to the equation $10LiI+5O_2=2LiIO_3+4Li_2O+4I_2$. S. K. TWEEDY.

Sodium hyponitrite. A. W. SCOTT (J. Amer. Chem. Soc., 1927, **49**, 986—987).—Sodium hyponitrite, which is not hygroscopic, is conveniently prepared as follows. To a saturated solution of 3·26 g. of hydroxylamine hydrochloride in anhydrous ethyl alcohol at −5° is added slightly more than the calculated amount of sodium dissolved in the least amount of alcohol. After filtering, 110 c.c. of anhydrous ether and 3·24 g. of sodium in the minimum amount of alcohol are added to the solution, which is then cooled to −5° and twice the calculated amount of either amyl or propyl nitrite added. After being kept at −5° for 1 hr., the sodium hyponitrite is collected, washed with alcohol, then with ether, and dried over sulphuric acid in a vacuum; the yield is 13·9%. S. K. TWEEDY.

Dehydration of borax. M. A. RAKUSIN and D. A. BRODSKI.—See B., 1927, 250.

Thermal dissociation of alkali fluoborates. J. H. DE BOER and J. A. M. VAN LIEMPT (Rec. trav. chim., 1927, **46**, 124—132).—The fluoborates of potassium (m. p. 530°), rubidium (m. p. 590°), and cæsium (m. p. 550°) were prepared by precipitation of solutions of the corresponding chlorides by hydro-

fluoboric acid solution, and those of sodium and lithium by placing solid boron fluoride and the solid alkali fluoride together in an evacuated vessel. Since the proportion of substance dissociating is small, the ratio of potassium fluoride to boron trifluoride in the liquid phase is sensibly constant over the whole temperature range, and the system is therefore univariant. The results fit the following equations: for KBF_4, $\log p$(mm. of mercury)$=-6317/T+8{\cdot}1\vartheta$, whence the heat of reaction Q of the equation KBF_4 (liquid)$=KF$(liquid)$+BF_3$(gas)$+Q$ g.-cal. is 28,900 g.-cal.; for $RbBF_4$, $\log p=-5900/T+7{\cdot}45$, and $Q=$ 26,960 g.-cal.; for $CsBF_4$, $\log p=-5880/T+7{\cdot}35$, and $Q-26{,}880$ g.-cal. By considering the formation of potassium fluoborate by the path $KF\longrightarrow K^{\cdot}+F'+U_{KF}$, $F'+BF_3\longrightarrow BF_4'-\phi_{BF_4}$, the value of ϕ_{BF_4} is deduced and applied to calcium fluoborate, the heat of formation of which is thus shown to be negative, in accordance with the fact that calcium fluoride will not combine with boron fluoride. The refractive indices of saturated solutions of the salts were also measured and shown to be close to that of water.

S. J. Gregg.

Azidodithiocarbonic acid. III. Azidodithiocarbonates of lithium, sodium, rubidium, and cæsium. A. W. Browne and A. F. Audrieth [with C. W. Mason] (J. Amer. Chem. Soc., 1927, **49**, 917—925; cf. A., 1926, 39).—The crystalline *azidodithiocarbonates*, $MS{\cdot}CS{\cdot}N_3{,}xH_2O$, of lithium ($x=1$), sodium ($x=4$, 2, and 0), rubidium ($x=0$), and cæsium ($x=0$) were prepared by the union of carbon disulphide with alkali azides (Browne and Hoel, A., 1922, ii, 848). The solubilities of the salts follow the order Li>Cs>Rb>Na; they are insoluble in carbon disulphide, chloroform, carbon tetrachloride, and benzene. They tend to decompose at the ordinary temperature: $MS{\cdot}CSN_3=MS{\cdot}CN+S+N_2$. The violence of the explosion on detonation varies directly as the atomic weight of M, except that the lithium salt is more explosive than the sodium salts. The explosion liberates a gas with a sulphurous odour, leaving a viscous, yellow residue, probably a polymeride of thiocyanogen. Microscopical observations are recorded. The rubidium and cæsium salts are very photosensitive; on alternate illumination and confinement in a dark space, "photolysis" occurs and the salt decomposes. The colour change on illumination is ascribed to free metal atoms held *in situ* in the crystal lattice, their valency electrons having been restored by some photo-process. It is suggested that the blue colour of Stassfurt halite may similarly be explained. S. K. Tweedy.

Reduction of copper oxide by gaseous reducing agents. W. G. Palmer (Trans. Amer. Electrochem. Soc., 1927, **51**, 87—90).—See A., 1923, ii, 474.

H. J. T. Ellingham.

Preparation of sodium aurothiosulphate. H. Brown (J. Amer. Chem. Soc., 1927, **49**, 958—959).—The following method is more rapid and economical than that described by McCluskey and Eichelberger (A., 1926, 255). A solution of 41·2 g. of hydrochloroauric acid in 75 c.c. of water is rendered faintly alkaline with 40% sodium hydroxide solution and a solution of 102 g. of sodium thiosulphate crystals in 200 c.c. of water is added. The mixture is mechanically stirred and 4*N*-nitric acid added dropwise until the red colour ceases to appear. When the mixture shows faint turbidity, it is filtered and precipitated with four times its volume of alcohol. The precipitate is redissolved in the minimum amount of water and, after filtration, reprecipitated. A further precipitation yields very pure sodium aurothiosulphate. The salt is dried over sulphuric acid in a vacuum and may be preserved in well-stoppered bottles in a refrigerator. It will keep at the ordinary temperature for 3 months if sealed in amber tubes under slightly reduced pressure.

S. K. Tweedy.

Reducing properties of beryllium. Isolation of barium, magnesium, potassium, and aluminium. C. Matignon and (Mlle.) G. Marchal (Compt. rend., 1927, **184**, 715—717).—On account of its high heat of oxidation, beryllium may be used to reduce certain metallic oxides. The oxide is well mixed with a slight excess of beryllium beyond the theoretical quantity required, pressed into a solid pastille, and heated in the electric furnace. Magnesium oxide and potassium hydroxide have been completely reduced by these means at 1280° and 700°, respectively. Barium and aluminium oxides are partly reduced to the corresponding metal at 1230° and 1280°, respectively, whilst lime forms a suboxide of calcium at 1230—1280°. J. Grant.

Preparation of beryllium chloride. C. Matignon and M. Piettre (Compt. rend., 1927, **184**, 853—855).—Beryllia may be converted into beryllium chloride by the action of sulphur chloride at 700—800°, phosphorus trichloride at 850°, phosphorus perchloride, or carbon tetrachloride. Carbon tetrachloride at 800° for 1·25 hrs. gives a yield of 68—80%, the other reagents giving low yields, slow reactions, or impure products. J. Grant.

[Non-existence of] magnesium sulphate octahydrate. A. Benrath and W. Schroder (Z. anorg. Chem., 1927, **161**, 155—158).—Attempts to confirm the existence of the magnesium sulphate octahydrate reported by Takegami (A., 1921, ii, 698) have been unsuccessful. R. Cuthill.

Reactions of metals with solid salts on heating. B. Garre (Z. anorg. Chem., 1927, **161**, 108—112).—The heating curves of mixtures of various metallic oxides and carbonates with magnesium and aluminium, respectively, have been determined. The reactions with magnesium start more gradually and at a lower temperature than those with aluminium. With binary mixtures of zinc and tin with lead oxide or cupric oxide, or of cupric oxide with lead or nickel, the reaction commences below the m. p. of either component. If the heat of reaction is less than about 15 kg.-cal., the reaction is not complete below the m. p., so that a little above this temperature there is a second evolution of heat, and if the products of reaction still prevent complete decomposition there may be a third evolution of heat at a still higher temperature. R. Cuthill.

Potentiometrical study of the reaction between calcium ferrocyanide and solutions containing rubidium and cæsium. C. del Fresno and J. Vázquez (Anal. Fís. Quím., 1927, **25**, 42—46, and

Z. Elektrochem., 1927, **33**, 149—150).—The potentiometric curves obtained by titrating 0·2*M*-solutions of calcium ferrocyanide against approximately 0·1*N*-solutions of rubidium chloride and cæsium bromide, respectively, show discontinuities corresponding with the completion of the reaction $Ca_2Fe(CN)_6+2MX=CaX_2+CaM_2Fe(CN)_6$, where M=Rb or Cs and X=halogen. The agreement with the equation is not sufficiently good for the method to be used for quantitative determinations. G. W. ROBINSON.

Analysis and preparation of cadmium sulphides. P. HULOT (Bull. Soc. chim., 1927, [iv], **41**, 313—316).—Ten different cadmium sulphides have been prepared, mainly by the reaction of a solution obtained by boiling sulphur with sodium carbonate solution with solutions of cadmium salts under varying conditions, and by the action of sodium monosulphide solution on a suspension of cadmium carbonate. Specimens were also prepared in the dry way; they contained 71 to 73·9% of cadmium and 21·2 to 19·2% of sulphur, whereas those prepared in the wet way contained 67 to 69·1% of cadmium and 16·3 to 18·4% of sulphur. The presence of free sulphur was carefully avoided. The products were analysed by fusing with potassium nitrate, extracting the cooled melt with water, and weighing the residue as cadmium oxide, the sulphate being determined in the extract. S. K. TWEEDY.

Fractional precipitation of barium and radium chromates. L. M. HENDERSON and F. C. KRACEK (J. Amer. Chem. Soc., 1927, **49**, 738—749).—The separation of barium and radium by fractional precipitation of the chromates in 0·05—0·3*N* acid solutions is as efficient as the bromide method of separation. The method is advantageous when only small quantities of the barium–radium mixture are available, or when the solution containing the mixture is too dilute to be concentrated economically by the chloride method. S. K. TWEEDY.

Causes of the surface devitrification of glasses. K. TABATA.—See B., 1927, 219.

Reduction of metallic chlorides by hydrogen. A. B. BAGDASARIAN (Trans. Amer. Electrochem. Soc., 1927, **51**, 1—46).—Equilibria involved in the reduction of lead, zinc, and cuprous and ferrous chlorides by hydrogen at various temperatures below the b. p. of the chlorides or the corresponding metals have been studied by analysing the gases obtained by passing a slow stream of hydrogen over the chloride or of hydrogen chloride over the corresponding metal. In the latter case, the reaction is relatively slow and measurements were made at various rates of gas flow, the true equilibrium composition of the resulting gases being obtained by extrapolation to zero gas velocity. Under these conditions, values of the equilibrium constant, K, were in good agreement, irrespective of the side from which the equilibrium was approached. The curve correlating $\log K$ with $1/T$ is a straight line except for ferrous chloride, where two breaks are obtained, due probably to the transition points of metallic iron. The free energy equations for the reduction of lead, zinc, and cuprous chlorides by hydrogen have been calculated, and by combining with existing data, the following quantities have been calculated: heats of formation of cuprous chloride (CuCl) and lead chloride, 31,280 and 85,145 g.-cal., respectively, at 25°; free energy of formation of cuprous chloride (CuCl), 28,435 g.-cal. at 25°; latent heats of fusion of cuprous chloride (CuCl) and zinc chloride, 2246 and 7380 g.-cal., respectively.

A process is suggested for the treatment of certain classes of complex ores and other metallurgical products, in which the material is chlorinated in the dry way with chlorine or hydrogen chloride at a suitable temperature and the metallic chlorides thus formed are reduced by hydrogen at elevated temperatures. Hydrogen and chlorine could be regenerated by electrolysis of the hydrogen chloride produced in the reduction process. H. J. T. ELLINGHAM.

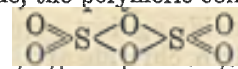
Active nitrogen. II. Reactions with gases. E. J. B. WILLEY and E. K. RIDEAL (J.C.S., 1927, 669—679).—The value 43,000 g.-cal./g.-mol. previously given by the authors (A., 1926, 893) for the mean energy content of active nitrogen has been confirmed by a study of the reactions of the gas with other gases of varying critical increments. Hydrogen, carbon monoxide, carbon dioxide, and water vapour, with their critical increments above 55,000 g.-cal./g.-mol., had no effect on the after-glow. The characteristic luminosity of iodine (dissociation energy 34,500 g.-cal./g.-mol.) and of bromine (46,200) were easily excited, but that of chlorine (55,000) only very slightly. Hydrogen iodide was readily, hydrogen bromide less readily, and hydrogen chloride not at all decomposed by active nitrogen, the respective energies of decomposition being 45,700, 50,000, and 90,000 g.-cal./g.-mol. On the other hand, from a mixture of hydrogen and chlorine a considerable quantity of hydrogen chloride was formed, probably owing to the intermediate excitation of the chlorine molecules by second-type collisions. Nitric oxide, the critical increment of which is below 55,000 g.-cal., was readily decomposed into nitrogen and oxygen, whereas nitrous oxide, with its energy of activation 60,300 g.-cal./g.-mol., was unaffected. The slight reactions that occur with substances of higher critical increment than the mean 43,000 are due to a statistical distribution in the after-glow of three species of active molecules, some just above and others below the mean values. S. J. GREGG.

Compounds of nitrosyl chloride with inorganic chlorides. H. RHEINBOLDT and R. WASSERFUHR (Ber., 1927, **60**, [*B*], 732—737; cf. this vol., 229; Gall and Mengdehl, *ibid.*, 219).—The following additive compounds are obtained from nitrosyl chloride and the inorganic chloride dissolved in well-cooled carbon tetrachloride: $SbCl_5$,NOCl, m. p. about 170° after darkening at about 150°; $SnCl_4$,2NOCl, m. p. about 188° after darkening at 100—110°, and becoming lighter at 150°; $TiCl_4$,2NOCl, which does not melt below 220°; $PbCl_4$,2NOCl. In absence of solvent, the following compounds are prepared: $AlCl_3$,NOCl, m. p. 108—110° after softening at 90—100°, decomp. 140—150°; $BiCl_3$,NOCl, m. p. 115—120° after softening at 80°, slight decomp. 150°; $FeCl_3$,NOCl, m. p. 128° after softening at about 115°. H. WREN.

Nitrosisulphonic acid. F. RASCHIG (Ber., 1927, 60, [*B*], 616—620).—In reply to Manchot and others (this vol., 32), the author maintains his conception that "blue acid" contains the compound, $O{:}N(OH){\cdot}SO_3H$. The following observations are cited in favour of this view. A solution of sodium nitrite in concentrated sulphuric acid in absence of air acquires under the action of mercury, copper, or silver an intense blue colour, which gradually fades; the colourless solution contains nitrous oxide. Nitrosulphonic acid forms with a solution of sulphur dioxide in sulphuric acid a blue solution from which nitric oxide is quantitatively evolved, $2NO_2{\cdot}SO_3H+SO_2+2H_2O=2NO+3H_2SO_4$. Nitric oxide is absorbed by copper sulphate dissolved in concentrated sulphuric acid in the molecular ratio 1 : 1 at atmospheric temperature and pressure; the conception that the dark blue solution contains the copper salt of nitrosisulphonic acid is strengthened by the observation that hydroxylaminesulphonic acid is oxidised by Caro's acid in presence of sulphuric acid and a trace of copper to a dark blue compound, whereas hydroxylamine is not similarly affected. H. WREN.

Stabilised aqua regia. E. BRINER (Bull. Soc. chim. Belg., 1927, **36**, 79—88).—When sealed tubes containing concentrated solutions of nitric and hydrochloric acids in the proportions usually used for the preparation of aqua regia are heated for a short time at 100°, or allowed to remain for several hrs. at the ordinary temperature, two conjugate solutions result. The heavier liquid phase, which has the characteristic colour of nitrosyl chloride, consists mainly of liquid chlorine and nitrosyl chloride formed as a result of the reaction $3HCl+HNO_3=Cl_2+NOCl+2H_2O$. This system is termed "stabilised aqua regia." Measurements of the vapour pressures of such systems show that within the limits of coexistence of two liquid phases the observed pressures (2·86 and 5·2 atm. at 0° and 20·5—21·0°, respectively) are dependent only on the temperature. Application of the phase rule leads to the conclusion that there are two independent components, nitric acid and hydrochloric acid. The thermal equation is $3HCl_{conc.}+HNO_{3conc.} \rightleftharpoons Cl_{liq.}+NOCl_{liq.}+2H_2O-21{\cdot}8$ kg.-cal. Measurements of the electrical conductivity at 0° and 20° of the aqueous phase after the establishment of equilibrium show that within the limits of coexistence of two liquid phases the specific conductivities at these two temperatures, 0·324 and 0·465 mho, respectively, are independent of the concentrations and proportions of the two acids. Mixtures of nitric and hydrobromic acids behave similarly, the vapour pressures of the univariant systems being, however, much smaller (0·25 and 0·50 atm. at 0° and 16°, respectively). Mixtures of nitric and hydriodic acid do not form a univariant system, the iodine formed as a result of the primary reaction being oxidised to iodic acid with production of nitric oxide. J. S. CARTER.

Behaviour and constitution of monosulphuric and disulphuric anhydrides. VI. G. ODDO and A. SCONZO (Gazzetta, 1927, **57**, 83—103; cf. this vol., 300, and following abstract).—On the supposition that monosulphuric anhydride (sulphur trioxide, α-form) has the structure $S[{:}O]_3$, and the β-form, or disulphuric anhydride, the polymeric constitution,



the resemblance to the polymerisation of an aldehyde suggested that negative catalysts might stabilise the α-form. With small quantities of sulphur, tellurium, carbon tetrachloride, or phosphorus oxychloride, the α-form was preserved for months; other substances gave less satisfactory or negative results. A tendency to the formation of the translucent or colloidal form was observed.

The α-form does not combine with sulphuryl chloride or with chlorosulphonic acid; with chlorinating agents, the two forms show different behaviour. Thus with phosphorus pentachloride the α-form gave sulphur dioxide, chlorine, and phosphorus oxychloride, with some pyrosulphuryl chloride. With the β-form no sulphur dioxide or chlorine was evolved, pyrosulphuryl chloride alone being formed, $S_2O_6+PCl_5 \longrightarrow S_2O_5Cl_2+POCl_3$. Sulphur monochloride with the α-form yielded sulphur dioxide and dichloride; with the β-form, no gas was evolved, the reaction being as before. The α-form reacted rapidly and the β-form slowly with carbon tetrachloride, giving carbonyl chloride and pyrosulphuryl chloride, for which the scheme $2SO_3+CCl_4 \longrightarrow [SO_2Cl{\cdot}O]_2CCl_2 \longrightarrow [SO_2Cl]_2O+COCl_2$ is suggested; the velocity constant shows that the reaction is unimolecular.

These results are considered to prove the structures assigned above to the α- and β-forms of sulphur trioxide. E. W. WIGNALL.

Sulphuric anhydrides and sulphuric [acids]. VII. G. ODDO (Gazzetta, 1927, **57**, 104—116).—A summary of papers on sulphuric anhydrides (sulphur trioxides) (A., 1901, ii, 650; preceding abstract) and sulphuric acids (A., 1908, ii, 353; 1909, ii, 377, 792; 1910, ii, 1035; 1911, ii, 717; 1918, ii, 189, 352). E. W. WIGNALL.

Colour of selenium dioxide. A. WELLER (Ber., 1927, **60**, [*B*], 649).—Selenium dioxide is not an isolated example of a colourless substance which gives a coloured liquid and vapour (cf. Meyer and Langner, this vol., 220). Similar behaviour is exhibited by tellurium dioxide and tetrachloride. H. WREN.

Colours of chromous, vanadous, and tervalent uranium ions. K. SOMEYA (Z. anorg. Chem., 1927, **161**, 46—50).—Reduction of a uranyl chloride solution with zinc amalgam and hydrochloric acid yields a reddish-purple solution, which on dilution with water or dilute hydrochloric acid becomes dark green. Addition of potassium thiocyanate to this diluted solution deepens the colour and turns it somewhat brown, whilst concentrated hydrochloric acid restores the purple colour. It therefore seems probable that the purple colour is not due to tervalent uranium ions, but to undissociated salt molecules or to complex ions. The violet solution obtained by reducing an ammonium vanadate solution fades on dilution and is restored by potassium thiocyanate or concentrated hydrochloric acid, probably for the same reason. Reduction of a very dilute solution of potassium dichromate gives an almost colourless solution, the chromous ion probably being colourless, whilst

addition of thiocyanate produces the blue colour of more concentrated solutions. R. CUTHILL.

Preparation and composition of the crystalline phospho- and arseno-conjugated ceruleo-molybdates. G. DENIGES (Compt. rend., 1927, **184**, 687—689).—The preparation from sodium molybdate and disodium phosphate of a molybdenyl phosphomolybdate, $[4(MoO_3)\cdot MoO_2]_2H_3PO_4,4H_2O$, sapphire-blue hexagonal plates, is described. The name phospho-conjugated ceruleo-molybdate is suggested for the compound, which is produced whenever the MoO_3 radical is reduced in presence of the phosphate ion. The corresponding arseno-compound is prepared analogously and has similar properties (cf. A., 1920, ii, 770). J. GRANT.

Occurrence of manganese homologues of atomic numbers 43, 61, and 75. W. PRANDTL (Ber., 1927, **60**, [*B*], 621—623).—Repetition of the work of Noddack, Tacke, and Berg (A., 1925, ii, 939) fails to yield evidence of the existence of elements 43 and 75 in columbite. The presence of ekamanganese in platinum ores cannot be regarded as established. There is no evidence of the existence of element 61, and its presence in cerite earths (cf. Rolla and Fernandes, A., 1926, 1083; this vol., 9) is regarded as impossible. H. WREN.

Interaction of manganese salts and permanganates. II. Action of manganese chloride on permanganates. J. G. F. DRUCE (Chem. News, 1927, **134**, 161—163; cf. this vol., 332).—When the residue of potassium chloride and manganese dioxide resulting from the reaction $2KMnO_4+2MnCl_2=Cl_2+2KCl+4MnO_2$, is treated with either concentrated sulphuric or hydrochloric acid, the extract from the final non-volatile residue yields an impure potassium manganichloride, K_2MnCl_5. Attempts to prepare the salt K_2MnCl_6 were unsuccessful. M. S. BURR.

Reduction of iron ores by hydrogen. I. G. GALLO.—See B., 1927, 278.

Behaviour of iron pyrites with hydrogen. II. G. GALLO.—See B., 1927, 279.

New ferromagnetic ferric oxide. R. CHEVALLIER (Compt. rend., 1927, **184**, 674—676).—The production of ferromagnetic ferric oxide (Fe_2O_3) from the oxide Fe_3O_4 depends on the conditions of the oxidation by hydrogen peroxide in presence of ferrous sulphate and sodium hydroxide. The specific moment of the product increases with the amount of the excess of sodium hydroxide present. The optimum temperature is 45—50°, and above this the magnetisation decreases rapidly, the ferric oxide being unstable, and contaminated with magnetite or free ferrous oxide at 100°. Such magnetic oxides show no hysteresis, as in the case of those prepared by dry oxidation of magnetite at 400° (Malaguti). The latter, however, are more stable at high temperatures. The ferromagnetism is attributed to a micellar structure rather than to the presence of simple polymerised molecules. J. GRANT.

Higher oxygen compounds of the metals of the eighth periodic group. I. Iron. D. K. GORALEVITCH (J. Russ. Phys. Chem. Soc., 1926, **58**, 1129—1158).—The preparation and properties of the salts of perferric acid are described. On fusing ferric oxide with potassium hydroxide and excess of potassium nitrate or, better, potassium chlorate, bright green *potassium perferrate* is obtained, which is more stable than potassium ferrate and can be purified by cautious sublimation. It decomposes very slowly when kept in air, explosively when warmed, on treatment with concentrated sulphuric acid, or on impact if mixed with sulphur, phosphorus, or charcoal.

It is quite stable in alkaline solutions, but acids readily decompose it, with evolution of oxygen and, in the case of hydrochloric acid, chlorine. Oxidising agents like chlorine and hydrogen peroxide give a deep red solution of potassium ferrate with evolution of oxygen. Neutral solutions of the perferrate give no reaction for ferric ions until, on the addition of acid, decomposition has commenced. Salts of the alkaline earths give white *precipitates* containing water of crystallisation. They are stable, non-explosive, and soluble in dilute acids, the solutions containing the unstable free perferric acid, since the green colour of potassium perferrate is obtained on addition of alkali. The *sodium* salt is also described. Analysis of the hydrated barium salt gave the formula $BaFeO_5,7H_2O$.

The decomposition of the free perferric acid was also investigated. At low temperatures, traces of a very volatile, unstable *anhydride*, probably FeO_4, were isolated, which was insoluble in water, but soluble with decomposition in dilute acids. The properties are compared with those of ruthenium and osmium tetroxides. M. ZVEGINTZOV.

Chlorides and chloro-salts of rhodium. M. DELÉPINE (Bull. Soc. chim. Belg., 1927, **36**, 108—118).—Rhodium trichloride has been prepared as the anhydrous salt and as the hydrate $RhCl_3,\frac{5}{2}H_2O$. The following salts have been prepared and analysed: hexachlororhodiates: sodium, $Na_3RhCl_6,12H_2O$; potassium, K_3RhCl_6,H_2O; lithium, $Li_3RhCl_6,12H_2O$; sodium lithium, $Na_{1\cdot5}Li_{1\cdot5}RhCl_6,12H_2O$; rubidium, Rb_3RhCl_6,H_2O; ammonium, $(NH_4)_3RhCl_6,H_2O$; aquopentachlororhodiates: potassium, ammonium, cæsium, *rubidium*, $M_2Rh(H_2O)Cl_5$; silver hydroxypentachlororhodiate, $Ag_3Rh(OH)Cl_5$. J. S. CARTER.

Determination of small quantities of hydrogen in nitrogen as hydrogen chloride. G. HEYNE.—See B., 1927, 217.

Reagents for standardisation of acids. K. O. SCHMITT (Z. anal. Chem., 1927, **70**, 321—340).—The loss in weight of analytical samples of sodium and potassium hydrogen carbonates at various temperatures is always greater than the theoretical. The tests of Lunge and of Sebelien for hydroxides in presence of large quantities of carbonates being found unsatisfactory, a new method of examination, based on titration of the hydrogen carbonate and of the resulting carbonate, taking into account the loss in weight, was employed; in this way, it was found that sodium carbonate, prepared by ignition of the hydrogen carbonate, contains both oxide and hydroxide. Potassium hydrogen carbonate of satisfactory purity (99·98—100·00%) may be obtained by recrystallisation; the saturated solution must be cooled

rapidly, with energetic stirring, a stream of carbon dioxide being continually passed through the mixture. S. I. LEVY.

Neutral litmus paper as indicator. W. EKHARD (Z. Spiritusind., 1927, **50**, 70—71).—The end-point, which is dependent to some extent on the colour sense of the observer, should be regarded as the point at which the colour just begins to alter. Fresh paper should always be used. At the neutral point, the paper should be compared with a control moistened with conductivity water. The paper, which should be kept hermetically enclosed from gases and protected from direct sunlight, should be of a medium violet colour of unvarying intensity. C. RANKEN.

Reference electrode for potentiometric titrations. T. R. BALL (Ind. Eng. Chem., 1927, **19**, 370).—As a substitute for a calomel electrode, an asbestos fibre is sealed into one end of a 5 mm. gauge glass tube, which is filled with 3*N*-sulphuric acid as electrolyte for oxidation–reductions in acid solution or with *N*-potassium chloride for acidimetric titrations. Connexion to the potentiometer is made by a platinum wire inserted in the electrode. Satisfactory results are obtained in oxidation–reduction and in precipitation determinations (such as zinc with potassium ferrocyanide or silver with sodium sulphide), but acidimetric titrations are less trustworthy. L. M. CLARK.

Application of the electron tube to potentiometric titrations. J. W. WILLIAMS and T. A. WHITENACK (J. Physical Chem., 1927, **31**, 519—524).—An apparatus for the general application of the electron tube ("valve") to potentiometric titrations is described. Results in agreement with the usual potentiometric and volumetric titrations were obtained in the oxidation of ferrous ammonium sulphate by potassium dichromate, in the reduction of permanganate, in the iodine–sodium thiosulphate reaction, and in the neutralisation of acetic acid by potassium hydroxide. In agreement with Kolthoff and Furman ("Potentiometric Titrations," 1926, 268), the potential break in the precipitation of zinc by potassium ferrocyanide occurs before the volumetric end-point is reached. L. S. THEOBALD.

Relation of titration acidity and p_H values [especially for mixtures of weak acids]. K. TAUFEL and C. WAGNER (Z. angew. Chem., 1927, **40**, 133—141).—Curves showing the variation in p_H during neutralisation of different types of acids and mixtures thereof are given. With a mixture of hydrochloric and acetic acids for which the curve shows two discontinuities, one part shows the relation of p_H to the concentration of free hydrochloric acid, one part to that of free alkali, and the intermediate curve gives the relation of p_H to the concentration of dissociated and undissociated acetic acid during the elimination of hydrogen ions. Here $p_H = -\log K + \log [A'] - \log [HA]$. In this way, the curve can be analysed into its component curves, and the principle is developed for other cases. By a suitable choice of indicators, one acid can therefore often be titrated in the presence of others. In some cases, *e.g.*, the determination of hydrochloric and other acids in gastric juice, no marked discontinuity occurs in the curve, and the correct value of p_H to take as the neutralisation point can then be fixed only by blank tests. If the acids present in the mixture are of the same order of dissociation, *e.g.*, lactic acid and acetic acid, the components are neutralised simultaneously and indirect methods of analysis are necessary, or the curves may be analysed mathematically. With complicated systems, the intermediate part of the curve may approach a straight line. The inclination of this line, *i.e.*, the rate of change in p_H within the limits of the zone, is of practical importance in brewing and other processes involving enzymes. It can be determined by pairs of titrations with suitable indicators. Other cases discussed are the variations of p_H in soils and the souring of wine. C. IRWIN.

Comparison of the accuracy of the titration of halides and thiocyanates by Fajans' method, the usual methods, and the potentiometric method. I. M. KOLTHOFF and L. H. VAN BERK (Z. anal. Chem., 1927, **70**, 369—394).—The potentiometric titration of chloride, bromide, iodide, and thiocyanate in neutral solution gives results within 0·02% of the theoretical when a slight deficiency of 0·1*N*-silver nitrate solution is added and the titration finished with 0·01*N*-silver nitrate. At the end-point, the solution has a potential of −0·08 volt against the mercuric sulphate–0·5*M*-potassium sulphate electrode in the case of chlorides, −0·17 volt in the case of bromides, −0·22 volt with iodides, and −0·18 volt with thiocyanates. In acid solutions, this potential is more negative in every case, but neutral salts have no effect. From numerous potentiometric titrations, the solubility products of the various silver salts have been calculated as silver chloride, $1{\cdot}5\times10^{-10}$; silver bromide $6{\cdot}5\times10^{-13}$; silver thiocyanate $1{\cdot}2\times10^{-12}$, and silver iodide 9×10^{-17}. The titration of chloride or bromide by Mohr's method gives good results if allowance is made for the amount of indicator (potassium chromate) added; titration of iodide or thiocyanate by this method, however, gives results which are generally 1—2% too high. Volhard's method is satisfactory for bromide, iodide, and thiocyanate if the solution is well shaken during the titration of the excess silver with thiocyanate. Titration of chloride with silver nitrate, using fluorescein as indicator, and of bromide, iodide, and thiocyanate, using eosin as indicator (Fajans and Wolff, A., 1924, ii, 776), gives excellent results in neutral or acetic acid solutions, provided that no great quantity of a strong electrolyte is present. A. R. POWELL.

Günzburg's reaction for free hydrochloric acid. P. N. VAN ECK (Pharm. Weekblad, 1927, **64**, 304—307).—The red coloration developed when a mixture of phloroglucinol and vanillin is brought into contact with hydrochloric acid is not a specific test for that acid; the same coloration is given by most mineral and many organic acids, and by various salts. S. I. LEVY.

Separation of hydrochloric from hydrobromic and hydriodic acids. G. G. LONGINESCU and (MLLE.) M. N. BĂDESCU (Bull. Sci. Acad. Roumaine, 1927, **10**, 2—4).—See this vol., 124.

Determination of perchlorate in Chile saltpetre with nitron. A. VÜRTHEIM.—See B., 1927, 250.

Argentometric determination of iodide in presence of chloride with the help of the absorption indicators of Fajans. I. M. KOLTHOFF (Z. anal. Chem., 1927, 70, 395—397; cf. Fajans and Wolff, A., 1924, ii, 776).—The determination of iodide in presence of chloride by Fajans' method is best carried out in presence of ammonium carbonate, using eosin as indicator; the solution becomes dark violet at the end-point. The results for iodide are accurate to 0·2—0·5% in the presence of up to 40 times the weight of chloride, but bromides interfere. A. R. POWELL.

Iodometric analysis of peroxides. C. WAGNER.—See B., 1927, 249.

Coalescence of an unfilterable precipitate of barium sulphate. H. M. TRIMBLE (J. Physical Chem., 1927, 31, 601—606).—The solution pressure of barium sulphate at approximately 100° ceases to be a function of particle size for particles larger than 2 μ in diameter. The coalescence of barium sulphate precipitates on digestion cannot be adequately explained as a growth of large from smaller particles, for long digestion at higher temperatures fails to bring this about in the case of particles of diameter greater than 2 μ, and the growth of large crystals themselves after digestion is inappreciable. Aggregates are formed by digestion without stirring, but not by digestion with stirring, in which case all the crystals present grow at the expense of any material separating from solution. The coalescence of precipitates is better explained by aggregation of particles followed by the cementation of individual particles in the aggregates by means of barium sulphate deposited, either from the still supersaturated solution or from the solution of particles of diameter less than 2 μ. L. S. THEOBALD.

Volumetric determination of sulphate in drinking water. A. BAHRDT.—See B., 1927, 238.

Preservation of standard solutions of sodium thiosulphate. I. YOSHIDA (J. Chem. Soc. Japan, 1927, 48, 26—27).—The alteration of 0·1*N*-sodium thiosulphate solution is only 1% after 10 months, with frequent exposure to air. For preservation, 0·05*M*-borax, 0·1*N*-disodium hydrogen phosphate, or carbon disulphide may be employed. Specially pure sodium thiosulphate and special distilled water need not be used. K. KASHIMA.

Application of mixtures of ammonium halide and sulphate in quantitative analysis. L. MOSER and W. MAXYMOWICZ (Ber., 1927, 60, [*B*], 646—649).—All salts of the alkali and alkaline-earth metals, of manganese, zinc, cadmium, lead, or (less advantageously) of cobalt and nickel which contain anions decomposable by hot halogen acids or sulphuric acid are quantitatively converted into sulphates when heated with a mixture of ammonium sulphate and ammonium halide. The effect can frequently be produced with ammonium sulphate alone, but much more slowly. The favourable action of the ammonium halide depends on the intermediate production of metallic halide which reacts with sulphur trioxide formed from the sulphate. The substance under investigation (0·1—0·4 g.) and 1—2 g. of a mixture ammonium sulphate and ammonium chloride (1 : 3 by weight) is gently heated in a porcelain or silica crucible so that slow but recognisable volatilisation of the ammonium salts occurs, and the operation is repeated until the weight of the residue remains constant. The proportion by weight of ammonium bromide or iodide to sulphate must not exceed 1 and 0·75, respectively. H. WREN.

Determination of traces of nitrogen peroxide in air. E. KOHN-ABREST.—See B., 1927, 251.

Gasometric determination of nitric oxide, with special reference to absorption by ferrous chloride. V. N. MORRIS (J. Amer. Chem. Soc., 1927, 49, 979—985).—A simple gas burette is described in which the absorbing liquid is allowed to drop into the gas, a fresh surface of the liquid thus continually being exposed. The apparatus is successfully applied to the determination of nitric oxide, the most suitable absorbing agent being concentrated ferrous chloride solution. S. K. TWEEDY.

Determination of phosphorus pentoxide as magnesium ammonium phosphate. W. M. MCNABB (J. Amer. Chem. Soc., 1927, 49, 891—896).—The determination is carried out by a combination of the methods of Schmitz (A., 1925, ii, 67) and Brookman (Repert. anal. Chem., 1882, 2, 297). The phosphate is precipitated (preferably, for accurate results, from monopotassium hydrogen phosphate solution) as magnesium ammonium phosphate, which is transferred to a tared crucible; particles clinging to the sides of the beaker are dissolved in warm dilute nitric acid and the solution added to the crucible. After rendering alkaline with ammonia (to prevent volatilisation of phosphorus pentoxide) the contents of the crucible are evaporated and ignited to constant weight. S. K. TWEEDY.

Electrometric study of the precipitation of phosphates. H. T. S. BRITTON (J.C.S., 1927, 614—630).—The dissociation constants $K_1=0{\cdot}94\times10^{-2}$, $K_2=1{\cdot}4\times10^{-7}$, and $K_3=2{\cdot}7\times10^{-12}$ satisfy the hydrogen electrode titration curve of phosphoric acid by sodium hydroxide. The alkaline-earth hydroxides when added to phosphoric acid solution give rise to supersaturated solutions from which the monohydrogen phosphate separates only gradually, and on addition of more alkaline earth becomes converted into the normal phosphate. With lime-water, further addition over two equivalents actually causes an increase in the hydrogen-ion concentration, since the calcium hydroxide decomposes the supersaturated solution of dicalcium phosphate, precipitating both di- and tri-calcium phosphates. The presence of sucrose prevents this anomalous increase. Calculations from Bassett's data on the system CaO–P_2O_5–H_2O at 25° show that calcium phosphate is not precipitated from solutions more acid than p_H 5·5. Hydrogen electrode titrations with trisodium phosphate of salt solutions of zirconium, thorium, aluminium, beryllium, chromium, zinc, manganese, magnesium, and calcium show that in all cases except the last two, basic salts are formed. The redissolution of the aluminium phosphate in excess of the precipitant is due to the formation of sodium aluminate, the necessary alkali being supplied by the hydrolysis of the trisodium phosphate. The possibility of the

phosphate separation is due to the fact that in a solution buffered at p_H 5 (by acetic acid and sodium acetate) the phosphates and, in presence of a deficiency of phosphoric acid, the hydroxides, only of aluminium, chromium, and iron can be precipitated. The importance of p_H data with reference to phosphate soil fertilisers is discussed. S. J. Gregg.

Titration of hypophosphoric acid and its salts by means of permanganate. D. Koszegi (Z. anal. Chem., 1927, **70**, 347—349; cf. A., 1926, 702; Kolthoff, *ibid.*, 1018).—The examples of unsatisfactory agreement in the author's earlier paper cited by Kolthoff are due to typographical errors, and not to any want of accuracy in the method. S. I. Levy.

Paper strips for the Gutzeit determination of arsenic. E. L. Green (Ind. Eng. Chem., 1927, **19**, 424).—It is important that papers to be used in the Gutzeit test for arsenic approximate closely to a standard size. A device for use with a print trimming machine is described whereby such approximation can be attained. L. M. Clark.

Micro-determination of carbon. Applications. M. Nicloux (Compt. rend., 1927, **184**, 890—892).—Sulphuric acid is added to a mixture of a solution of the substance to be analysed with potassium dichromate, silver chromate, and sodium sulphate contained in an evacuated vessel. On warming, carbon dioxide is evolved and is absorbed in potassium hydroxide solution and determined by titration. A degree of accuracy of 0·003 mg. has been obtained using solutions containing 2·0—2·5 mg. of a number of organic compounds. Quinolinesulphonic acid alone resists complete oxidation. The method is useful in biochemical work. J. Grant.

Rapid determination of silicon in steel and iron. J. Verfurth.—See B., 1927, 255.

Determination of excess of alkali in hypochlorite solutions. A. Wachter (J. Amer. Chem. Soc., 1927, **49**, 791—792).—An aqueous suspension of nickelous hydroxide (5 g./litre) is added to the solution: $2Ni(OH)_2+NaClO+H_2O=NaCl+2Ni(OH)_3$. The mixture is heated and filtered, the filtrate being titrated with acid as usual. The method is inapplicable in presence of ammonium salts and also when the alkali is calcium hydroxide. S. K. Tweedy.

Specific reagent for sodium. I. M. Kolthoff (Z. anal. Chem., 1927, **70**, 397—400).—Zinc uranyl acetate gives a yellow, crystalline precipitate of the compound $(UO_2)_3ZnNa(CH_3{\cdot}CO_2)_9{,}9H_2O$ with neutral solutions of sodium salts containing more than 50 mg. of sodium per litre. Acid solutions are preferably neutralised with zinc oxide before applying the test. The reagent is prepared by dissolving 10 g. of uranyl acetate and 30 g. of zinc acetate in 100 c.c. of water and adding 9 g. of 33% acetic acid. For the detection of traces of sodium in potassium salts, 2 c.c. of a 1% solution of the salt are mixed with 2 c.c. of the reagent and 2 c.c. of absolute alcohol; in the presence of sodium, a precipitate appears within 15 min. A. R. Powell.

Determination of calcium in aluminium alloys P. G. Ward.—See B., 1927, 282.

Schlagdenhaufen's reaction [for magnesium]. A. Hamy.— See B., 1927, 217.

New reactions of zinc, copper, and cadmium. R. Montequi (Anal. Fís. Quím., 1927, **25**, 52—76).—The reactions of salts of copper, zinc, and cadmium with alkali mercurithiocyanates are described. Photomicrographs are given of the complex copper zinc and cadmium zinc mercurithiocyanates formed. The theory of the reactions is discussed. G. W. Robinson.

Determination and separation of copper by means of 8-hydroxyquinoline. R. Berg (Z. anal. Chem., 1927, **70**, 341—347; cf. J. pr. Chem., 1927, **115**, 178).—Copper is precipitated quantitatively from a solution containing 5 g. of sodium acetate in 100 c.c. of 10% acetic acid by addition of a 2% alcoholic solution of 8-hydroxyquinoline; the results using a solution containing about 5 g. of sodium tartrate and 20 c.c. of 2*N*-sodium hydroxide per 100 c.c. (total) are also satisfactory. As the precipitate may be filtered, washed, and dissolved in dilute acids, and the copper determined quantitatively by the iodide method, the reagent permits of exact determination of copper in presence of ferric iron, bismuth, tin, arsenic, and antimony, which are not easily precipitated in the alkaline tartrate solution, and of zinc, which is precipitated with the copper, but does not interfere with the iodide titration. S. I. Levy.

Separation of copper and mercury. J. Krauss (Z. angew. Chem., 1927, **40**, 354—355).—The usual methods of separating copper and mercury are criticised, and a new method, based on that of Rivot, and depending on the precipitation of the copper as cuprous thiocyanate, is described. The solution (200 c.c.), containing approximately 0·15 g. each of the two metals, is treated with 50 c.c. of a solution of 53·5 g. of ammonium chloride and 3 g. of hydroxylamine sulphate per litre, and heated to boiling. The copper, now in the cuprous condition, is precipitated with 30 c.c. of 0·1*N*-ammonium thiocyanate, the solution allowed to cool with stirring, the precipitate collected, and dried at 105—110°. The filtrate containing the mercury is acidified with 25 c.c. of hydrochloric acid, *d* 1·126 (25%), and mixed with 10 c.c. of a solution containing 5 c.c. of bromine in 50 c.c. of sodium hydroxide solution (*d* 1·168—1·172). After removing the excess of bromine, the mercury is precipitated from the warm solution (50—70°) by passing in hydrogen sulphide. E. Holmes.

Determination and separation of rare metals. VIII. Determination of thallium as thallous chromate. L. Moser and A. Brukl (Monatsh., 1926, **47**, 709—725).—Thallium is best determined after reduction to a thallous salt by the following method (cf. Mach and Lepper, B., 1926, 390). The boiling ammoniacal solution is treated with 2% by weight of solid potassium chromate and kept for 12 hrs. The precipitate of thallous chromate is filtered on an asbestos mat, washed with 1% potassium chromate solution, then with 50% aqueous alcohol, and dried at 120°. A quantitative separation of lead and thallous salts may be effected by treating the acid solution with 20 c.c. of 33% sulphosalicylic

acid solution and excess of ammonium phosphate. After making alkaline with ammonia, the lead phosphate is collected and thallium determined as above in the filtrate. Manganous salts may be removed in the same way. In presence of sulphosalicylic acid, thallium may be precipitated from faintly alkaline solutions containing aluminium, ferric, or chromic salts. Thallium is separated from zinc, cadmium, nickel, or cobalt by precipitation as the chromate from solutions rendered strongly alkaline with ammonia. From the filtrate, zinc is best recovered as the phosphate, cadmium as the sulphide, nickel by means of dimethylglyoxime, and cobalt as hydroxide. In presence of silver, mercury, or copper, thallium is precipitated from a faintly alkaline solution containing potassium cyanide or, in the case of the first two, sodium thiosulphate. The filtrate is boiled with an excess of sodium thiosulphate, when silver, mercury, or copper sulphide separates. Bismuth in 0·1% solution is separated from thallium by precipitation as the phosphate, $BiPO_4$, thallium being determined in the filtrate. The separation of arsenic and thallium has been previously described (*loc. cit.*), and the method is also applicable to antimony–thallium mixtures. Stannic salts may be removed by precipitation as oxide from a boiling, neutral 0·1—0·2% solution. Double precipitation is necessary in presence of large quantities of tin. Quadrivalent selenium does not interfere with the precipitation of thallium chromate from ammoniacal solutions.

H. E. F. Notton.

Colorimetric determination of iron. A. Sagaidatchni and M. Ravitch (J. Russ. Phys. Chem. Soc., 1926, 58, 1018—1022).—Methods for the determination of small quantities of iron in presence of other ions are summarised. The depth of the violet colour obtained by the addition of salicylic acid to slightly acid (0·01*N*), very dilute (<0·3%) solutions of ferric iron depends on the concentration of the ferric ion, which can be determined to within 2%. The solutions are compared with a standard the details of preparation of which are given.

The method can be used in presence of cations of the first three groups, sulphate, chloride, nitrate, acetate, moderate amounts of phosphate, and small quantities of organic matter. Free alkali or organic polybasic acids destroy the colour. M. Zvegintzov.

Precipitation of zirconium with picric acid. M. Speter.—See B., 1927, 255.

Delicate colour test for antimony and tungsten. E. Eegriwe (Z. anal. Chem., 1927, 70, 400—403).—Addition of a solution of antimony pentachloride in hydrochloric acid to a solution of a dye of the xanthone group produces a violet to blue fluorescence in the previously red solution. The metal is separated as in the usual course of group analysis and the chloride solution oxidised to the quinquevalent state by boiling with sodium nitrite; a few drops of the solution added to 5 c.c. of a 0·05% solution of tetraethylrhodamine produce a blue to violet colour in transmitted light if only 0·005 mg. of antimony is present. Large quantities of stannic chloride and relatively small amounts of iron do not interfere. Similar reactions are given by solutions containing 0·01 mg. of molybdenum, 0·007 mg. of bismuth, 0·015 mg. of thallium (as $TlCl_3$), or 0·0012 mg. of gold. Mercuric chloride also gives the coloration in a concentration of 1 mg. of mercury per c.c. To test for tungsten in a solution free from any of the above-named metals, hydrochloric acid is added so as to obtain a colloidal solution of tungstic acid. One drop of this solution containing only 0·005 mg. of tungsten will produce a perceptible violet tint with 5 c.c. of the reagent.

A. R. Powell.

Grating-spectrometer (wave-length spectrometer) of Loewe and Schumm for the spectrochemical investigation of natural pigments. O. Schumm (Z. physiol. Chem., 1927, 164, 58—60).—An apparatus is described which gives a spectrum of which the red is much broader, and the blue and violet are much narrower, than in the prism spectrum. Absorption phenomena in the blue and violet are therefore clearer and more defined. A. Wormall.

Illuminator for use in metallographic microscopy. L. E. Jewell (J. Opt. Soc. Amer., 1927, 14, 159—167).—A modification is described of George's method (Trans. Amer. Soc. Steel Treating, 1923) of securing, with medium and high powers, in the photomicrography of opaque objects, an approach to the relief effects ordinarily obtained with oblique illumination at low magnifications. L. F. Gilbert.

Graphic correction for the exposed thread for readings of mercury-in-glass thermometers. E. Berl and A. Kullmann (Ber., 1927, 60, [*B*], 815—817).—An arrangement is made whereby the correction can be ascertained graphically from the number of degrees in the exposed thread and the difference between the recorded temperature and the mean temperature of the exposed thread. H. Wren.

Determination of m. p. E. Berl and A. Kullmann (Ber., 1927, 60, [*B*], 811—814).—The m. p. of a substance as observed in Thiele's apparatus depends on the position of the burner, thermometer, and capillary tube. These difficulties are avoided by the use of a cylindrical metal block in which two holes are bored for thermometers and two for capillary tubes. The block is heated by a small burner. The ends of the capillary tubes are visible through a tunnel drilled through the block; the ends of the tunnel can be covered with a strip of mica.

H. Wren.

Apparatus for determining the softening point of paraffin and other waxes, pitches, etc. H. Herbst.—See B., 1927, 244.

Glass water still. G. G. Kretchmar (J. Opt. Soc. Amer., 1927, 14, 187—189).—A simple apparatus capable of distilling 700 c.c. of water per hr. is described. The heater is a 600-watt nickel–chromium wire element. The efficiency is about 85%.

L. F. Gilbert.

Laboratory fractionating columns. J. B. Hill and S. W. Ferris (Ind. Eng. Chem., 1927, 19, 379—382).—The efficiency of various types of fractionating column is investigated, comparison being established in such manner that the ability to produce contact between refluxing liquid and distilling vapour is the factor influencing efficiency. The columns are therm-

ally insulated, the vapour is distilled at a constant rate while a constant, controlled amount of reflux is fed back at the top of the column, a portion of the issuing vapour being removed for analysis. Of the long type of column, the Snyder floating-ball column is most efficient over a wide range of distillation rate; columns packed with glass tube or rod, iron chain, or Lessing rings show approximately equal efficiencies, whilst the Young rod and disc fractionator, except at low distillation rates, is the least efficient apparatus examined. Using a similar method, short columns of types in general service are found to depend largely on fractional condensation in the column, and not to the production of intimate contact between ascending vapour and descending condensate. L. M. CLARK.

Adapter. G. N. QUAM (Ind. Eng. Chem., 1927, **19**, 425).—An adapter for use in alcohol distillation has a drying tube sealed on to the side and fits into the stopper of the receiving vessel, which can therefore be changed with minimum exposure of the anhydrous distillate. L. M. CLARK.

Distillation flasks. A. MÜLLER (Z. angew. Chem. [Chem. App. u. Maschinenw.], 1927, **40**, 19).—Entrainment of liquid particles is prevented by extending the side tube slightly into the neck of the flask, the end of the extension being drawn out and bent downwards. The flask may have two necks, one carrying the side tube. For vacuum distillation, the side tube is widened to avoid any constriction. C. IRWIN.

Kjeldahl digestion apparatus. E. G. HASTINGS, E. B. FRED, and W. H. PETERSON (Ind. Eng. Chem., 1927, **19**, 397).—A wide, horizontal lead fume pipe has a series of side tubes which carry adjustable lead stoppers, on to which is fitted the battery of Kjeldahl distillation flasks. Fumes from the digestion are carried away by the current of air produced by a leaden water injector in the fume pipe. No hood or suction fan is required. The apparatus is economical in the amount of acid used, and the time of digestion is less than that required in the usual hood method. L. M. CLARK.

Laboratory stirring apparatus. A. MÜLLER (Z. angew. Chem. [Chem. App. u. Maschinenw.], 1927, **40**, 18).—The cover of the vessel has five equal ground-glass connexions which serve for a thistle funnel, the gas outlet, a thermometer, a Soxhlet condenser, and the stirrer. The latter is designed with a liquid seal to render it gas-tight. C. IRWIN.

Pipette. A. MÜLLER (Z. angew. Chem. [Chem. App. u. Maschinenw.], 1927, **40**, 18).—At the upper end of the pipette is a bulb closed by a ground-glass stopper connected to a cock, a right-angle bend, and an expansion filled with a suitable absorbent. The latter is closed by a mouth-piece. One such attachment serves for a range of pipettes. C. IRWIN.

Apparatus for extraction by dialysis. P. W. DANCKWORTT and E. PFAU (Arch. Pharm., 1927, **265**, 65—68).—It is convenient to use dialysis for separating, *e.g.*, soluble toxic compounds from such colloidal material as stomach contents. An apparatus for this purpose, in which the volume of solvent used is relatively small, is described and figured. The extraction is based on the Soxhlet principle. The collodion bag to contain the colloidal material is of any capacity up to about 2 litres, and is suspended in a specially constructed glass vessel, capable of being evacuated. W. A. SILVESTER.

Apparatus for measuring the turbidity of opalescent glass. W. EWALD.—See B., 1927, 252.

Gauge for measurement of high vacua. R. E. BURK (J. Physical Chem., 1927, **31**, 591—595).—A gauge combining the principles of the ordinary manometer, the McLeod gauge, and the quartz fibre manometer is described. The gauge can be easily made from pyrex glass, and can be baked out and calibrated *in situ* without a previous knowledge of its dimensions. Pressures from several decimetres to 1×10^{-7} mm. of mercury can be measured. A 2-way stop-cock of large bore which greatly accelerates evacuation is also described. L. S. THEOBALD.

Apparatus for circulating gases. H. N. STEPHENS (Ind. Eng. Chem., 1927, **19**, 425).—A circulating capacity of 25—30 litres per hr. can be attained by the use of two 500 c.c. levelling bulbs and two reversed mercury traps. Mercury is raised into one of the bulbs by an aspirator and on admission of air through an automatic control falls into the second bulb. On the compression stroke, gas passes through one air trap and into the reaction chamber, and on the expansion stroke it flows back through the second air trap into the higher levelling bulb. L. M. CLARK.

Vacuum oven and thermoregulator. D. H. BRAUNS (J. Amer. Chem. Soc., 1927, **49**, 985—986).—The oven consists of a long, wide pyrex tube, sealed at one end and flanged at the other in such a way that a tubulated desiccator lid can be fitted.

The initial adjustment of the mercury in a thermoregulator is facilitated by a reservoir sealed on to the stem of the regulator and communicating with the latter through a plug or stop-cock. The stem and capillary of the regulator are filled with mercury and the reservoir is attached to a water-pump. By manipulating the stop-cock, the mercury can readily be adjusted to any desired height within the capillary. S. K. TWEEDY.

Anhydrous barium perchlorate and mixed alkaline-earth perchlorates as dehydrating reagents. G. F. SMITH (Ind. Eng. Chem., 1927, **19**, 411—414).—Barium perchlorate trihydrate on dehydration in a vacuum at 100—140° gives the anhydrous salt without fusion, and this equals sulphuric acid in drying efficiency. A mixture of barium perchlorate with up to 35% of magnesium perchlorate (A., 1922, ii, 850) can be dehydrated at 250° and 102 mm. pressure without fusing; the granules of such a mixture containing 26·5% of magnesium perchlorate in a drying column 15 cm. long and 2·5 cm. in diameter allow only 0·001 g. of water to remain unabsorbed when air 60% saturated with moisture is passed through for 5·5 hrs. at the rate of 53 litres per hr. L. M. CLARK.

Apparatus for removing the supernatant liquid from centrifuged precipitates. W. KRANE (Z. physiol. Chem., 1927, **164**, 50—51).

Grüneisen's criteria for the capillary viscosimeter. N. E. DORSEY (J. Opt. Soc. Amer., 1927, **14**, 45—53).—The manner of derivation of Grüneisen's criteria for use in designing capillary viscosimeters (Wiss. Abhandl. Physikal. Tech. Reichsanst., 1904, **4**, 151) is unsatisfactory and the criteria themselves are erroneous. Other criteria, in accordance with Bond's observations (Proc. Physical Soc., 1921, **33**, 225; 1922, **34**, 139), are formulated.

L. F. GILBERT.

Laboratory emulsifier. R. C. SMITH (Rev. gén. Colloïd., 1927, **5**, 412—414).—The apparatus consists of a vertical revolving axis to the end of which is fixed a brass tube with an orifice above the two end discs situated one above the other and joined by four curved blades covered with brass gauze. The liquid to be dispersed enters at the orifice and is passed through the gauze into the dispersion medium. When the dispersed phase is denser than the dispersion medium, the apparatus is reversed, the orifice is covered with gauze, and the two discs are made of equal diameter so that the liquid is sucked in by the revolving blades and passed out of the orifice. A band of brass on the side and bottom of the containing test-tube has the effect of keeping the denser liquid to the centre of the tube. The apparatus may be readily adapted for continuous emulsification.

D. G. HEWER.

Modification of Mohr's pinch-cock for burettes. L. MOSENDS (Z. anal. Chem., 1927, **70**, 404—405).—The ordinary Mohr pinch-cock is provided with an adjustable screw so that the arms may be kept sufficiently apart to permit the liquid to flow from the burette drop by drop. A titration is started in this manner, then the cock is opened full to allow a steady stream of solution to run out, and finally, by releasing the cock again, the titration is finished by drops. A note by W. FRESENIUS (*ibid.*, 405) states that this modification has been in use in his laboratory for 50 yrs., but has not previously been published.

A. R. POWELL.

Mercury and ammonia vapour an explosion hazard. C. VAN BRUNT (Science, 1927, **65**, 63—64).—The circumstances of an accidental explosion indicate the possibility of the formation, during 10 yrs. at the ordinary temperature, of a mercuri-ammonium oxide from mercury in the safety-valve of a carboy containing concentrated ammonia solution.

CHEMICAL ABSTRACTS.

Interchangeable laboratory furniture. A. H. WHITE (Ind. Eng. Chem., 1927, **19**, 404—405).—Standardised benches, balance cases, and apparatus cupboards are described. Benches are separate from the standardised plumbing arrangements for water, gas, or fume hoods and are removed bodily when the latter need attention.

L. M. CLARK.

Mineralogical Chemistry.

Measurements of the amount of ozone in the earth's atmosphere and its relation to other geophysical conditions. II. G. M. B. DOBSON, D. N. HARRISON, and J. LAWRENCE (Proc. Roy. Soc., 1927, **A**, **114**, 521—541; cf. A., 1926, 493).—Simultaneous measurements of the amount of ozone in the earth's atmosphere have been made, by the method previously described (*loc. cit.*), at various places in N.-W. Europe. Exposures were made, where possible, three times daily. A determination of the monthly means of the ozone values at Oxford shows the dates of maximum and minimum to be April and October, respectively. This result is unexpected. The general annual variation is very similar over the two years investigated (1925 and 1926). The connexion between the amount of ozone and *H* (horizontal component of the earth's magnetic force) range is much more marked on days of high magnetic character, the days of low character showing little differentiation between the amounts of ozone corresponding with high and low *H* range. For 1925, the ozone values at Oxford tended to be higher on days of low rather than high sunspot number, but for 1926 the opposite effect was found. The most marked relation between the ozone content of the atmosphere and any geophysical quantity is found in the case of pressure distribution. Almost without exception, the ozone value is high in marked cyclonic systems and low in anticyclonic systems. The reasons for the connexion between the amount of ozone and the meteorological upper-air conditions are discussed.

L. L. BIRCUMSHAW.

Gold in sea-water. F. HABER (Z. angew. Chem., 1927, **40**, 303—314).—Numerous analyses of sea-water from various parts of the world show that the average gold content of the South Atlantic, round latitude 48° S., is 0·008 mg. per m.^{3}, with a highest single value of 0·044 mg. For the Bay of San Francisco, it is very little higher, in spite of the fact that these waters are fed by streams passing through a gold-bearing country. In a few cases, especially round the Newfoundland Bank, concentrations from 2·25 to 8·46 mg. per m.^{3} have been found. In Arctic regions the mean value is 0·04 to 0·047 mg., but a few samples of surface ice gave remarkably high values, in one case as much as 4·843 mg. per m.^{3} The concentrations of silver are of about the same order of magnitude, but vary between wider limits. Analytical methods for the determination of very small quantities of gold and silver are described.

M. S. BURR.

Origin of the earth's surface structure. J. JOLY and J. H. J. POOLE (Nature, 1927, **119**, 524—525).

Highly penetrating radiation from the earth. L. N. BOGOIAVLENSKY and A. A. LOMAKIN (Nature, 1927, **119**, 525).—The radiation, which is complex, appears to originate from radio-elements diffused in the soil.

A. A. ELDRIDGE.

Occurrence of platinum in Norwegian rocks and minerals. G. LUNDE (Z. anorg. Chem., 1927, **161**, 1—20).—The amounts of platinum and silver in a number of Norwegian rocks and minerals have been

determined. For analysis, the material was fused with six times its weight of a mixture of equal parts of lead acetate, fusion mixture, and anhydrous borax, and the metallic bead cupelled. The bead of silver and platinum so obtained was measured microscopically, then fused repeatedly with boric acid to remove the silver, and measured again.

R. CUTHILL.

Anhydrous silicas containing clays. Composition of ochres. A. P. BIGOT.—See B., 1927, 253.

Organic Chemistry.

Preparation of octane. H. F. LEWIS and G. R. YOHE (Proc. Iowa Acad. Sci., 1925, **32**, 327—328).—Using butyl bromide (50 g.), sodium (10·5 g.), and ether (40 c.c.), a 73% yield of octane is obtained, with agitation, in 5 hrs.; without agitation, the yield is 44%. High yields can be obtained in less than 1 hr. by dropping butyl bromide on to sodium in a pyrex flask. CHEMICAL ABSTRACTS.

Preparation of βε-dimethylhexane. H. F. LEWIS and J. W. FLEMING (Proc. Iowa Acad. Sci., 1925, **32**, 328).—Nearly quantitative yields of βε-dimethylhexane are obtained by interaction of *iso*butyl bromide and sodium in a reflux apparatus in absence of a solvent. CHEMICAL ABSTRACTS.

Preparation of hydrocarbons by reduction of organic substances. Use of carbon and carbon monoxide. J. CAMPARDOU (Compt. rend., 1927, **184**, 828—830).—By the use of carbon monoxide in presence of wood charcoal as catalyst at 400—450°, yields up to the theoretical of vinyl or ethylenic hydrocarbons are obtained with organic compounds containing hydrogen and oxygen, alcohols and ethers affording vinyl hydrocarbons, whilst acids, ketones, and aldehydes yield olefines. The two reactions (1) $C+H_2O \longrightarrow CO+2H_2$ and (2) $CO+H_2O \longrightarrow CO_2+H_2$ thus appear general in organic chemistry. Reduction according to equation (2) is practically always exothermic and is independent of pressure, and is accordingly best conducted at the lower limit of the activity of the catalyst. Reduction according to equation (1) is often endothermic, and requires a relatively high temperature, limited by decomposition of the hydrocarbons. The conversion of phenol into benzene according to equation (1) absorbs 20 g.-cal., whereas reduction by equation (2) liberates 22·4 g.-cal. (cf. Stadnikov, A., 1926, 1110).

R. BRIGHTMAN.

Catalytic preparation of unsaturated hydrocarbons from carbon monoxide and hydrogen. C. R. HOOVER, M. J. DORCAS, W. D. LANGLEY, and H. G. MICKELSON (J. Amer. Chem. Soc., 1927, **49**, 796—805).—When a mixture of equal parts of carbon monoxide and hydrogen is passed, together with a little oxygen, at 100°, over a nickel–palladium catalyst, supported on aluminium or pumice, at the rate of 1500—2000 c.c. per c.c. of catalyst per hr., the exit gas contains 1—3% of ethylene. The catalyst loses one half of its activity in 30 hrs. The following catalysts, in order of decreasing activity, also effected the production of ethylene: nickel–copper–palladium, iron–nickel–palladium, nickel–platinum, copper–cobalt–iron, copper–palladium, copper–cobalt–nickel, carbon–palladium, nickel–copper, and copper–cobalt. The favourable effect of aluminium as a catalyst support is ascribed to the formation of traces of aluminium oxide. Catalysts prepared by precipitation with sodium or potassium carbonates appeared to be the most active. Cobalt, and possibly copper, were the only single-component catalysts by means of which unsaturated hydrocarbons could be obtained. The formation of acetylene or benzene could not be observed. Nickel–palladium and nickel–platinum catalysts, at 100°, yielded small amounts of nickel carbonyl. Nickel and nickel–palladium catalysts yield 20—25% of methane at about 250°, the activity of the catalysts being only slightly diminished after several days' use. F. G. WILLSON.

Propylene derivatives. H. GOUDET and F. SCHENKER (Helv. Chim. Acta, 1927, **10**, 132—140).—Catalytic reduction of *n*- and *iso*-propyl alcohols with anhydrous alumina at the optimum temperature, 460—470°, gives propylene in 89 and 98% yields, respectively, provided the catalyst is frequently renewed. When an equimolecular mixture of propylene and chlorine is passed slowly through an illuminated cooled tube and the product washed immediately with sodium carbonate solution, an 80% yield of αβ-dichloropropane, n_D^{20} 1·4388, together with small amounts of αββ-trichloro- and ααββ-tetrachloro-propane, is obtained. Treatment of the αβ-dichloropropane with alcoholic potassium hydroxide solution under specified conditions gives a mixture of α- and β-chloropropylenes in 95% yield, which, on fractional distillation, gives 25—30% of the β-isomeride, n_D^{63} 1·404, the remainder being a mixture of constant b. p. (b. p. 30—32°) consisting mainly of the α-isomeride (cf. Reboul, A., 1879, 127). By the action of *m*-xylene on ββ-dichloropropane, β-chloropropylene, or a mixture of these in presence of aluminium chloride, a 25—27% yield of *xylylpropane*, m. p. 174·5°, is obtained. This yields a *dinitro*-derivative, m. p. 256° (decomp.), when treated with ordinary nitric acid, a *tetranitro*-derivative, decomp. 295—300°, when nitrated with fuming nitric acid, and a *hexanitro*-derivative, decomp. 205°, when treated with a mixture of fuming nitric and sulphuric acids. J. W. BAKER.

Polymerisation of the amylenes. J. F. NORRIS and J. M. JOUBERT (J. Amer. Chem. Soc., 1927, **49**, 873—886).—The five isomeric amylenes were prepared by improved methods in pure condition, and their behaviour was studied with concentrations of sulphuric acid varying from 46% upwards. β-Methyl-Δ^{β}-butene and β-methyl-Δ^{α}-butene are the most readily polymerised, and the acid solutions obtained yield *tert.*-amyl alcohol when saturated with am-

monium sulphate, and consequently contain no alkyl hydrogen sulphate. The solutions obtained when Δ^{α}-pentene and Δ^{β}-pentene were used gave *sec.*-amyl alcohol only after dilution and hydrolysis. γ-Methyl-Δ^{α}-butene is the only amylene which is polymerised without first dissolving in the acid used. The formation of the diamylenes appears to be the result of the dehydration of the amyl alcohol in solution, or of that formed as the result of hydrolysis of an alkyl hydrogen sulphate. The diamylenes did not condense with primary or secondary alkyl halides when heated at 100° with calcium oxide or zinc oxide. β-Methyl-Δ^{β}-butene condensed with tertiary alkyl halides under these conditions, but γ-methyl-Δ^{α}-butene did not; in general, the diamylenes, although olefines, are much less reactive than the amylenes. A study of the decomposition of the ozonide indicates that the diamylene from β-methyl-Δ^{β}-butene is $CMe_2{:}CMe{\cdot}CMe_2{\cdot}CH_2Me$. F. G. WILLSON.

Reaction of magnesium and tribromopropane. W. KRESTINSKI (J. Russ. Phys. Chem. Soc., 1926, 58, 1078—1080; cf. A., 1913, i, 1145; 1915, i, 365).—The action of metallic magnesium on symmetrical tribromopropane gives, under the conditions of Grignard's synthesis, an 85% yield of diallyl, which crystallises from a mixture of alcohol and ether in two forms, m. p. 53—54° and 64°.

M. ZVEGINTZOV.

Semi-hydrogenation of the acetylenic linking and dependence of the geometrical configuration of the ethylenic compound so formed on the rate of reaction. E. OTT and R. SCHROTER (Ber., 1927, 60, [*B*], 624—642).—During the preparation of ethylenedicarboxylic acids by reduction of acetylenedicarboxylic acid by (accidentally) impure hydrogen in presence of palladised charcoal, it is found that a gradual change in the proportion of maleic to fumaric acid is induced by repeated use of the same catalyst in the sense that the proportion of the latter acid increases as the activity of the catalyst decreases (cf. Zalkind, A., 1923, i, 176). It is shown that alteration in the amount of catalyst and the method of agitation influences the period of reaction within wide limits, but does not affect the relative proportion of the stereoisomeric ethylenic compounds, provided the activity of the catalyst remains unchanged. In the heterogeneous system, therefore, the rate of reaction does not bear the same relationship to the period as in a homogeneous system, and the rate of addition of hydrogen to the multiple linking is influenced definitely only by the activity of the catalyst. In all cases, the product formed when the rate of reaction is greatest is the most labile stereoisomeride with the highest energy content, whether this be the *cis*- or the *trans*-form. Zalkind's observation that *cis*-$\beta\varepsilon$-dihydroxy-$\beta\varepsilon$-dimethyl-Δ^{γ}-hexene is preferentially produced by rapid reduction of the corresponding hexinene is not connected with the rate of the reaction, but is due to diminution of the period by increase in the amount of catalyst; with the most highly active catalysts, *trans*-$\beta\varepsilon$-dihydroxy-$\beta\varepsilon$-dimethyl-Δ^{γ}-hexene is produced. Reduction of diphenyldiacetylene with highly active palladised charcoal affords up to 90% of the most labile *cis–trans*-diphenylbutadiene; increasing diminution of the activity of the catalyst increases the yield of the moderately stable *cis–cis*-form to more than 50%. Controlled and reproducible limitation of the activity of the catalyst has been achieved towards $\beta\varepsilon$-dihydroxy-$\beta\varepsilon$-dimethyl-Δ^{γ}-hexinene, diphenyldiacetylene, and phenylpropargylidenemalonic acid; simple exposure to air or previous use in the reduction of sparingly soluble acetylenic compounds suffices to reduce the activity of the palladium. Hydrogen sulphide or carbon monoxide does not alter the proportion of maleic to fumaric acid produced from acetylenedicarboxylic acid in presence of palladium, whence it follows that a portion of the metal is completely poisoned, whereas the remainder retains its efficiency, the net result being the reduction of the amount of catalyst.

Reduction of diphenyldiacetylene in presence of colloidal palladium, nickelised charcoal, and highly active palladised charcoal gives 25%, 33%, and 8%, respectively, of the moderately stable *cis–cis*-diphenylbutadiene. Tolane yields exclusively *iso*stilbene in presence of colloidal palladium or nickelised charcoal, whereas cobalt affords 8% of stilbene. Zalkind's $\beta\varepsilon$-dihydroxy-$\beta\varepsilon$-dimethyl-Δ^{γ}-hexinene is equally sensitive to change in the catalyst, but irregularities in the action render it unsuitable as a standard for comparison of activities.

Comparison of the effects of highly active palladised charcoal and colloidal palladium shows that the latter never exhibits the maximum activity of the metal, the protective colloid causing delay in the reaction. The period of reaction under equivalent conditions is shorter with the colloidal metal than with the activated charcoal by reason of the greater surface exposed.

The most suitable standard for the comparison of the activities of catalysts is diphenyldiacetylene; methods for the approximate separation of the labile *cis–trans*-, moderately stable *cis–cis*-, and stable *trans–trans*-diphenylbutadienes are given. Tolane is less suitable, whilst acetylenedicarboxylic and phenylpropiolic acids cannot be used on account of the readiness with which they lose carbon dioxide.

The laws governing the addition of hydrogen to the acetylenic linking cannot be stereochemical, as universally assumed; the course of the change is a question of energy. H. WREN.

Thermal investigation of certain olefinic and acetylenic derivatives. W. A. ROTH and F. MULLER (Ber., 1927, 60, [*B*], 643—645).—In connexion with the work of Ott and Schroter (preceding abstract), the heats of combustion of $\beta\varepsilon$-dihydroxy-$\beta\varepsilon$-dimethyl-Δ^{γ}-hexinene, m. p. 94°, and of the $\beta\varepsilon$-dihydroxy-$\beta\varepsilon$-dimethyl-Δ^{γ}-hexenes (α-form, m. p. 76—77°, β-form, m. p. 68—69°) have been found to be 8028 ± 4, 8122 ± 5, and 8145 ± 2 g.-cal./g., respectively. As expected from other lines of reasoning, the β form of the hexene is found to be richer in energy.

H. WREN.

Propylene–halogen hydride reaction. B. P. SUTHERLAND and O. MAASS (Trans. Roy. Soc. Canada, 1927, [iii], 20, III, 499—505).—In the mixture of products obtained when propylene and hydrogen chloride are allowed to react in the liquid state,

*iso*propyl chloride was identified by vapour-pressure measurements. A new *hexyl chloride*, $C_6H_{13}Cl$, which from vapour-pressure measurements appeared to have a b. p. of 110·0—110·8°, was also separated, but its structure was not ascertained. A third product was probably a hydrocarbon of mol. wt. about 260, and b. p. about 163°. R. CUTHILL.

Preparation of substituted vinyl bromides. A. KIRRMANN (Bull. Soc. chim., 1927, [iv], **41**, 316—323).—α-Bromo-Δ^{α}-olefines are obtained by the general method of Lespieau (A., 1921, i, 490) and Bourguel (A., 1923, i, 1170). The β-bromo-Δ^{α}-isomerides are less readily obtained. Kirrmann's method (A., 1926, 934) affords mixtures which in the case of the higher members are incapable of separation. Bruylant's method (Ber., 1875, **8**, 406) gives poor yields in consequence of by-reactions affording the α-bromo-substituted aldehyde, and the tribromo-derivative, $R{\cdot}CHBr{\cdot}CHBr_2$ or $R{\cdot}CBr_2{\cdot}CH_2Br$ through addition at the double linking. By use of the acetals in place of the aldehydes, the β-bromo-Δ^{α}-olefine is ultimately obtained in at least 25% yield free from its isomeride. The acetals are readily obtained in 90% yield, and with phosphorus trichlorodibromide afford upwards of 60% of the ααβ-tribromo-derivative, $R{\cdot}CHBr{\cdot}CHBr_2$. Excess of the reagent affords a tetrabromo-derivative. The ααβ-tribromo-derivative is then treated with zinc dust, $R{\cdot}CHBr{\cdot}CHBr_2+Zn \longrightarrow R{\cdot}CH{:}CHBr+ZnBr_2$.

By the above methods, a number of known vinyl bromides have been prepared in a greater state of purity. No attempt was made to separate the *cis*- and *trans*-forms of the α-bromo-Δ^{α}-olefines. The following compounds are new: *βγ-dibromo-Δ^{α}-propene*, $d^{21(?)}$ 1·9794, n_D^{21} 1·15352; *αα-dibromobutane*, b. p. 53°/13 mm., 158°/760 mm., d 1·733, 1·4991; n-*αα-dibromoheptane*, b. p. 98—99°/11 mm., d 1·500, n^{15} 1·4959; *ααβ-tribromo-γ-methylbutane*, b. p. 106—108°/16 mm., d 2·032, n^{21} 1·5522; *ααβ-tribromoheptane*, b. p. 144—145°/19 mm., d 1·792, n^{-1} 1·5293, n-*heptaldehyde-dimethylacetal*, b. p. 75°/17 mm., 182°/760 mm., d 0·849, n^{20} 1·4130, *α-bromo-β-methylbutaldehyde*, b. p. 43—44°/16 mm., d 1·353, n^{21} 1·4610, *α-bromoheptaldehyde*, b. p. 80°/11 mm., d 1·256, n^{20} 1·4652. The *tetrabromo*-derivative, $C_5H_8Br_4$, b. p. 150—152°/17 mm., d 2·305, n^{17} 1·5940, was isolated from the action of phosphorous trichlorobromide on the acetal of *iso*valeraldehyde, b. p. 128—129°, d 0·847, n^{15} 1·3992 (cf. Alsberg, Jahresber., 1864, 486). Octane and butyl alcohol afford an azeotropic mixture, b. p. 110°, d^{17} 0·778, n^{17} 1·4022 (cf. Young, J.C.S., 1902, **81**, 760). R. BRIGHTMAN.

Action of phosphorus pentahalides on derivatives of *as*-methylethylethylene glycol. W. F. SEYER and W. CHALMERS (Trans. Roy. Soc. Canada, 1926, [iii], **20**, III, 337—341).—By the action of phosphorus pentachloride on the oxide, glycol, and chlorohydrin of *as*-methylethylethylene (β-methyl-Δ^{α}-butylene), or by the action of thionyl chloride on the oxide, there is produced, not the dichloride, but a *chlorinated amylene*, (?) $CH_2Me{\cdot}CMe{:}CHCl$, b. p. 102—104°. Distillation of the chlorohydrin gives the same substance with an *isomeride*, (?) $CHMe{:}CMe{\cdot}CH_2Cl$, b. p. 117—120°. Further action of phosphorus pentachloride on the chloroamylene yields a *trichloride*, $C_5H_9Cl_3$, b. p. 180—184°. R. CUTHILL.

Action of halogen acids and phosphorus halides on the acetylenic γ-glycols. W. N. KRESTINSKI (J. Russ. Phys. Chem. Soc., 1926, **58**, 1067—1077).—The physical properties and reactions of βε-dibromo-βε-dimethyl-Δ^{γ}-hexinene (cf. Dupont, A., 1911, 173) and of the product of the action of phosphorus tribromide on βε-dimethyl-Δ^{γ}-hexinene-βε-diol are studied, to determine the structure of the bromo-compounds. Dupont's dibromide, m. p. 39°, is inert towards bromine and potassium permanganate. The mol. refractivity is 55·7 in alcohol, 54·83 in toluene. It gives a yellow colour with tetranitromethane and is oxidised by potassium permanganate on boiling to acetone and oxalic and α-hydroxy-α-methylpropionic acids. The ethylenic structure, $CMe_2{:}CBr{\cdot}CBr{:}CMe_2$, and not Dupont's acetylenic structure, is therefore probably correct. Reduction with zinc dust in alcohol is rapid, giving a solid hydrocarbon, m. p. 35°, which rapidly passes in air into an amorphous mass, insoluble in organic solvents, which explodes when strongly heated and contains oxygen. Phosphorus tribromide and the glycol give in benzene solution at 0° a mixture of isomeric bromo-compounds, b. p. 100—118°/13 mm. No dibromide, m. p. 39°, is obtained, but the fraction boiling below 104°/13 mm. deposits an *isomeride*, m. p. 46—48°. It is very unstable, and does not give a yellow colour with tetranitromethane. It probably has the acetylenic structure, and readily passes into the ethylenic isomeride. The fractions of b. p. 110—111°/13 mm. and 116—118°/13 mm. seem to contain two dibromides with an ethylenic structure, differing in colour and density. The second fraction on reduction gives a liquid *hydrocarbon*, C_8H_{12}, b. p. 126—127°, d_4^{20} 0·768, n_D^{20} 1·48143, mol. ref. 40·09, which rapidly resinifies on keeping in air. The original γ-glycol on oxidation gives oxalic and α-hydroxy-α-methylpropionic acids together with traces of acetic and formic acids. The possible structures of the glycol and its bromides, together with the mechanism of the reactions, is discussed. M. ZVEGINTZOV.

Trifluoro-alcohols. I. Trifluoro-*tert.*-butyl alcohol. F. SWARTS (Bull. Soc. chim. Belg., 1927, **36**, 191—205).—iso*Amyl trifluoroacetate*, b. p. 119·3°/757 mm., d 1·1047, n_D 1·35295, reacts with magnesium methyl iodide to form *trifluoro*-tert.-*butyl alcohol*, m. p. 20·75°, b. p. 81·6—81·7°/761 mm., $d_4^{22·6}$ 1·1903, n_D 1·33241, the fluorine being unattacked. The alcohol is converted by phosphorus pentabromide at 50—60°, but not by concentrated sulphuric acid, into *γγγ-trifluoroisobutylene*, b. p. 6·3—6·4°, d_4^0 1·056; which combines slowly with bromine to give *γγγ-trifluoro-αβ-dibromoisobutane*, m. p. —53—55°, b. p. 130·8°/754 mm., d_4^{15} 1·9825, n_D 1·44104, and with hydrogen bromide to give a *trifluorobromoisobutane*, b. p. 79—81°, d^{17} 1·550. By the action of phosphorus pentabromide on trichloro-*tert.*-butyl alcohol, a small quantity of a *substance*, $C_4H_5Cl_3Br_2$, b. p. 243°, is obtained. C. HOLLINS.

Action of halogen acids on acetylenic glycols. (I) Hydrobromic and (II) hydriodic acids and

βε-dimethyl-Δ$^{\gamma}$-hexinene-βε-diol. J. S. SALKIND and (I) M. P. SIGOVA and (II) B. RUBIN and A. A. KRUGLOV (J. Russ. Phys. Chem. Soc., 1926, 58, 1039—1043, 1044—1051).—I. The action of hydrobromic acid in water and glacial acetic acid solutions at different temperatures and concentrations on βε-dimethyl-Δ$^{\gamma}$-hexinene-βε-diol gives the same products under all conditions, the best yield being obtained with excess of aqueous hydrobromic acid on keeping for several hrs. at the ordinary temperature. On pouring into cold water, a solid dibromide, m. p. 36—37°, separates (together with some oil). It is very inert, does not react with chlorine or bromine, decolorise cold permanganate, lose bromine on prolonged treatment with potassium hydroxide, or add hydrogen in presence of palladium or platinum-black. Prolonged oxidation with potassium permanganate gives, on warming, formic and acetic acids, together with traces of α-hydroxy-α-methylpropionic acid. Treatment of the glycol with excess of cold phosphorus tribromide yields an isomeric dibromide, m. p. 46°. If the residual oil is purified by steam distillation, a further yield of the crystalline isomeride, m. p. 37°, is obtained. The isomeride of higher m. p. is also very inert, but reacts slowly with potassium hydroxide. It is never obtained by the action of hydrobromic acid. The formulæ $CMe_2Br{\cdot}C{:}C{\cdot}CMe_2Br$ and $CMe_2{:}CBr{\cdot}CBr{:}CMe_2$, respectively, are suggested for the isomerides of higher and lower m. p. The latter formula accounts for the production of the α-hydroxy-α-methylpropionic acid on oxidation, *via* the formation of a dibromoglycol by the addition of hydroxyl groups in the αδ-position.

II. The action of excess of aqueous hydriodic acid in the cold and on warming on βε-dimethyl-Δ$^{\gamma}$-hexinene-βε-diol gives in every case a crystalline *product*, $C_8H_{14}I_2$, m. p. 75°, inert and analogous in properties to the dibromide, m. p. 37°. On reduction by zinc dust in boiling alcohol, a white *solid*, decomp. 180—190°, is obtained which contains oxygen, but not halogen. It does not give reactions for either a hydroxyl or a carbonyl group, and is rapidly oxidised by permanganate, giving acetic, traces of formic, and a little α-hydroxy-α-methylpropionic acids. If the di-iodide is reduced in absence of air, an unsaturated *hydrocarbon*, m. p. 105—106°, is obtained. It is rapidly oxidised in air to the compound containing oxygen.

Cautious oxidation of the hydrocarbon with permanganate in absence of air gives mainly acetone and oxalic acid, with traces of formic and acetic acids. The formulæ $CMe_2{:}C{:}C{:}CMe_2$ and $\begin{matrix}CMe_2{\cdot}C{:}C{:}CMe_2\\ \llcorner\!\!-\!\!O\!\!-\!\!\lrcorner\end{matrix}$ or $\begin{matrix}CMe_2{:}C\!\!-\!\!C{:}CMe_2\\ \llcorner\!\!-\!\!O\!\!-\!\!\lrcorner\end{matrix}$ are suggested for the hydrocarbon and its oxide, although the latter is probably a polymeride. Prolonged oxidation of the di-iodide with potassium permanganate gave a product (b. p. 135—138°), probably α-hydroxy-α-methylpropaldehyde. It gave on keeping a *solid*, m. p. 59—63°, probably a polymeride, and a *semicarbazone*, m. p. 156°. Besides the aldehyde, small quantities of formic, acetic, oxalic, and α-hydroxy-α-methylpropionic acids were obtained. The formula suggested for the di-iodide is $CMe_2{:}CI{\cdot}CI{:}CMe_2$. M. ZVEGINTZOV.

Action of halogen acids on acetylenic glycols. III. Hydrobromic acid and αδ-diphenyl-Δ$^{\beta}$-butinene-αδ-diol. J. S. SALKIND and A. A. KRUGLOV (J. Russ. Phys. Chem. Soc., 1926, 58, 1052—1061).—The action of acetic acid solutions of hydrobromic acid at different temperatures and concentrations on one of the stereoisomerides (m. p. 140°) of αδ-diphenyl-Δ$^{\beta}$-butinene-αδ-diol yields five products. Solid *dibromide I*, m. p. 114—115°, is obtained in 90% yield by treating the glycol for 30 min. at the ordinary temperature with a large excess of hydrobromic acid in 95% acetic acid solution. It slowly decolorises alkaline permanganate, does not react with cold bromine or potassium hydroxide, and is very slowly hydrolysed by moist silver oxide. On oxidation for 4 days at the ordinary temperature with potassium permanganate, only benzoic acid is obtained. Alcoholic potassium hydroxide gives some αδ-diphenyl-Δ$^{\beta}$-butinene, m. p. 87°, together with an amorphous polymeride containing bromine. Solid *dibromide II*, m. p. 92—95°, is obtained if the original reaction mixture is kept at 0° and poured into ice-water. On boiling the solution in most solvents except benzene and cooling, the isomeride of higher m. p. separates.

The action of alcoholic potassium hydroxide is the same as with dibromide I. Liquid *dibromide III* is obtained by the action of a saturated solution of hydrogen bromide in 95% acetic acid on the solid dibromide I. On pouring into water, the liquid dibromide separates as an oil, together with some solid tribromide. It decomposes on distillation under 50 mm. A liquid *monobromide*, $C_{16}H_{13}OBr$, is obtained as an oily by-product in the preparation of solid monobromide I. Larger yields result if a saturated solution of hydrogen bromide in glacial acetic acid is used. The liquid decomposes on distillation under 80 mm. It gives no reaction for a hydroxyl group, and is oxidised to the extent of about 50% by potassium permanganate, benzoic acid only resulting. The formula suggested is $\begin{matrix}CH\!\!-\!\!CHPh\\ |\quad\quad|\\ CBr{\cdot}CHPh\end{matrix}\!\!>\!O$. A solid *tribromide*, m. p. 155°, is obtained by the action for 1—2 days of a saturated solution of hydrogen bromide in glacial acetic acid on the glycol, or by the further action of such a solution on the mono- and di-bromides. It does not decolorise permanganate or react with bromine, and is very slowly hydrolysed by potassium hydroxide and moist silver oxide on heating. Potassium permanganate in acetone solution oxidises it very slowly, giving benzoic acid only. Alcoholic potassium hydroxide gives a product similar to that with the dibromides.

The theoretical significance of these results is discussed. The monobromide gives on further bromination only the tribromide and no dibromides, so that the formation of the latter must be an independent parallel reaction. The tribromide is formed from the monobromide and the dibromide I by the direct addition of hydrogen bromide and consequently must be $CHPhBr{\cdot}CH{:}CBr{\cdot}CHPhBr$, and dibromide I $CHPh{:}CBr{\cdot}CH{:}CPhBr$. Dibromide II can either be $CHPhBr{\cdot}C{:}C{\cdot}CHPhBr$ or $CPhBr{:}CH{\cdot}CH{:}CPhBr$.

M. ZVEGINTZOV.

Syntheses of glycol derivatives of ethers. M. Godchot (Compt. rend., 1927, **184**, 820—822).—The action of magnesium methyl iodide on ethyl diglycollate affords *di-β-hydroxy-β-methylpropyl ether*, m. p. 65°, b. p. 125—128°/25 mm., 230—235°/760 mm., which is not dehydrated in acetic acid. Similarly, magnesium phenyl bromide affords *di-β-hydroxy-ββ-diphenylethyl ether*, m. p. 126°, converted on warming in acetic acid alone into *αα'α'-tetraphenyldiethylene dioxide*, $O<\frac{CH_2\cdot CPh_2}{CH_2\cdot CPh_2}>O$ m. p. 178—179°; in presence of hydrochloric acid also the glycol affords *di-ββ-diphenylvinyl ether*, an oil, oxidised to benzophenone by chromic acid. Ethyl α-methyl-α'-ethyl diglycollate (A., 1908, i, 126) and magnesium phenyl bromide afford the *ether*, $OH\cdot CPh_2\cdot CHEt\cdot O\cdot CHMe\cdot CPh_2\cdot OH$, m. p. 142—143°, which loses water on warming in acetic acid and affords αα'α'-tetraphenyl-β-methyl-β'-ethyldiethylene dioxide, m. p. 65°. Ethyl methyldiglycollate and ethyl dimethyldiglycollate afforded only viscous products with magnesium phenyl bromide.

R. Brightman.

Displacement of alkyl groups from sulphurous esters. E. Bourgeois and A. V. Casteele (Bull. Soc. chim. Belg., 1927, **36**, 149—152).—Compounds of the type Cl·S(:O)·OR are obtained in good yield by the action of phosphorus pentachloride on sulphurous esters. The following compounds are described in which R is the alkyl group: ethyl, b. p. 72°/117 mm.; n-*propyl*, b. p. 87·5°/88 mm.; iso*butyl*, b. p. 93°/68 mm.; iso*amyl*, b. p. 87·5°/25 mm. These react in the cold with alcohols, forming normal sulphites, $R\cdot SO_2\cdot R'$. The mixed sulphites obtained when R and R' are different are converted on keeping into equilibrium (?) mixtures of the two simple normal esters and the mixed ester. *Methyl ethyl sulphite*, b. p. 139—144°, *methyl* iso*amyl sulphite*, b. p. 121°/76 mm., and *ethyl* iso*amyl sulphite*, b. p. 120—121°/50 mm., are described.

When ethyl sulphite is heated at 100° with excess of *iso*amyl alcohol for some hrs. it is converted completely into ethyl alcohol, *iso*amyl sulphite, and ethyl *iso*amyl sulphite. Under similar conditions, excess of ethyl alcohol has little action on *iso*amyl sulphite.

C. Hollins.

Interaction of sulphur dichloride with substances containing the reactive methylene group or substituted methylene group. K. G. Naik and G. V. Jadhav (J. Indian Chem. Soc., 1926, **3**, 260—272).—The action of sulphur dichloride on substituted malonamides and methylmalonamides in benzene solution has been investigated. With malondianilide and -di-*o*-tolylamide, both hydrogen atoms of the methylene group react to yield *compounds* of the type $(CO\cdot NHR)_2C(SCl)_2$, m. p. 164—165° (R=Ph) and 160—161° (R=C_6H_4·Me), respectively, which are less stable than those obtained by the action of sulphur monochloride (Naik, J.C.S., 1921, **119**, 379), and on treatment with fuming nitric acid yield, respectively, *malon-dinitroanilide*, m. p. 90° (decomp.), and *-dinitro-o-tolylamide*, m. p. 85° (decomp.). Methylmalon-dianilide and -di-*o*-tolylamide yield the *compounds* $(CO\cdot NHR)_2CMe\cdot SCl$, m. p. 132° (R=Ph) and 150° (R=C_6H_4·Me). With malon-di-*n*-propylamide, -di-α-naphthylamide, and -di-β-naphthylamide, only one methylene hydrogen atom reacts, yielding *compounds* of the type $(CONHR)_2CH\cdot SCl$, m. p. 141—142° (R=Pr[n]), m. p. 145° (decomp.) (R=α-naphthyl), m. p. 230—231° (decomp.) (R=β-naphthyl). The latter on nitration yields *malondinitro-β-naphthylamide*, m. p. 185° (decomp.). Malon-di-*p*-tolylamide and -dibenzylamide react to yield chlorinated *compounds* of the type $(CO\cdot NHR)_2CCl\cdot SCl$, m. p. 158° (R=·$C_6H_4$Me), m. p. 149—150° (R=·$CH_2$Ph), which in presence of a trace of moisture are reconverted into the original amides. On nitration, the former compounds yield *malondinitro-*p*-tolylamide*, m. p. 120° (decomp.). In the case of methylmalondi-*p*-tolylamide, the methyl group is also attacked to yield the *compound* $(CO\cdot NH\cdot C_6H_4Me)_2C<^{CH_2}_{SCl}$, m. p. 157—158°, which is similarly decomposed with traces of moisture. The authors conclude that sulphur dichloride is a definite compound, SCl_2.

J. W. Baker.

Varying valency of platinum with respect to mercaptanic radicals. IV. Inadequacy of Werner's theory to explain certain anomalous cases. P. C. Ray, B. C. Guha, and K. C. Bose-Ray (J. Indian Chem. Soc., 1926, **3**, 358—370).—In continuation of previous work (A., 1926, 1023), the action of primary, secondary, and tertiary bases on the mercaptanic platinum compounds previously described (A., 1925, ii, 1121) has been investigated. The action of ethylamine on the isomerides, m. p. 77° and 104°, of the compound $(Et_2S)_2,PtCl_2$, and of benzylamine on those of m. p. 77°, 96°, and 100°, yields *compounds* of the type $PtCl_2,4B$, which have m. p. 142° (B=NH_2Et) and 196° (B=$NH_2\cdot CH_2Ph$), respectively. Diethylamine on the isomeride, m. p. 108°, yields the *compound* $PtCl_2,Et_2S,NHEt_2$, m. p. 176°, quinoline on the form, m. p. 77°, yields the *compound* $PtCl_2,2C_9H_7N$, m. p. 165°. Pyridine acts on the compound $(Et_2S)_2,PtCl_3$ to give the *compounds* $PtCl_3,2C_5H_5N$, $PtCl_3,4C_5H_5N$, and, probably, $PtCl_4,2C_5H_5N$; benzylamine yields $PtCl_2,4NH_2\cdot CH_2Ph$ (above), and aniline the *compound* $PtCl_2,2NH_2Ph$. The action of benzylamine on the compound $PtCl_4,2Et_2S$ yields the compound $PtCl_2,4NH_2\cdot CH_2Ph$, whilst aniline yields two isomeric *compounds*, $PtCl_2,2NH_2Ph$, m. p. 100° and 190°, respectively. All the above compounds can be represented in accordance with Werner's co-ordination theory. The compound $Et_2S,PtCl$, however, cannot be so represented, and a mol. wt. determination shows that it is bimolecular and most probably has the structure $(SEt_2\cdot PtCl)_2$. With benzylamine, it yields the *compound* $Pt_2Cl,NH_2\cdot CH_2Ph,Et_2S$, together with $PtCl_2,4NH_2\cdot CH_2Ph$ and a *substance*, m. p. 110°. Pyridine yields the *compound* Pt_2Cl,C_5H_5N,Et_2S and the compound $PtCl_2,2C_5H_5N$ (*loc. cit.*). Piperidine yields the *compound* $Pt_2Cl,2C_5H_{11}N,0{\cdot}5Et_2S$, whilst ethylamine yields the *compound* Pt_2Cl,NH_2Et,Et_2S and the compound $PtCl_2,4NH_2Et$. In each case, simultaneous oxidation and reduction have occurred. The action of pyridine on the compound $Et_2S,PtCl_5,2H_2O$ yields the *compound* $PtCl_4,2C_5H_5N$, and ethylamine gives the *compound* $PtCl_5,2NH_2Et$.

J. W. Baker.

Catalytic decomposition of formic acid. J. B. SENDERENS (Compt. rend., 1927, **184**, 856—859).—Decomposition of formic acid by sulphuric acid is catalytic, since the latter acid may be used in as small a proportion as 0·05 vol., even when diluted with water. Aluminium sulphate favours the decomposition only when sulphuric acid is present, but potassium hydrogen sulphate and orthophosphoric acid are both catalysts in its absence. The products of decomposition, carbon monoxide and water, are also obtained when alumina is used as catalyst (cf. Wescott and Engelder, A., 1926, 693).

E. W. WIGNALL.

Manufacture of acetic acid. H. DREYFUS.—See B., 1927, 268.

Optical resolution of chloroiodoacetic acid. A. M. MCMATH and J. READ (J.C.S., 1927, 537—543).—*dl*-Chloroiodoacetic acid has been resolved, using *l*-hydroxyhydrindamine and brucine, the less soluble diastereoisomeride in each case being of the form *l*B*l*A. Ammonium *d*- and *l*-chloroiodoacetates racemise rather less readily than ammonium *d*- and *l*-chlorosulphoacetates. Slow racemisation occurs in hot aqueous solution, and in presence of an equivalent of sodium hydroxide complete racemisation takes place in a few hrs. at the ordinary temperature. The following are described: l-*hydroxyhydrindamine* l-*chloroiodoacetate*, m. p. 149° (decomp.), $[M]_D$ −126° in dilute aqueous solution, $[M]_D$ declining from −135° to −103° in 5 days in methyl alcohol, $[M]_D$ −118° in chloroform containing a little methyl alcohol; l-*hydroxyhydrindamine* d-*chloroiodoacetate*, $[M]_D$ −7° in dilute aqueous solution, giving +53·5° for the acid ion; *brucine* l-*chloroiodoacetate*, m. p. 158—160° (decomp.); *brucine* d-*chloroiodoacetate*; *ammonium* l-*chloroiodoacetate*, $[M]_D$ −60°, and *ammonium* d-*chloroiodoacetate*, decomp. 149—150°, $[M]_D$ +56° in dilute aqueous solution.

M. CLARK.

Determination of mixtures of isomeric unsaturated compounds. I. Bromine additive method. R. P. LINSTEAD (J.C.S., 1927, 355—362).—The rate of addition of bromine to four pairs of isomeric unsaturated acids in an inert solvent has been determined. Previous observations that addition takes place more rapidly at the $\beta\gamma$ than at the $\alpha\beta$ double linking are confirmed. Substitution of positive groups for hydrogen increases the velocity of reaction. The statement of Kon and Linstead (A., 1925, i, 633) that β-ethyl-Δ^{β}-pentenoic acid (p-*toluidide*, m. p. 94°; *amide*, m. p. 114°) is a $\beta\gamma$-unsaturated acid is confirmed. Measurements have been made of the amount of bromine adding to known mixtures of the isomerides in a standard time, the results being used to determine the percentage of each isomeride in equilibrium mixtures obtained by boiling the acids in potassium hydroxide solution.

M. CLARK.

Undecenoic acid and its homologues. II. P. CHUIT, F. BOELSING, J. HAUSSER, and G. MALET (Helv. Chim. Acta, 1927, **10**, 113—131).—Undecenyl bromide (this vol., 40) yields successively *dodecenonitrile*, $CH_2{:}CH{\cdot}[CH_2]_9{\cdot}CN$, b. p. 142—143°/12 mm., 0·844, and *dodecenoic acid*, m. p. 19°, b. p. 171—172°/13 mm., d^{20} 0·907 (*barium* salt; *methyl* ester, b. p. 138—139°/13 mm., d^{15} 0·885; *ethyl* ester, b. p. 154·5—155·5°/18 mm. d^{15} 0·879), which on ozonisation yields nonane-$\alpha\iota$-dicarboxylic acid and sebacic acid in yields corresponding with the presence of 10% of iso*dodecenoic acid*, $CHMe{:}CH{\cdot}[CH_2]_8{\cdot}CO_2H$, b. p. 166—168°/9 mm. (*methyl* ester, b. p. 138—140°/14 mm., d^{15} 0·888). The latter is also obtained (1) by the hydrolysis of the nitrile obtained by the action of alcoholic potassium cyanide solution on βλ-dibromoundecane (together with undecane-βλ-dinitrile); (2) by hydrolysis of dodecenonitrile (together with the Δ^{κ}-acid and hydroxydodecoic acid); and (3) by heating the Δ^{κ}-acid with potassium hydroxide at 230° for several hrs. At 350—370°, the main product of the fusion is decoic acid, but fission also occurs at all other points in the chain. By reduction of the corresponding esters with sodium and alcohol are obtained Δ^{λ}-*dodecenol*, b. p. 138—140°/11 mm., d^{15} 0·848 (*phenylurethane*, m. p. 59—60·2°), and Δ^{κ}-*dodecenol*, b. p. 143—144°/13 mm., d^{15} 0·850, respectively. *Dodecalactone*, b. p. 170—171°/11 mm., d^{15} 0·9382, is obtained by the action of sulphuric acid at 90° on dodecenoic acid, and on hydrolysis yields *γ-hydroxydodecoic acid*, m. p. 62·5—63·5°. Heated for 4 hrs. at 150° with ethyl sodiomalonate in alcohol solution, undecenoyl bromide yields *ethyl undecenylmalonate*, b. p. 185°/8 mm., which on hydrolysis yields *tridecenoic acid*, m. p. 38—38·2°, b. p. 185°/15 mm. (*methyl* ester, b. p. 143°/8 mm., d^{15} 0·885; *ethyl* ester, b. p. 150°/8 mm., d^{15} 0·880; *tridecenyl* ester, m. p. 18°; b. p. 230—235°/13 mm.). Reduction of the methyl ester yields Δ_{μ}-*tridecenol*, m. p. 15°, b. p. 149—150°/9 mm. (*acetate*, b. p. 154—155°/9 mm., d^{15} 0·8795; *phenylurethane*, m. p. 58·2—58·6°), which with hydrogen bromide yields *tridecenyl bromide*, b. p. 141—143°/8 mm., d^{15} 1·037, and βν-*dibromotridecane*, b. p. 185°/8 mm., d^{15} 1·217. The latter on acetylation yields the *diacetate*, b. p. 180—190°/8 mm. (together with some iso*tridecenyl acetate*, b. p. 140°/8 mm.), which on hydrolysis yields *tridecane-βν-diol*, m. p. 60—61°. This glycol is readily oxidised with chromic and acetic acids to λ-*ketotridecoic acid*, m. p. 70—71°, b. p. 185—186°/1 mm. (*methyl* ester, m. p. 30°, b. p. 185—186°/15 mm.). *Tridecalactone*, m. p. 17—18°, b. p. 178—180°/9·5 mm., d^{15} 0·9327, obtained by the action of sulphuric acid on tridecenoic acid, on hydrolysis yields *γ-hydroxytridecoic acid*, m. p. 66—66·5°. iso*Tridecenoic acid*, $CHMe{:}CH{\cdot}[CH_2]_9{\cdot}CO_2H$, m. p. 28—29°, b. p. 183—185°/13·5 mm., 161—162°/4 mm., is obtained as a by-product in the reaction between ethyl sodiomalonate and βλ-dibromoundecane (cf. following abstract), or by the action of potassium hydroxide at 220° on the Δ^{λ}-acid. At 300—360°, fission of the chain occurs as in the analogous cases of the lower homologues. Reduction of *methyl* iso*tridecenoate*, b. p. 147—148°/10 mm., yields Δ^{λ}-*tridecenol*, m. p. 6°, b. p. 150—152°/11 mm., d^{15} 0·852 (*phenylurethane*, m. p. 64—64·5°). Condensation of ethyl methylmalonate with undecenyl bromide in presence of dry sodium ethoxide yields *ethyl methylundecenylmalonate*, b. p. 160°/3 mm., d^{15} 0·939, which on hydrolysis yields α-*methyl*-Δ^{λ}-*tridecenoic acid*, m. p. 8—9°, b. p. 182—184°/10 mm., d^{15} 0·893 (*methyl* ester, b. p. 148—149°/10 mm., d^{15} 0·879; *ethyl* ester, b. p. 160·4—161°/10 mm., d^{15} 0·873; *amide*, m. p. 86—86·5°), which on oxidation yields

undecane-βκ-dicarboxylic acid. By analogous methods are obtained: *β-methyl-Δ$^{\lambda}$-tridecenol*, b. p. 159—160°/12 mm., d^{15} 0·848 (*phenylurethane*, m. p. 66·5—67·5°); *methyltridecenyl bromide*, b. p. 140—144°/4 mm., d^{15} 1·014; *αι-dibromo-β-methyltridecane*, b. p. 161—162°/2·5 mm., d^{15} 1·129; *β-methyltridecane-αμ-diol*, b. p. 195—196°/12 mm., m. p. —2°, d^{15} 0·911; *λ-keto-α-methyltridecoic acid*, m. p. 46·5—47·2°, b. p. 198—199°/3 mm. (*methyl* ester, b. p. 181—183°/11 mm., d^{15} 0·936); *methyltridecen-α-ol*, b. p. 159—161°/13 mm., d^{15} 0·852 (*phenylurethane*, m. p. 69·5—70·5°); *methyl tridecenylmalonate*, b. p. 178—180°/3 mm., d^{15} 0·947; *pentadecenoic acid*, m. p. 49·8—50°, b. p. 195°/8 mm. (*methyl* ester, b. p. 167—168°/8 mm., d^{15} 0·881; *ethyl* ester, b. p. 174—176°/8 mm., d^{15} 0·875; *pentadecenyl* ester, m. p. 35—35·5°, b. p. 290—295°/10 mm.); *Δ$^{\xi}$-pentadecen-α-ol*, m. p. 32—33°, b. p. 170—172°/10 mm. (*phenylurethane*, m. p. 60·5—61°); *pentadecenyl bromide*, b. p. 180—185°/3 mm., d^{15} 1·009; *αξ-dibromopentadecane*, b. p. 180—185°/3 mm., d^{15} 1·170; *pentadecane-αξ-diol*, m. p. 70·6—71·6°, b. p. 205—207°/10 mm. (*diacetate*, b. p. 195—200°/8 mm.); *ν-ketopentadecoic acid*, m. p. 78·4—79·5° (*methyl* ester, m. p. 43·2—43·8°, b. p. 205—206°/15 mm.); iso*pentadecenoic acid*, m. p. 42·2—43°, b. p. 174—176°/1·25 mm. (*methyl* ester, 166—168°/8 mm., d^{15} 0·883; *ethyl* ester, b. p. 175—177°/8 mm., d^{15} 0·877); *Δ$^{\nu}$-pentadecenol*, m. p. 40—40·5°, b. p. 170—172°/8 mm. (*phenylurethane*, m. p. 68—68·4°); *methyl γ-methylpentadecenoate*, b. p. 167—173°/10 mm.; *δ-methyl-Δ$^{\xi}$-pentadecenol*, b. p. 176—182°/12 mm., d^{15} 0·831; *α-methylheptadecenoic acid*, m. p. 43—43·5°, b. p. 186—187°/3 mm. (*methyl* ester, b. p. 158—159°/3 mm., d^{15} 0·876).

J. W. Baker.

Monomethylated polymethylenedicarboxylic acids and their derivatives. P. Chuit, F. Boelsing, and G. Malet (Helv. Chim. Acta, 1927, **10**, 167—194; cf. Ruzicka, this vol., 57).—Condensation of ethyl sodiomethylmalonate and methyl θ-bromopelargonate and hydrolysis of the *ester*, b. p. 200°/2 mm., formed yields *decane-βι-dicarboxylic acid*, m. p. 80—80·5°. Ozonisation of α-methyltridecenoic acid (preceding abstract) yields the *aldehydo-acid*, b. p. 184—186°/1 mm. (*semicarbazone*, m. p. 129·5—130·5°), which is readily oxidised to *undecane-ακ-dicarboxylic acid*, m. p. 76—76·5° (*dimethyl* ester, b. p. 187—188°/13 mm., d^{15} 0·966; *diethyl* ester, b. p. 197°/12 mm., d^{15} 0·940), which is also obtained by the interaction of ethyl methylmalonate and methyl ι-bromodecoate, and on hydrolysis of the dinitrile obtained by the action of potassium cyanide on βλ-dibromoundecane (preceding abstract). The action of chloromethyl ether on the magnesium compound of βλ-dibromoundecane yields *αμ-dimethoxy-β-methyldodecane*, b. p. 156—168°/12 mm. (together with a little *methoxydodecenol*, b. p. 77—88°/11 mm.), which, treated with hydrogen bromide at 170—180°, yields *αι-dibromo-β-methyldodecane*, b. p. 190—200°/8 mm., d^{15} 1·275; this, converted into the *diacetate* and hydrolysed, yields *β-methyldodecane-αμ-diol*, b. p. 186—189°/8·5 mm., 169—172°/1 mm., m. p. 18°, d^{15} 0·917, which changes spontaneously to a white, crystalline mass, m. p. 42°. The same glycol is better obtained by the reduction of methyl α-methyldecane-ακ-dicarboxylate. Condensation of ethyl malonate with methyl bromoundecoate (Walker and Lumsden, J.C.S., 1901, 79, 1191) and hydrolysis of the product yields *β-methyldecane-ακ-dicarboxylic acid*, m. p. 82°, b. p. 237—238°/7 mm., 210—211°/1 mm. (*dimethyl* ester, b. p. 175—176°/8 mm., d^{15} 0·975; *diethyl* ester, b. p. 187—189°/8 mm., d^{15} 0·947; cf. Komppa, A., 1901, i, 365, who described this acid as the normal undecanedicarboxylic acid). Reduction of the methyl ester yields *γ-methyldodecane-αι-diol*, b. p. 190—191°/8 mm., d^{15} 0·916 (*dibromide*, b. p. 187·5—189°/7 mm., d^{15} 1·272). By the continued application of these methods, the following are obtained: *dodecane-αλ-dicarboxylic acid*, m. p. 87·5—88·5° (*dimethyl* ester, b. p. 185°/9 mm.); *β-methyltridecane-αν-diol*, m. p. 46—47°, b. p. 195°/9 mm. (*dibromide*, b. p. 198—200°/9 mm., d^{15} 1·229); *β-methylundecane-αλ-dicarboxylic acid*, m. p. 68·5—69·5°, b. p. 182—185°/8 mm., d^{15} 0·958; *β-bromo-λ-cyanoundecane*, d^{15} 1·100 (decomposes on distillation); *γ-methyltridecane-αν-diol*, b. p. 196—197°/8 mm., d^{15} 0·912, which spontaneously changes into a white, crystalline mass, m. p. 24° (corresponding *dibromide*, b. p. 196—197°/8 mm., d^{15} 1·241); β-methyldodecane-αμ-dicarboxylic acid, m. p. 75·2°, b. p. 239—241°/4 mm. (*dimethyl* ester, b. p. 194—196°/9 mm., d^{15} 0·957; *diethyl* ester, b. p. 205—207°/9 mm., d^{15} 0·938), which was also obtained by hydrolysis of the *dinitrile*, b. p. 229—232°/16 mm., d^{15} 0·901; *γ-methyltetradecane-αο-diol*, m. p. 17°, b. p. 204—205°/8 mm., d^{20} 0·909; *αο-dibromo-γ-methyltetradecane*, b. p. 207—208°/8 mm., d^{15} 1·218; α-methyltridecane-αν-dicarboxylic acid, m. p. 93·5—94·5°, b. p. 228—230°/4 mm. (*dimethyl* ester, b. p. 193—195°/5 mm., d^{15} 0·941). Dodecane-αι-diol yields a *monoacetate*, b. p. 185°/8 mm., which with hydrogen bromide is converted into a *bromoacetate*, b. p. 160—161°/3·5 mm., d^{15} 1·083; this on hydrolysis yields the *bromohydrin*, m. p. 28·6°, b. p. 155—156°/4 mm., which is converted into *α-cyanododecan-μ-ol*, m. p. 23—24°, b. p. 173—175°/4 mm., which on treatment with hydrogen bromide yields a mixture of the *bromonitrile*, *bromoamide*, m. p. 42—43°, and the *hydroxyamide*, m. p. 82—84°; the first two on hydrolysis with methyl-alcoholic sulphuric acid yield *methyl μ-bromotridecoate*, b. p. 174—179°/4 mm., d^{15} 1·090; β-methyltridecane-αν-dicarboxylic acid, b. p. 215—220°/1 mm. (*dimethyl* ester, b. p. 203—204°/8 mm., d^{15} 0·950; *monoamide*, m. p. 110—111°; *dinitrile*, b. p. 227°/9 mm., d^{15} 0·908); γ-methyltridecane-αν-dicarboxylic acid, b. p. 226—227°/3 mm. (*dinitrile*, b. p. 177—178°/3 mm., d^{15} 0·905). Condensation of ethyl malonate with *βθ-dibromo-octane*, b. p. 137—138°/15 mm., d^{15} 1·449, yields iso*decenoic acid*, $CHMe{:}CH{\cdot}[CH_2]_6{\cdot}CO_2H$, b. p. 155—157°/14 mm., d^{15} 0·930 (*methyl* ester, b. p. 121—123°/20 mm., d^{15} 0·896), and *β-methylnonane-αι-dicarboxylic acid*, b. p. 210—215°/5 mm. (m. p. 40—42°, but sample may not be pure) (*dimethyl* ester, b. p. 174—178°/15 mm., d^{15} 0·955); *γ-methylundecane-αλ-diol*, b. p. 192—195°/15 mm., d^{15} 0·923 (corresponding *dibromide*, b. p. 185—188°/15 mm., d^{15} 1·297); δ-methyltridecane-αν-dicarboxylic acid, b. p. 229—230°/2·5 mm. (*dimethyl* ester, b. p. 210—215°/14 mm.). *Pentadecane-αζ-dicarboxylic acid*, m. p. 89—90°, b. p. 223—225°/0·2 mm. (*dimethyl* ester, b. p. 172—180°/1 mm., d^{15} 0·9465, m. p. 3—4°, but changes spontaneously into a white, crystalline mass, m. p. 19—21°), is pre-

pared by the ozonisation or permanganate oxidation of α-methylheptadecenoic acid and by the oxidation of *ο-hydroxy-α-methylpentadecanecarboxylic acid*, m. p. 62—63°, obtained by the condensation of *α-bromotetradecan-ο-ol*, m. p. 46·4°, b. p. 192—195°/12 mm., d^{35} 1·123, with ethyl sodiomethylmalonate; *β-methyltetradecane-αζ-dicarboxylic acid*, m. p. 77·2—77·4°, b. p. 250°/3 mm. (*dimethyl* ester, b. p. 198—200°/3·5 mm., d^{15} 0·946; *diethyl* ester, b. p. 209—211°/3·5 mm., d^{15} 0·931). *γ-Methyltetradecane-αζ-dicarboxylic acid*, m. p. 78—78·4° (*dimethyl* ester, b. p. 203—204°/4 mm., d^{15} 0·948; *diethyl* ester, b. p. 223—225°/8 mm., d^{15} 0·934; dinitrile, m. p. 36·6—36·8°, b. p. 235—245°/8 mm.); *δ-methyltetradecane-αζ-dicarboxylic acid*, m. p. 78·8—79°, b. p. 252—253°/3 mm. (*dimethyl* ester, b. p. 200—202°/3 mm., d^{15} 0·950; *diethyl* ester, b. p. 234—236°/9 mm., d^{15} 0·931). *Methyl κ-bromoundecoate*, m. p. 15·8°, b. p. 164·5°, and *ethyl κ-bromoundecoate*, m. p. 10°, b. p. 172—174°, d^{15} 1·1295, are described. J. W. Baker.

Oxidation of oleic acid by perbenzoic acid. G. W. Pigulevski and M. A. Petrova (J. Russ. Phys. Chem. Soc., 1926, **58**, 1062—1066).—Oleic acid was oxidised at 0° in ethereal solution of perbenzoic acid and the benzoic acid removed by gaseous ammonia. The ethereal mother-liquor gave a 78% yield of a solid *oxide*, m. p. 57·5—58°. On hydrolysis by boiling with dilute acids, or heating in a sealed tube at 150°, this gave a solid dihydroxystearic acid, m. p. 94—94·5°, which corresponds, not with oleic, but with elaidic acid. Hydrolysis of the oxide corresponding with elaidic acid, on the other hand, according to Albitzky (A., 1899, i, 862), gives dihydroxystearic acid, m. p. 137°, corresponding with oleic acid. It is probable that the isomerisation takes place during hydrolysis. M. Zvegintzov.

Oxidation of ricinoleic acid with nitric acid. Conditions underlying the formation of suberic acid. P. E. Verkade (Rec. trav. chim., 1927, **46**, 137—143).—The relative amounts of suberic and azelaic acids produced in this oxidation vary considerably. The following factors influence the reaction. (1) It is immaterial whether the ricinoleic acid is added to the nitric acid, or *vice versa*. (2) A higher temperature lowers the total yield. (3) A higher temperature or less concentrated nitric acid gives a mixture in which suberic acid predominates. (4) Prolonged oxidation reduces the amount of azelaic acid, since it undergoes further oxidation more rapidly than suberic acid. On the basis of these facts, methods of preparing suberic and azelaic acids are described. J. M. Gulland.

Preparation of α-ketonic acids. Barré (Compt. rend., 1927, **184**, 825—826).—Ethyl diethyloxamate, $CO_2Et{\cdot}CO{\cdot}NEt_2$, and magnesium ethyl bromide (1·5 mols.) in 1 hr. at −15° afford 75—80% of the theoretical yield of *α-hydroxy-α-ethylbutyrdiethylamide*, b. p. 120°/11 mm., together with 5—10% of *propionylformdiethylamide*, b. p. 100°/11 mm. (*semicarbazone*, p. 140°). Excess of Grignard reagent, higher temperatures, and prolonged reaction favour formation of the latter compound. Traces of dipropionyl are formed and about 10% of the ethyl diethyloxamate is unchanged. Rapid hydrolysis of the ketone amide with hydrochloric acid affords the α-ketonic acid in 70% yield. Propionylformic acid has m. p. 31—32°, b. p. 80—82°/16 mm. (*phenylhydrazone*, m. p. 161°; *oxime*, m. p. 167°; *semicarbazone*, m. p. 210°); on slow heating these derivatives give m. p. 152°, 161°, and 190°, respectively). R. Brightman.

Electrolysis of aqueous solutions of pure oxalic acid. E. Doumer.—See this vol., 427.

Preparation of maleic and succinic acids from furfuraldehyde. Zaidan Hojin Rikagaku Kenkyujo.—See B., 1927, 268.

Effect of *gem*-dialkyl groups on the formation and stability of the anhydrides of dicarboxylic acids. E. H. Farmer and J. Kracovski (J.C.S., 1927, 680—685).—Adipic and β-methyladipic acids form unimolecular anhydrides readily hydrolysed by atmospheric moisture when the acids are boiled with acetic anhydride. The stability is progressively increased in the anhydrides of ββββ′β′- and ααα′α′-tetramethyladipic acids, the former anhydride being unaffected by boiling water or by sodium carbonate solution. Ring closure of *ethyl α-bromo-ββββ′β′-tetramethyladipate* could not be effected by treatment with potassium hydroxide in methyl alcohol. The following are described: *adipic anhydride*, m. p. 97°; *β-methyladipic anhydride*, b. p. 165°/1 mm.; *ααα′α′-tetramethyladipic anhydride*, m.p. 166° (*anilic acid*, m.p. 218°); *βββ′β′-tetramethyladipic anhydride*, m. p. 189° (*anilic acid*), when heated gives 1 : 1 : 2 : 2-*tetramethylcyclopentan-4-one*, b. p. 186—189°. M. Clark.

Shellac. Constitution of aleuritic acid. W. Nagel (Ber., 1927, **60**, [*B*], 605—609; cf. Harries and Nagel, A., 1923, i, 120).—Oxidation of aleuritic acid by 3% potassium permanganate affords azelaic acid and non-crystalline ζ-hydroxyheptoic acid, identified by further oxidation to pimelic acid. With 1% potassium permanganate at the atmospheric temperature, aleuritic acid gives azelaic acid and non-crystalline aldehydic acids, which are oxidised further to pimelic acid. More drastic oxidation with Beckmann's mixture or potassium permanganate yields mainly azelaic and pimelic acids, whereas with hydrogen peroxide and ferrous sulphate, non-crystalline, aldehydic compounds are formed. Aleuritic acid is therefore regarded as 9ω-trihydroxypalmitic acid. H. Wren.

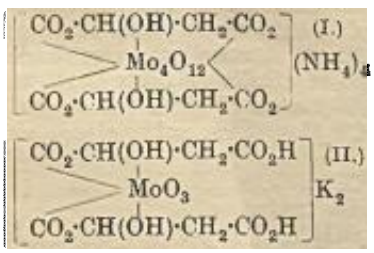
Ring-chain tautomerism. XV. Hydroxylactone type. E. Rothstein and C. W. Shoppee (J.C.S., 1927, 531—534).—Introduction of a second *gem*-dimethyl group into Balbiano's acid (cf. *ibid.*, 1922, **121**, 654) leads to stabilisation of the hydroxylactone form, $\begin{matrix}CO\text{——}O\\ |\\ CMe_2{\cdot}CMe_2\end{matrix}>C(OH){\cdot}CO_2H$. *α-Keto-ββγγ-tetramethylglutaric acid*, m. p. 140° (*dimethyl* ester, m. p. 103°, b. p. 170°/15 mm.), yields an *acetyl* derivative, m. p. 149°. It titrates as a monobasic acid, but the presence of alkalis or acids tends to shift the equilibrium in favour of the ketonic form, $CO_2H{\cdot}CO{\cdot}CMe_2{\cdot}CMe_2{\cdot}CO_2H$. The acid gives an additive *product*, $CO_2H{\cdot}[CMe_2]_2{\cdot}C(OH)(CO_2H){\cdot}NH{\cdot}C_6H_4{\cdot}NH_2$, m. p. 160°, and a condensation *product*, $\begin{matrix}N{\cdot}C_6H_4{\cdot}NH\\ ||\\ CO_2H{\cdot}[CMe_2]_2{\cdot}C\text{——}CO\end{matrix}$, m. p. 240°, with enediamine. M. Clark.

Oxidation [of organic compounds]. W. H. HATCHER (Trans. Roy. Soc. Canada, 1926, [iii], 20, III, 327—335).—The action of alkaline permanganate on tartaric acid yields 2 mols. of oxalic acid, whilst acid permanganate gives carbon dioxide and 2 mols. of formic acid, and sodium hypoiodite has no effect. Dihydroxymaleic acid is oxidised by alkaline permanganate to oxalic acid, and by acid permanganate to carbon dioxide, formic acid not being produced in either case, whereas with sodium hypoiodite the product is mesoxalic acid. With all three oxidising agents, dihydroxytartaric acid is formed as an intermediate stage. Permanganate oxidises mesoxalic acid to oxalic acid or carbon dioxide, and sodium hypoiodite slowly converts it into oxalic acid. Mesoxalic acid does not seem to be formed in the oxidation of dihydroxymaleic acid by permanganate. Formic acid is rapidly and completely oxidised by alkaline permanganate, but with acid permanganate the reaction is not complete. R. CUTHILL.

Compounds of the tartar emetic type. Classification. E. DARMOIS (Bull. Soc. chim. Belg., 1927, **36**, 64—75; cf. A., 1923, i, 299, 535, 751; 1924, ii, 618; 1925, ii, 184, 357; 1926, 337, 457, 559, 661, 778, 1201).—Compounds of the tartar emetic type are formed from a variety of oxides of metals or metalloids (beryllium, boron, aluminium, titanium, zirconium, arsenic, antimony, bismuth, copper, molybdenum, tungsten, uranium) and all organic compounds containing two adjacent hydroxyl groups, whether alcoholic, phenolic, or acidic. The constitution, $CO_2H{\cdot}CH(OH){\cdot}CH(OSbO){\cdot}CO_2H$, suggested by Jungfleisch for tartar emetic does not account for the immediate change in optical rotation on adding alkali to tartar emetic or yellow molybdic acid to malic acid, nor the inability of tartaric esters to form emetics until hydrolysis has occurred. Co-ordination formulæ of a single type are also not satisfactory for all emetics.

Emetics are grouped in three classes: (i) those possessing a p_H of maximum stability; *e.g.*, the compound $[4MoO_3,2C_3H_4O_5]Na_4$, formed by gradual addition of alkali to a solution of molybdic and tartaric acids, represents a point of maximum stability at p_H 3·7; (ii) those stable in acid media, and (iii) those stable in basic media; *e.g.*, tartar emetic and mixtures of antimony trioxide or boric acid with mannitol, form stable complexes on addition of excess of concentrated alkali.

The formation of complexes of the emetic type is readily followed by means of polarimetric measurements. The molybdomalates are derivable from acids $4MoO_3,2H_2O$ and MoO_3,H_2O; *e.g.*, the dextrorotatory ammonium salt is (I), and the lævorotatory potassium salt is (II). Emetics stable in acid are usually formed only from strongly acidic oxides; those of class iii are derived from weakly acidic oxides combined with alcoholic hydroxyl groups. Thus in sodium boromannitol, $[C_6H_{13}O_5{\cdot}B_2O_3{\cdot}C_6H_{13}O_5]Na_2$, neighbouring pairs of hydroxyl groups are linked to the boric oxide group, and one hydroxyl group of each pair becomes acidic, and the hydrogen atom is replaced by sodium. In the alkali-stable complex from tartar emetic, neutral potassium tartrate takes the place of mannitol.



C. HOLLINS.

Muconic and hydromuconic acids. IV. Geometrical form and reducibility. E. H. FARMER and W. M. DUFFIN (J.C.S., 1927, 402—412).—Addition of bromine to *trans–trans*-methyl muconate gives two isomeric *dibromides*, A, m. p. 104—105°; B, m. p. 50°. When treated with diethylamine in ether, A gives (i) trans–trans-*methyl α-bromomuconate*, m. p. 89° (*amide*, m. p. 235°), whilst B gives (ii) cis–cis-*methyl α-bromomuconate*, m. p. 68° (*amide*, m. p. 197°), and (iii) cis–trans-*methyl-α-bromomuconate*, m. p. 55° (*amide*, m. p. 156°). The geometrical configurations of these isomerides are determined by the relative ease of formation of the amides. Reduction with zinc and acetic acid readily gives with (i) and (iii) *methyl Δ$^\beta$-dihydromuconate*, m. p. 16°, whilst with (ii) no reduction occurs. Treatment with zinc dust in alcohol or acetone removes bromine from (i) to give *trans–trans*-methyl muconate, but does not affect (ii) or (iii). Reduction of the three isomeric ethyl-αα′-dibromomuconates and of the analogous dichloro-compounds with zinc and acetic acid gives, in each case, *ethyl Δ$^\beta$-dihydromuconate* (trans ?), m. p. 2°. The two isomeric methyl muconates (J.C.S., 1923, 121, 2531), on reduction with zinc and acetic acid, give methyl Δ$^\beta$-dihydromuconate, with sodium amalgam give Δ$^\beta$-dihydromuconic acid, and with palladium and hydrogen give methyl adipate. The isomeric methyl αα′-dibromoadipates (*loc. cit.*) treated with zinc and acetone give methyl Δ$^\beta$-dihydromeconate, m. p. 16°. *meso*- and *r*-Ethyl ββ′-diphenyl-ββ′-dihydroxyadipates (Beschke, A, 1912, i, 889) react with phosphorus tribromide to give two isomeric *ethyl -diphenylmuconates*, (iv), m. p. 136°, and (v), m. p. 174°. These are also produced by the action of zinc dust and acetone or of acetic anhydride on the dihydroxy-compounds; (v) rapidly changes on keeping to a third isomeride (vi), m. p. 72°. Hydrolysis of (iv) yields *-diphenylmuconic acid*, m. p. 142°, whilst (vi) gives 2 : 3-diphenylcrotonolactone-3-acetic acid (?), m. p. 181° (Beschke, *loc. cit.*). Reduction of (iv) with sodium amalgam after hydrolysis gives *-diphenyl-Δ$^\beta$-dihydromuconic acid*, m. p. 195 (*ethyl* ester, m. p. 56°), whilst (vi) under similar treatment gives a mixture of this acid with trans-*-diphenyl-Δ$^\beta$-dihydromuconic acid*, m. p. 297 (*ethyl* ester, m. p. 86°). Oxidation of each of these acids with ozone gives the same benzoylacetic acid.

M. CLARK.

Catalytic oxidation by air of alcohols to aldehydes or ketones in presence of zinc oxide. R. OTTENSOOSER (Bull. Soc. chim., 1927, [iv], **41**, 324—325).—The following yields of aldehydes or ketones are obtained by oxidation by air of the alcohol named in the presence of zinc oxide catalyst prepared from ammonium zincate (cf. Adkins and Lazier, A., 1925, i, 878). The optimum temperature is indicated: Propyl alcohol, 85·6% (315—325°); *iso*propyl, 84·5% (315—325°); *sec.*-butyl, 93·0% (335—340°);

butyl, 85·7% (335—340°); *iso*butyl, 74·0% (340—350°), *iso*amyl, 60·5% (345—355°); *sec.*-octyl, 79·1% (330—340°); *n*-decyl, 70% (390—400°), benzyl, 67·2% (330°), phenylethyl alcohol, 50% (430—440°). In the first three cases, yields are calculated on the air used, less than the theoretical amount being employed. In the last two cases, the reaction was effected under reduced pressure. R. BRIGHTMAN.

Catalytic condensation of acetone at high temperatures and pressures. II. W. N. IPATIEV and A. D. PETROV (Ber., 1927, **60**, [*B*], 753—755; cf. A., 1926, 1130).—Mesitylene is the main product formed when acetone is heated with aluminium oxide at 350° under high pressure; in addition, mesityl oxide, *iso*phorone, xylitone, and a terpene hydrocarbon are obtained. Hexamethylbenzene is not produced by the condensation of acetone with methyl alcohol in presence of aluminium oxide under pressure. H. WREN.

Catalytic condensation of acetone at high temperatures and pressures. I. W. N. IPATIEV and A. D. PETROV (J. Russ. Phys. Chem. Soc., 1926, **58**, 1028—1033).—See A., 1926, 1130, and preceding abstract.

Condensation of acetaldehyde with methyl *n*-propyl ketone. J. COLONGE (Bull. Soc. chim., 1927, [iv], **41**, 325—328).—Methyl propyl ketone and acetaldehyde in presence of methyl-alcoholic potassium hydroxide at 10° afford (yield 50—55%) *γ-ethylpentan-δ-ol-β-one*, b. p. 80—82°/3 mm., d^{15} 0·977, n_D^{15} 1·4418, which gives iodoform with sodium hypoiodite, but does not form a hydrogen sulphite compound. Dehydration in presence of iodine or oxalic acid at 145° affords *γ-ethyl-Δγ-penten-β-one*, b. p. 85—86°/80 mm., $d^{17·5}$ 0·865, 1·4479 (*oxime*, b. p. 110—113°/5 mm.; *semicarbazone*, m. p. 200°), which does not give a hydrogen sulphite compound, but on hydrogenation in presence of nickel is converted into γ-ethylpentan-β-one. Reduction with sodium in moist ether affords γ-ethyl pentan-β-ol (yield 30%), and oxidation with sodium hypochlorite, α-ethylcrotonic acid, m. p. 42°. R. BRIGHTMAN.

Study of the molecular constitution of certain organic compounds by the absorption of light. H. E. ACLY and H. S. FRENCH (J. Amer. Chem. Soc., 1927, **49**, 847—856).—The absorption of acetylacetone, acetylacetone dioxime, acetylacetone monoxime anhydride, copper acetylacetone, dimethyl diketone monoxime, dimethylglyoxime anhydride, and copper dimethylglyoxime, dissolved in 95% alcohol, was investigated in the ultra-violet; the visible absorption of the copper compounds was also studied. The conclusion is reached that acetylacetone in 95% alcohol is an equilibrium mixture of keto- and enolic forms, about 55·7% of the latter being present. Dimethyl diketone monoxime also appears to be an equilibrium mixture.

F. G. WILLSON.

Ring-chain tautomerism. XVI. Effect of two adjacent *gem*-dimethyl groups on the ease of formation of the *cyclo*pentane ring. I. VOGEL (J.C.S., 1927, 594—600).—αδ-Diacetyl-ββγγ-tetramethylbutane, $\begin{matrix}CMe_2 & CH_2 & c\\ | & & \\ CMe_2{\cdot}CH_2Ac & & \end{matrix}$ (I), reacts exclusively in the form of the ring isomeride, $\begin{matrix}CMe_2 & —CH_2\\ | & \\ CMe_2{\cdot}CHAc & \end{matrix}>CMe{\cdot}OH$ (II), as would be expected from the modified strain theory of Thorpe and Ingold. In addition to purely chemical evidence, confirmation of the structure (II) is obtained from measurements of the parachor. This compound, obtained by reduction of mesityl oxide by moist aluminium amalgam (cf. Law, J.C.S., 1912, **101**, 1016), exists in two modifications, a solid (α) and a liquid (β) form, to which *cis* and *trans* configurations, respectively, are ascribed. The α-form, m. p. 45°, gives a monosemicarbazone, m. p. 185°, and a *monobenzoyl* derivative, m. p. 115°. The β-form, b. p. 122—124°/20 mm., gives a *monosemicarbazone*, m. p. 165°, and a *monobenzoyl* derivative, m. p. 42°. Oxidation of either form with chromic acid gives tetramethylsuccinic acid. Sodium hypochlorite and potassium permanganate are almost without effect. Oxidation with sodium hypobromite gives a quantitative yield of bromoform corresponding with one acetyl group and a small quantity of *acid*, m. p. 122—123° (sparingly soluble *silver* and *barium* salts).

M. CLARK.

Selenoketones. R. E. LYONS and W. E. BRADT (Ber., 1927, **60**, [*B*], 824—826).—Selenoketones are obtained as heavy red oils by the action of hydrogen selenide on ketones mixed with concentrated hydrochloric acid. They cannot be distilled without decomposition. Chlorine decomposes them with production of selenium tetrachloride. *Diselenoacetone*, $(CH_3{\cdot}CSe{\cdot}CH_3)_2$, *di(methyl ethyl selenoketone)* and *diselenoacetophenone* are described. H. WREN.

Constitutional studies in the monocarboxylic acids derived from sugars. IV. Isomeric lactones obtained from arabinose. J. PRYDE and R. W. HUMPHREYS (J.C.S., 1927, 559—565).—Direct chemical proof of the amylene-oxide structure of trimethyl-β-methylarabinoside is adduced in that this substance, like the α-stereoisomeride, is converted by simultaneous hydrolysis and oxidation with hydrobromic acid and bromine into *d*-2 : 3 : 4-trimethylarabonolactone (cf. A., 1925, i, 366). The isomeric *l*-2 : 3 : 5-trimethylarabonolactone is obtained by synthesis of the mixed methyl-γ-arabinosides and subsequent methylation, followed by simultaneous hydrolysis and oxidation. It is obtained alternatively by bromine oxidation of arabinose, followed by methylation. The results of Baker and Haworth (A., 1925, i, 365) and of Haworth and Nicholson (A., 1926, 1025) are confirmed. Simultaneous formation of amylene and butylene oxide derivatives occurs when arabinose is condensed with methyl alcohol in presence of hydrogen chloride at 100°, since both *d*-2 : 3 : 4- and *l*-2 : 3 : 5-trimethylarabonolactones can be obtained from the initial condensation product. The auto-condensation of γ-arabinose derivatives to form a dipentoside is described. M. CLARK.

Action of sugar in the organism. II. Decomposition of dextrose by very dilute alkali. F. FISCHLER (Z. physiol. Chem., 1927, **165**, 53—67).—The previous observation (A., 1926, 1170) that, on distilling a solution of dextrose in dilute sodium carbonate, methylglyoxal appears in the distillate, is confirmed. If the experiment be conducted in the

absence of air and so that the sugar solution is dropped slowly into boiling sodium carbonate, it is further possible to isolate from the residual solution the osazone of glyceraldehyde (or of dihydroxyacetone); the osazone so obtained was always more or less contaminated with a red pigment. Distillation with dilute sulphuric acid, after treatment of the dextrose with carbonate, yields a further amount of methylglyoxal, which must have been derived from the dihydroxyacetone; moreover, dihydroxyacetone, on distillation with sodium carbonate, gives half the amount of methylglyoxal which is yielded by an equimolecular quantity of dextrose under the same conditions. It is therefore thought that the primary degradation of dextrose, under the influence of very dilute alkali, is into two molecules of glyceraldehyde (or dihydroxyacetone), from which the methylglyoxal is formed secondarily. C. R. HARINGTON.

Acetone compounds of the sugars and their derivatives. VIII. Monoacetone-*l*-arabinose [*l*-arabinose *iso*propylidene ether]. H. OHLE and G. BEREND (Ber., 1927, 60, [*B*], 810—811).—*l*-Arabinose is converted by acetone in presence of anhydrous copper sulphate into *l-arabinose isopropylidene ether*, m. p. 110° after softening at 103° (also *semihydrate*, m. p. 80°, $[\alpha]_D^{20}$ +128·8° in water). Since it reduces Fehling's solution, it appears to represent a new type of "acetone sugar." H. WREN.

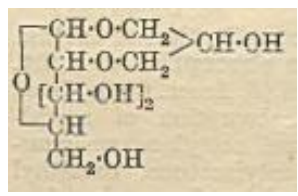
Detection of sugar in presence of proteins and the supposed condensation of carbohydrates with albumin. C. NEUBERG and E. SIMON (Ber., 1927, 60, [*B*], 817—824).—The observation of Pringsheim and Winter (A., 1926, 1274) that reducing hexoses combine instantaneously with proteins, albumoses, and peptones is not in harmony with the slight optical effect of proteins on sugars and the ready decomposability of amino-acid–sugar complexes (cf. Neuberg and Kobel, A., 1926, 151). If, however, a mixture of a protein with only half the quantity of sugar with which, according to Pringsheim, it can combine is heated with Fehling's solution, reduction is observed. Pringsheim's observations appear to be vitiated by the retention in colloidal solution of a part of the cuprous oxide by the protective action of the albumin or alkali albuminate. That proteins do not combine with sugars in the proportions indicated by Pringsheim and Winter is established by the observations (1) that sugars can be almost completely removed from such mixtures by dialysis, (2) that the sugar remains in solution when the protein is precipitated from neutral solution by colloidal ferric hydroxide, (3) that proteins can be precipitated by alcohol from the protein–carbohydrate mixtures, and (4) by titrimetric determination of the sugar by a method which does not involve the separation of the cuprous oxide formed. H. WREN.

Constitution of the disaccharides. XII. Lactose. W. N. HAWORTH and C. W. LONG (J.C.S., 1927, 544—548).—Methylation of the barium salt of lactobionic acid, obtained by oxidation of lactose, yields *methyl octamethyl-lactobionate*, b. p. 157—164°/0·05 mm., $[\alpha]_D$ +34°, n_D^{13} 1·4632. Hydrolytic cleavage of this product gives 2 : 3 : 4 : 6-tetramethylgalactose and 2 : 3 : 5 : 6-tetramethyl-γ-gluconolactone. The biose linking in lactobionic acid must therefore occupy the 4-position in the hexonic acid chain, and the constitution already ascribed to lactose by Charlton, Haworth, and Peat (A., 1926, 273) is confirmed. M. CLARK.

Synthetic melibiose. A. PICTET and H. VOGEL (Helv. Chim. Acta, 1927, **10**, 280).—The following additional data are given concerning the synthetic melibiose previously obtained (A., 1926, 1229): $[\alpha]_D$ +127·1° in water (after 24 hrs.); *hydrazone*, m. p. 142°; *osazone*, m. p. 177°; *octa-acetate*, m. p. 175°, $[\alpha]_D$ +97·3° in alcohol-chloroform solution. J. W. BAKER.

Melezitose and turanose. G. C. LEITCH (J.C.S., 1927, 588—594; cf. Zemplen and Braun, A., 1926, 1229).—Treatment of melezitose with methyl sulphate and sodium hydroxide gives hendecamethylmelezitose, b. p. 236°/0·01 mm., n_D 1·4680, $[\alpha]_D$ +114° in methyl alcohol, +108·6° in ethyl alcohol. Hydrolysis with hydrochloric acid gives amylene-oxidic tetramethylglucose and trimethyl-γ-fructose, n_D 1·4660, $[\alpha]_D$ +55·5° in alcohol (Zemplen gives +24°) in the proportion 2 : 1. From the behaviour of the trimethylfructose on distillation, a definite structure, agreeing with that already suggested by Zemplen and Braun, is ascribed to it. An improved method of isolating the hexose derivatives after hydrolysis is given. M. CLARK.

Complete depolymerisation of starch. A. PICTET and R. SALZMANN (Helv. Chim. Acta, 1927, **10**, 276—279).—Trihexosan, obtained from starch, when heated with twice its weight of glycerol for 15 hrs. at 200—210°, yields an exceedingly hygroscopic *compound*, m. p. about 40°, $[\alpha]_D$ +69·21°, of α-glucosan and glycerol (*tetrabenzoate*, m. p. 65°; *tetra-acetate*, m. p. 36—37°) which does not reduce Fehling's solution or form an osazone. The same compound is obtained when an equimolecular mixture of glucosan and glycerol is heated at 165° in a vacuum for 10 hrs. It yields dextrose on hydrolysis with dilute mineral acids and acraldehyde when heated with potassium hydrogen sulphate, and, therefore, is probably represented by the annexed formula. Thus α-glucosan is the ultimate depolymerisation product of trihexosan (and therefore of starch), but careful search failed to detect the presence of any β-glucosan in the product, as would be expected, since trihexosan is probably β-glucosylmaltosan (Pictet and Salzmann, A., 1926, 52). The formation of the glucosan is, however, in good agreement with the author's relation between the rotatory power and mol. wt. of starch depolymerides (Pictet, A., 1926, 387). J. W. BAKER.



Catalytic and specific dynamic actions of certain amino-acids. J. M. ORT and J. L. BOLLMAN (J. Amer. Chem. Soc., 1927, 49, 805—810).—The action of 0·03% hydrogen peroxide on dextrose in presence and absence of certain amino-acids was studied by the method of oxidation potentials. Cystine, glycine, alanine, phenylalanine,

leucine, histidine, and valine were found to catalyse this action; glutamic acid, aspartic acid, and tyrosine were without effect. This division of amino-acids closely parallels their division *in vivo* according to their specific dynamic actions. F. G. WILLSON.

Structure of amino-acids, polypeptides, and related compounds. E. ABDERHALDEN and R. HAAS (Z. physiol. Chem., 1927, **164**, 1—9; cf. A., 1926, 959).—A significant rise in the absorption of ultra-violet light by amino-acids takes place on formation of salts, but no appreciable increase occurs on salt formation by polypeptides. In polypeptides, therefore, the amino-carboxyl form is the principal type, and this would account for the greater ease of chlorination of these compounds compared with amino-acids. Great differences are exhibited in the absorption curves of creatine and creatinine, and this is attributed to the closure of the ring and the consequent loss of its "Zwitterion" properties. From absorption curves, it is shown that solutions of amino-acids react with freshly-precipitated ferric hydroxide, since there is a distinct increase in the absorption. Large quantities of ferric hydroxide, however, cause a decrease, due to the adsorption of glycine, and possibly the iron compound also, by the ferric hydroxide. A. WORMALL.

Copper salts of optically active amino-acids and similar polypeptides in polarised light. E. ABDERHALDEN and E. SCHNITZLER (Z. physiol. Chem., 1927, **164**, 37—49).—The specific rotatory powers of the copper salts of amino-acids, and those of polypeptides, increase with decreasing concentration. The significance, with regard to the structure of these substances in solution, is briefly discussed. A. WORMALL.

Copper salts of amino-acids and polypeptides. E. ABDERHALDEN and E. SCHNITZLER (Z. physiol. Chem., 1926, **163**, 94—119).—Copper salts of glycine, sarcosine, *d*-alanine, *dl*-serine, α- and β-aminobutyric acids, α-amino*iso*butyric acid, *dl*-valine, *l*-leucine, *d*-, *l*-, and *dl*-tyrosines, aspartic acid, asparagine, *d*-glutamic acid, glycylglycine, leucylglycine, and leucyl-leucine are prepared by boiling a concentrated aqueous solution of the amino-acid with a neutral aqueous suspension of freshly-precipitated copper oxide for some time and crystallising from the dark blue filtrate or precipitating with alcohol. For the cystine salt, the components are shaken together in the cold and excess of copper oxide is removed from the sparingly soluble copper salt by means of hydrochloric acid. The copper salt of histidine cannot be dried without decomposition. The electrical conductivities of the copper salts of the monobasic acids at varying concentrations are of the order of 10^{-5}, and differ little for different acids, that of copper leucine being the smallest for simple amino-acids, and that of copper leucyl-leucine one tenth as great. The copper salts of dibasic amino-acids show special behaviour. The conductivity of monocopper glutamate, $(C_5H_8O_4N)_2Cu$, is ten times that of the other amino-acid copper salts examined. The normal copper salts of aspartic and glutamic acids have about the same conductivity as salts of monobasic acids. Copper *l*-tyrosine shows a higher conductivity than the

C. HOLLINS.

β-Amino-β-aryl-aliphatic acids. II. β-Amino-β-aryl*iso*succinic ester. W. M. RODIONOV and A. M. FEDOROVA (Ber., 1927, 60, [*B*], 804—807; cf. this vol., 137).—Ethyl malonate is converted by benzaldehyde and boiling alcoholic ammonia into a mixture of benzylidenemalondiamide, m. p. 190°, ethyl benzylidenemalonate, and ethyl α-aminobenzylmalonate isolated as the *hydrochloride*, m. p. 158—160°, which is converted by boiling hydrochloric acid into β-amino-β-phenylpropionic acid hydrochloride, m. p. 223°. Ethyl piperonylidenemalonate and *ethyl α-aminomethylenedioxybenzylmalonate hydrochloride*, m. p. 155°, converted by hydrochloric acid into β-amino-β-piperonylpropionic acid hydrochloride, m. p. 233°, are derived similarly from piperonal. *Ethyl α-methylaminomethylenedioxybenzylmalonate hydrochloride*, m.p. 130°, is described. *Ethyl α-amino-*m*-nitrobenzylmalonate hydrochloride* has m. p. 150°. H. WREN.

Influence of groups and associated rings on the stability of certain heterocyclic ring systems. I. Substituted glutarimides. S. S. G. SIRCAR (J.C.S., 1927, 600—605).—The rate of hydrolysis of various ββ-disubstituted glutarimides shows that, in accordance with Thorpe and Ingold's modified strain theory, there is an increase in stability in the ascending series, H, H; Me, H; Et, H; Me, Me; Me, Et; Et, Et; *cyclo*pentane; *cyclo*hexane.

The following compounds are new: ββ-*Dimethyl-*, β-*methyl*-β-*ethyl-*, and ββ-*diethyl-glutarimide*; cyclo*pentanediacetimide* [ββ-(α′δ′-*tetramethylene*)*glutarimide*] and cyclo*hexanediacetimide* [ββ-(α′ε′-*pentamethylene*)-*glutarimide*]. They melt, respectively, at 147°, 127°, 146—147°, 153—154°, and 169°.

B. W. ANDERSON.

Mustard oils. II. [Reactions with semicarbazide and piperazine.] L. ROSENTHALER (Arch. Pharm., 1927, **265**, 111—114; cf. A., 1924, i, 949).—The mustard oils react with semicarbazide and piperazine, giving stable compounds of the types $NHR{\cdot}CS{\cdot}N(NH_2){\cdot}CO{\cdot}NH_2$ (I), and (II), $NHR{\cdot}(S)CN<\begin{matrix}CH_2{\cdot}CH_2\\CH_2{\cdot}CH\end{matrix}>NC(S){\cdot}NHR$. The *compounds*, m. p. 195—196° and 203—204°, were obtained from semicarbazide and allyl- or phenyl-thiocarbimides in aqueous alcoholic solution. The sparingly soluble *piperazine* derivatives, m. p. 219°, 156°, and 255—260° (decomp.), were prepared from ethyl-, allyl-, and phenyl-thiocarbimides, respectively. S. COFFEY.

Reactions of magnesium alkyl halides. E. SPATH (Ber., 1927, 60, [*B*], 702—704).—The fission of the methylenedioxy-group into hydroxyl and methoxyl under the action of magnesium methyl iodide (Kafuku, A., 1925, i, 1413) has been observed previously by the author (A., 1914, i, 506, 650). The assumption that the product of high b. p. obtained by the action of magnesium methyl iodide on benzyl chloride is α-phenyl-β-*p*-benzylphenylethane, and not αβγ-triphenylpropane, appears arbitrary (cf. Spath, A., 1914, i, 1; Fuson, A., 1926, 1237; this vol., 46).

H. WREN.

Formation of peroxides in the oxidation of organo-magnesium compounds. H. WUYTS (Bull. Soc. chim. Belg., 1927, 36, 222—238; cf. A.,

1909, i, 448).—Peroxides can be detected in the products of the action of pure, dry oxygen on Grignard reagents in dry ether, especially if the ether solution is diluted with dry toluene. The peroxide is less persistent in the case of magnesium phenyl bromide than in that of the corresponding ethyl and *cyclo*hexyl compounds, and numerous by-products of oxidation are formed, including diphenyl, *p*-diphenylbenzene, ethyl alcohol, and α-phenylethyl alcohol, the last two involving reaction of the ether present.

C. HOLLINS.

Reactions of lead tetraethyl. O. H. BROWNE and E. E. REID (J. Amer. Chem. Soc., 1927, **49**, 830—838).—Lead triethyl chloride can be obtained in 86% yield by the gradual addition of lead tetraethyl to concentrated hydrochloric acid below 34°. Lead triethyl hydroxide is obtained in 74% yield by treatment of the chloride, in benzene solution, with aqueous sodium hydroxide (cf. Buckton, Annalen, 1859, **112**, 226), but the product is not free from chlorine. The hydroxide absorbs atmospheric carbon dioxide. The decomposition of lead tetraethyl by acids is catalysed by silica gel, and the following lead triethyl salts were obtained by boiling lead tetraethyl with the appropriate acid in presence of silica gel, the fourth ethyl group being always eliminated as ethane: acetate, m. p. 160·4° (decomp.) (cf. Klippel, J. pr. Chem., 1881, [i], **81**, 287); *propionate*, m. p. 141—142°; iso*butyrate*, m. p. 119·4—121·8°; iso*valerate*, m. p. 119·4—119·8°; *hexoate*, m. p. 94·7—95·8°; *heptoate*, m. p. 90·0—90·8°; *octoate*, m. p. 85·0—87·5°; and n-*nonoate*, m. p. 88·0—90·0°; *chloroacetate*, m. p. 146—146·5°; *dichloroacetate*, m. p. 113·5—114·5°; *trichloroacetate*, m. p. 135·5—138·6°; *bromoacetate*, m. p. 121°, and *dibromoacetate*, m. p. 98·6—101·8°. The following salts were prepared by double decomposition from lead triethyl acetate and the appropriate sodium or potassium salt in aqueous solution: *cyanide*, m. p. 194°; *benzoate*, m. p. 127°; *ferrocyanide*, buff-coloured, decomp. above 200°; *ferricyanide*, brick-red, similar, and *valerate*, m. p. 115·6—117·0°. All the above m. p. are dependent on the rate of heating. Attempts to prepare the chromate or dichromate always yielded products which appeared to be mixtures of these two salts. A solution of lead tetraethyl in carbon disulphide deposits a black, flocculent *precipitate*, m. p. not below 300°. Acetyl chloride, phosphorus pentachloride, aluminium chloride, and silicon tetrachloride react with lead tetraethyl, with formation of lead triethyl chloride. Treatment of the latter with sodium phenoxide, *p*-nitrophenoxide, β-naphthoxide, and ethoxide, in absolute alcohol, gave oils. The above lead triethyl salts of the halogenated acetic acids, the reaction of which with lead tetraethyl is vigorous, are strongly sternutatory.

F. G. WILLSON.

Spontaneous oxidation of a saturated cyclic hydrocarbon. G. CHAVANNE (Bull. Soc. chim. Belg., 1907, **36**, 206—221; cf. A., 1926, 1130).—Dry 1 : 3-dimethyl*cyclo*pentane absorbs oxygen at the ordinary temperature in diffused light even under reduced pressure, giving a compound of the peroxide type, which on decomposition with potassium iodide yields a mixture of methyl *iso*amyl ketone, b. p. 143—145° (semicarbazone, m. p. 145°), and δ-methylhexan-β-one, b. p. 146—147° (*semicarbazone*, m. p. 129°). The mixture is not separated, but its components are synthesised, the first by catalytic reduction of *iso*butylideneacetone, the second by the action of magnesium ethyl bromide on ethylideneacetone.

C. HOLLINS.

Transformation of phenols into hydrocarbons by hydrogen under pressure in presence of catalysts. A. KLING and D. FLORENTIN (Compt. rend., 1927, **184**, 885—887; cf. A., 1926, 381).—When heated at 480° with alumina and hydrogen under a pressure of 70—80 kg./cm.², phenol gives mainly benzene; a mixture of the cresols, mainly toluene; *cyclo*hexanol, a mixture of hydrocarbons, only slightly unsaturated, and containing aliphatic hydrocarbons of low b. p. (cf. Ipatiev, A., 1911, i, 25).

E. W. WIGNALL.

Halogenation. I. Iodination. P. S. VARMA and D. A. KULKARNI. **II. Direct iodination in the presence of sodium nitrite and fuming sulphuric acid.** P. S. VARMA and K. G. R. PANICKAR (J. Indian Chem. Soc., 1926, **3**, 291—296, 342—344).—I. The yields of aromatic iodo-compounds obtained by the method of Datta and Chatterjee (A., 1917, i, 327) are considerably increased by the addition of glacial acetic acid and 50% nitrosulphonic acid (obtained by passing sulphur dioxide into nitric acid, *d* 1·5). The authors believe that the iodine reacts with nascent nitrobenzene.

II. A 70% yield of iodobenzene may be obtained by the gradual addition of fuming sulphuric acid (*10%* SO_3) to a mixture of sodium nitrite, iodine, and benzene, and a little glacial acetic acid. Iodination of toluene and xylene may be similarly effected.

J. W. BAKER.

Preparation of *p*-bromobenzyl chloride. R. QUELET (Bull. Soc. chim., 1927, [iv], **41**, 329—331).—*p*-Bromobenzyl chloride is obtained in 50% yield by the action of hydrogen chloride on a mixture of trioxymethylene and bromobenzene in presence of stannic chloride. In presence of zinc chloride (cf. Blanc, A., 1923, i, 549), only traces of *p*-bromobenzyl chloride are formed. The crude product (yield 80%) contains about 30% of the *ortho*-isomeride. Boeseken's method (A., 1904, i, 384) affords only 35% of *p*-bromobenzyl chloride, higher chlorinated compounds forming the bulk of the reaction product. The method of Stephen, Short, and Gladding (J.C.S., 1920, **117**, 510) also failed to give the yield claimed.

R. BRIGHTMAN.

***p*-Bromobenzyl chloride and the Grignard reaction.** R. QUELET (Compt. rend., 1927, **184**, 888—890).—*p*-Bromobenzyl chloride reacts with magnesium and ether in the side-chain only, to give a *monomagnesium* derivative, decomposed by sulphuric acid to *p*-bromotoluene, together with *pp'*-dibromo-αβ-diphenylethane in increasing amounts if the vigorous reaction is not controlled by cooling. The Grignard derivative reacts with allyl bromide to give *p-bromo-*Δ$^{\gamma}$*-butenylbenzene*, b. p. 106°/12 mm., d_4^{11} 1·259, n_D^{11} 1·554, which combines with bromine to give *αβ-dibromo-δ-p-bromophenylbutane*, b. p. 190—191°/12 mm., d_4^{9} 1·859, n_D^{9} 1·610, and reacts with perbenzoic acid to form *δ-p-bromophenylbutylene oxide*, b. p. 142°/10 mm.

E. W. WIGNALL.

Walden inversion. XI. Evidence for the bivalency of carbon from some reactions of α-chloroethylbenzene. αα′-Diphenyldiethyl ether. A. M. WARD (J.C.S., 1927, 445—458).—The displacement of the halogen in *r*-α-chloroethylbenzene in aqueous-alcoholic solution at 28·7° and at 50°, alone and in presence of sodium hydroxide, yields a mixture of phenylethylcarbinol (identified as the p-*nitrobenzoate*, m. p. 47—48°) and ethyl α-phenylethyl ether. The velocity coefficients are identical in each case, and agree with a unimolecular reaction, the sodium hydroxide playing no part in the halogen replacement. Velocity coefficients obtained from the change in rotation of *d*-α-chloroethylbenzene under comparable conditions confirm this conclusion. *r*-α-Chloroethylbenzene on boiling with water yields mainly αα′-diphenyldiethyl ether, together with styrene and phenylmethylcarbinol. The same products are obtained by boiling αα′-diphenyldiethyl ether or phenylmethylcarbinol with 0·5*N*-hydrochloric acid. It is concluded that these reactions proceed through a phase, CPhMe<, in which only two groups are momentarily attached to carbon. The mechanism of the Walden inversion is discussed from this point of view. Displacement of halogen from β-chloroethylbenzene is negligibly slow in aqueous-alcoholic solution, but proceeds according to the bimolecular law in presence of sodium hydroxide.

M. CLARK.

Thermal decomposition of sulphonic esters. Z. FOLDI (Ber., 1927, 60, [*B*], 656—664; cf. A., 1920, i, 828).—Allyl benzenesulphonate, b. p. 120—122°/1 mm., decomposes somewhat violently at 180°, slowly at the atmospheric temperature, yielding benzenesulphonic acid and an amorphous, saturated hydrocarbon of high mol. wt. which could not be identified and is probably formed by polymerisation of vinylmethylene under the action of benzenesulphonic acid. Attempts to counteract the effect of the latter by addition of magnesium or zinc oxides were unsuccessful. In boiling xylene, the radical enters the benzenoid nucleus, yielding unsaturated hydrocarbons of high b. p. Methyl benzenesulphonate and *p*-toluenesulphonate are thermostable. From ethyl benzenesulphonate, the hydrogen atom required for the production of benzenesulphonic acid is withdrawn from the β-position of the ethyl group, since ethylene is almost quantitatively produced. This is also the case with the β-chloroethyl and ββ′-dichloro-*iso*propyl esters, which yield, respectively, vinyl chloride and γ-chloroallyl chloride. Fission of the halogenated esters is more complex than that of the ethyl ester. *Ethylene dibenzenesulphonate*, m. p. 49—50°, b. p. 190°/1 mm., prepared from ethylene glycol and benzenesulphonyl chloride in presence of aqueous sodium hydroxide (20%), gives benzenesulphonic acid, acetylene, and paracetaldehyde. Benzyl benzenesulphonate, m. p. 59—60°, decomposes at a relatively very low temperature into benzenesulphonic acid and an amorphous, polymeric hydrocarbon; if decomposition takes place at the ordinary temperature, the intermediate phenylated *cyclo*paraffins can be isolated as liquids which are immediately polymerised by concentrated sulphuric acid. *Benzenesulphonylbenzoin*, m. p. 99—100°, decomposes at 160° without production of recognisable material other than benzenesulphonic acid.

H. WREN.

Action of ethyl nitrate on diphenyl and its derivatives. H. RAUDNITZ [with H. BOHM] (Ber., 1927, 60, [*B*], 738—743).—Ethyl nitrate acts as a vigorous nitrating agent towards aromatic compounds suspended or dissolved in concentrated sulphuric acid at −5°. Anthraquinone is transformed into dinitroanthraquinone. Diphenyl affords *trinitrodiphenyl*, m. p. 175·5°. Carbazole is converted into 1 : 3 : 6 : 8-tetranitrocarbazole, m. p. 289° after darkening at 200° (cf. Borsche and Scholten, A., 1917, i, 390), and an isomeric *tetranitrocarbazole*, decomp. above 200°. *oo′*-Dimethoxydiphenyl gives 3 : 3′ : 5′ : 5-tetranitro-2 : 2′-dimethoxydiphenyl, m. p. 187° (Borsche and Scholten, *loc. cit.*, record m. p. 177—178°), dealkylated to 3 : 3′ : 5 : 5′-tetranitro-2 : 2′-dihydroxydiphenyl, m. p. 248—249°, which is also obtained by direct nitration of *oo′*-dihydroxydiphenyl. Diphenylene oxide and ethyl nitrate yield *trinitrodiphenylene oxide*, m. p. 228°.

Trinitrodiphenyl is converted by thionyl chloride at 180° into *trichlorodiphenyl*, m. p. 55°; similarly, tetranitrocarbazole yields 1 : 3 : 6 : 8-*tetrachlorocarbazole*, m. p. 180° after softening at 168°.

H. WREN.

Addition of hydrogen to acetylene derivatives. XVII. Hydrogenation of tolane. J. S. SALKIND and N. W. ILYIN (J. Russ. Phys. Chem. Soc., 1926, 58, 994—997; cf. A., 1922, 1134; ii, 835).—Tolane, m. p. 62—63·5°, was hydrogenated in alcohol solution by Paal's method, the unimolecular constant of the reaction being determined. This remains steady until 80% conversion is reached, and then falls gradually. There is no increase of velocity, as in the case of phenylacetylene (*loc. cit.*), when the triple linking is reduced to a double linking, the presence of a second phenyl group apparently slowing down the reduction of the latter. This is proved by the fact that stilbene is reduced more slowly than either tolane or styrene.

M. ZVEGINTZOV.

Hydrogenation of naphthalene and anthracene at high temperatures and under high pressures in presence of non-hydrogenating catalysts. A. KLING and D. FLORENTIN (Compt. rend., 1927, 184, 822—824; cf. A., 1926, 381).—The threshold temperatures for hydrogenation both in presence and absence of a non-hydrogenating catalyst are dependent to some extent on the pressure. Thus at an initial hydrogen pressure of 90—100 kg./cm.², hydrogenation of naphthalene is appreciable at 475—480°, or at 450° in presence of aluminium chloride; the corresponding temperatures for anthracene are 440° and 425—430° (with ferric chloride). The presence of the catalyst increases the proportion of liquid products, and particularly the proportion of benzene hydrocarbons. Thus naphthalene under the conditions cited affords 17·6% of liquid products, 36% of which distil below 160°, whilst in presence of a catalyst 64% of liquid products is obtained, 54% of which distils below 160°. Similarly, anthracene affords 67% of liquid products in presence of a catalyst 19% of which distils below 180°, the corresponding figures in absence of the catalyst being 60% and

3·75%. The fractions of high b. p. consist of hydronaphthalenes and hydroanthracenes. In the case of anthracene, a crystalline product, m. p. 68—69°, distilling at 200—250°, was isolated. R. BRIGHTMAN.

Nitration. III. Nitration of naphthalene. P. S. VARMA and C. K. MENON (J. Indian Chem. Soc.; 1926, 3, 328—334).—The maximum yield (86%) of α-nitronaphthalene obtained by using a mixture of nitric and sulphuric acids is also produced when plaster of Paris, quicklime, or phosphoric oxide is used as a dehydrating agent in place of sulphuric acid, although they are not effective in the nitration of benzene. The b.-p. curve for mixtures of naphthalene and α-nitronaphthalene has been plotted, and the percentage of the nitronaphthalene in the product was determined by this means. J. W. BAKER.

Rate of conversion of naphthalene-2 : 7-disulphonic acid into the isomeric 2 : 6-acid at 160° in presence of sulphuric acid. J. L. HEID (J. Amer. Chem. Soc., 1927, 49, 844—846).—When heated with 1 mol. of sulphuric acid (95%) at 160° in a glass vessel, naphthalene-2 : 7-disulphonic acid is converted, to the extent of 42%, into the 2 : 6-disulphonic acid, in 19 hrs. Further heating results in a diminution of the proportion of the 2 : 6-isomeride present, due apparently to the formation of sulphonated tars (cf. Ebert and Merz, A., 1876, ii, 408; Fierz-David and Hasler, A., 1923, i, 1190). F. G. WILLSON.

Constitution of thiocyanoaniline and some derivatives. J. W. DIENSKE (Rec. trav. chim., 1927, 46, 154—157; cf. Soderback, A., 1920, i, 219; Kaufmann and Oehring, A., 1926, 392).—Confirmation is obtained of Soderback's conclusion that the thiocyano-group in thiocyanoaniline is in the *p*-position. The calculated quantity of bromine in acetic acid converts *p*-thiocyanoaniline (*acetyl* derivative, m. p. 189°) into 2 : 6-*dibromo*-4-*thiocyanoaniline*, m. p. 118° (*acetyl* derivative, m. p. 174°; *diacetyl* derivative, m. p. 102°), whilst further bromination yields 2 : 4 : 6-tribromoaniline. The thiocyano-group is not removed by superheated steam in 70% sulphuric acid, but it is oxidised to the sulpho-group by permanganate, and the resulting sulphonic acid yields 2 : 6-dibromoaniline when distilled in steam. Chlorine water in acetic acid converts 2 : 6-dibromothiocyanoaniline into a mixture which probably contains 4-chloro-2 : 6-dibromoaniline. J. M. GULLAND.

Action of phosphorus, arsenic, and antimony trichlorides on dimethylaniline. H. RAUDNITZ [with H. HELLER] (Ber., 1927, 60, [*B*], 743—748).—Phosphorus trichloride is converted by the successive action of dimethylaniline and aqueous sodium hydroxide into a mixture of the compound, $NMe_2{\cdot}C_6H_4{\cdot}P{:}O$, m. p. 162°, the *substance*, $(NMe_2{\cdot}C_6H_4)_2P{\cdot}OH,2H_2O$, m. p. 165°, and tridimethylaminophenylphosphine, m. p. about 275°. Similar products are derived from arsenic trichloride. Dimethylaminophenylarsenious oxide, m. p. 95° (Michaelis records m. p. 75°), is identified by reduction with sodium hyposulphite to bisdimethylaminoarsenobenzene, m. p. 202°. Tridimethylaminophenylarsine, m. p. 240°, and *bisdimethylaminophenylarsenious acid*, m. p. 169°, are described. The action of the chlorides of phosphorus, arsenic, and antimony on dimethylaniline is accompanied by the production of crystal-violet, the formation of which is most pronounced in the case of the antimony chloride; in addition, hexamethyltriaminotriphenylmethane and tetramethyldiaminodiphenylmethane (obtained from the former by the action of antimony trioxide formed by hydrolysis) are isolated. H. WREN.

Alternating effect in carbon chains. XII. Nitration of some derivatives of methyl benzylaminoformate. J. W. BAKER (J.C.S., 1927, 565—571).—Nitration of (*a*) methyl benzylaminoformate, (*b*) *methyl benzylmethylaminoformate*, b. p. 118°/5 mm., prepared from benzylmethylamine and methyl chloroformate, (*c*) *methyl dibenzylaminoformate*, b. p. 199°/13 mm., gave the following amounts of *m*-nitro-derivative, calculated by oxidation to the corresponding benzoic acid with subsequent analysis: (*a*) 11%, (*b*) 12%, (*c*) 14%. These values are of the same order as those obtained for the nitration of the acyl substituted benzylamines (Goss, Ingold, and Wilson, A., 1926, 1133). *Methyl* p-*nitrobenzylaminoformate* and *methyl* pp′-*dinitrodibenzylaminoformate* have m. p. 109·5° and 140°, respectively. H. BURTON.

Azo dyes [from new derivatives of aminodiphenyl]. I. G. FARBENIND. A.-G.—See B., 1927, 213.

Condensations with alkylene bromides. H. F. LEWIS and C. FORDYCE (Proc. Iowa Acad. Sci., 1925, 32, 323).—The corresponding butylenes and substituted diphenylethylenediamines are among the products of condensation of various butylene bromides with aniline. CHEMICAL ABSTRACTS.

Reducing action of sodium methoxide. H. S. FRY and J. L. CAMERON (J. Amer. Chem. Soc., 1927, 49, 864—873).—Klinger's equation (cf. A., 1882, 1061) for the reduction of nitrobenzene to azoxybenzene by sodium methoxide has been verified by comparison of the relative amounts of azoxybenzene and sodium formate produced. In absence of water, the yield of azoxybenzene is 86—87%. Addition of water progressively reduces this, and in presence of 1 mol. of water the yield is 55%. In presence of pyridine, the yield of azoxybenzene may be increased to 90%, but azobenzene is formed simultaneously, the production of sodium formate then being equivalent to that of the azoxy- and azo-benzene combined. The reducing action of sodium methoxide is ascribed to its acidic dissociation, $MeOH+NaOH \rightleftharpoons H{\cdot}CO_2Na+2H_2$, the effects of water and pyridine on the reduction being due to their respective inhibition and promotion of this dissociation (cf. Fry and Schulze, A., 1926, 710). F. G. WILLSON.

Derivatives of 4 : 4′- and 2 : 2′-dihydroxyazobenzene. D. BIGIAVI and P. GUARDUCCI (Gazzetta, 1927, 57, 145—159).—4 : 4′-Dihydroxyazobenzene is benzoylated in presence of sodium carbonate to 4-*hydroxy*-4′-*benzoyloxyazobenzene*, m. p. 234—235°, which is acetylated to the 4-*acetoxy*-derivative, m. p. 130—134°, and on bromination gives 3 : 5-*dibromo*-4-*hydroxy*-4′-*benzoyloxyazobenzene*, m. p. 168—169°, hydrolysed to 3 : 5-*dibromo*-4 : 4′-*dihydroxyazobenzene*, m. p. 192°. During bromination, some diazo-scission

occurs: with β-naphthol, the solution gives *p*-benzoyloxyazo-β-naphthol, m. p. 164°. By the action of nitrous acid, the benzoyl derivative gives 3-*nitro*-4-*hydroxy*-4′-*benzoyloxyazobenzene*, m. p. 175—176°, hydrolysed to the 3-*nitro*-4 : 4′-*dihydroxy*-compound, m. p. 170—172°.

4 : 4′-Dihydroxyazoxybenzene is benzoylated to a mixture, m. p. 180°, of the two *benzoyl* derivatives, $BzO{\cdot}C_6H_4{\cdot}NO{:}N{\cdot}C_6H_4{\cdot}OH$, m. p. 200—201°, and $BzO{\cdot}C_6H_4{\cdot}N{:}NO{\cdot}C_6H_4{\cdot}OH$, m. p. 212°. The latter forms an *acetyl* derivative, m. p. 129—132° to a cloudy liquid, clearing at 220°; it is unaffected by nitrous acid. The former gives an *acetyl* derivative, m. p. 108—111°, liquid clearing at 210°; with nitrous acid it gives a *nitro*-derivative, hydrolysed to nitroazoxyphenol (Bigiavi and Carrara, A., 1923, i, 715), which forms a *dibenzoyl* derivative, m. p. 164°, liquid clearing at 240°, and a *monobenzoyl* derivative, m. p. 178—179°; the *benzoyl-acetyl* derivative has m. p. 154—157°, clearing at 164°.

2 : 2′-Dihydroxyazobenzene gives a 2 : 2′-*diacetoxy*-compound, m. p. 150°, which is not affected by peracetic acid; 2 : 2′-dibenzoyloxyazobenzene is, however, oxidised to the corresponding *azoxybenzene*, m. p. 108—109°. E. W. Wignall.

***cyclo*Hexylhydrazine.** M. Busch and K. Linsenmeier (J. pr. Chem., 1927, [ii], **115**, 216—234).—When an alcoholic solution of *cyclo*hexyl bromide and hydrazine hydrate is heated at 140° in a sealed tube, *cyclo*hexene and 25% of the theoretical yield of *cyclo*hexylhydrazine (cf. Kijner and Beloff, A., 1911, i, 678; Harkins and Lochte, A., 1924, i, 435) are obtained. The latter is now the most readily accessible hydrazine derivative of aliphatic nature. It forms a *dihydrate*, m. p. 36—38°, which readily absorbs oxygen and carbon dioxide. The *carbonate* has m. p. 70°; the *hydrochloride*, m. p. 110—111°, *hydrogen sulphate*, and *hydrobromide*, m. p. 120°, are stable. The abnormal benzylidene compound, m. p. 183°, of Harkins and Lochte is actually *benzaldehyde-cyclohexylhydrazone hydrochloride*; the oily free *hydrazone* rapidly absorbs oxygen, forming a crystalline *dioxide*, m. p. 72—73° (decomp.). The *cyclohexylhydrazones* of *p*-anisaldehyde, m. p. 55—56° (*hydrochloride*, m. p. 159—160°; *dioxide*, m. p. 79—80°); salicylaldehyde, m. p. 58—59° (*hydrochloride*, m. p. 166—167°); *p*-dimethylaminobenzaldehyde, oily (*hydrochloride*, m. p. 190°; *dioxide*, m. p. 72—73°); *p*-nitrobenzaldehyde, m. p. 110—111° (*hydrochloride*, m. p. 130—132°); *m*-nitrobenzaldehyde, m. p. 104—105° (*hydrochloride*, m. p. 137—138°); cinnamaldehyde (*hydrochloride*, m. p. 158°), and acetaldehyde, oily (*hydrochloride*, m. p. 83—86°), and *acetone-cyclohexylhydrazone dioxide hydrochloride*, m. p. 224—226°, are described. *cyclo*Hexylhydrazine gives an *acetyl* derivative, m. p. 148—149°, and a *dibenzoyl* derivative, p. 195—196°; with potassium cyanate solution, it forms *cyclohexylhydrazinedicarboxylamide*, $NH_2{\cdot}CO{\cdot}N(C_6H_{11}){\cdot}NH{\cdot}CO{\cdot}NH_2$, m. p. 135—136°, which is partly converted by boiling water into *cyclohexylsemicarbazide*, $C_6H_{11}{\cdot}NH{\cdot}NH{\cdot}CO{\cdot}NH_2$, p. 175—176° (*hydrochloride*, m. p. 173—174°, but cf. A., 1924, i, 226); and with phenylcarbimide, *1-cyclohexyl-4-phenylsemicarbazide*, $C_6H_{11}{\cdot}N(NH_2){\cdot}CO{\cdot}NHPh$, m. p. 165—166° (1-*benzylidene* derivative, m. p. 135°), together with its 1-*phenylurethane*, m. p. 202°. The so-called thioureide, m. p. 144°, of Kijner and Beloff must be 2-cyclo*hexyl*-4-*phenylthiosemicarbazide*, since with benzaldehyde it affords the corresponding *semicarbazone*, m. p. 222°. H. E. F. Notton.

Dicyclohexyl derivatives. H. Hartmann (Rec. trav. chim., 1927, **46**, 150—153).—The interaction of hydrazine sulphate, potassium cyanide, and *cyclo*hexanone at the ordinary temperature yields 1 : 1′-*dicyanohydrazocyclohexane*, m. p. 145°, in quantitative yield. Bromine water converts this into the colourless 1 : 1′-*dicyanoazocyclohexane*, m. p. 100°, which loses nitrogen in boiling toluene, passing into 1 : 1′-*dicyanodicyclohexyl*, m. p. 220°. The hydrolysis of this nitrile is difficult, and proceeds only as far as the formation of 1-*cyanodicyclohexyl*-1′-*carboxylic acid*, m. p. 185°; even fusion with potassium hydroxide failed to produce the dicarboxylic acid, and the cyano-group was not reduced by sodium and alcohol. The hydrolysis of 1 : 1′-dicyanohydrazo*cyclo*hexane by alcoholic potassium hydroxide yields 1-amino-1-cyano-*cyclo*hexane. J. M. Gulland.

Constitution of normal diazohydrates. A. Hantzsch (Ber., 1927, 60, [*B*], 667—668).—In reply to Angeli (A., 1926, 947), reasons are advanced for considering the normal and *iso*diazotates to be stereoisomeric and not structurally isomeric. H. Wren.

***cis–trans*-Isomerism and steric hindrance. IV. 2-*iso*Propyl*cyclo*hexanols.** G. Vavon and A. Callier (Bull. Soc. chim., 1927, [iv], **41**, 357—367).—In continuance of earlier work (A., 1926, 837, 1033, 1042), the *iso*propyl radical is shown to exert a marked steric effect on the reactions of the *cis*- and *trans*-forms of 2-*iso*propyl*cyclo*hexanol, the reactions of the *cis*-form being distinctly slower than those of the *trans*-isomeride. To the same influence is attributed the small proportion (14%) of *ortho*- as compared with *para*-derivative (86%) in the nitration of *iso*propylbenzene with nitric acid (*d* 1·5), acetic acid, and acetic anhydride; with acetyl nitrate (10% excess), the nitration product (yield 83%) consists of 22% *ortho*- and 78% *para*-derivative, whereas the nitration of toluene by this method affords the *ortho*- and *para*-derivatives in the ratio 10 : 1. *o*-Nitro*iso*propylbenzene, b. p. 106—107°/9 mm., n_D^{13} 1·5286, d^{12} 1·101, on reduction with hydrogen and platinum-black in acetic acid, gives an 84% yield of the amine, b. p. 220—221°/745 mm., 92—94°/8 mm., from which *o-iso*propylphenol, b. p. 90—91°/8 mm., 212—213°/745 mm., is obtained by the diazo-reaction. Hydrogenation of the phenol in presence of platinum-black affords a mixture in which cis-2-iso*propyl*cyclo*hexanol*, m. p. 50—50·5°, preponderates. The cis-*hydrogen phthalate* has m. p. 129—130°, the *hydrogen succinate*, m. p. 61·5—62°, and the *phenylurethane*, m. p. 95—95·5°. Oxidation of the hexanol with chromic and sulphuric acids affords 80% of 2-*iso*propyl*cyclo*hexanone, b. p. 72—73°/9 mm., n_D^{13} 1·4585, d^{12} 0·923 [*oxime*, b. p. 118—119°/10 mm., m. p. 37—39°, giving, by hydrogenation, the β-*hydroxylamine*, m. p. 63—64°, semicarbazone, m. p. 178—179° (cf. Bouveault, A., 1906, i, 513; Kotz and Michels, A., 1907, i, 58)],

reduction of which with sodium and boiling alcohol yields mainly trans-2-iso*propyl*cyclo*hexanol*, b. p. 86°/10 mm., m. p. 63·5—64°. The latter is also obtained by heating the *cis*-isomeride at 220° for 6 hrs. The trans-*hydrogen phthalate* exists in two forms, m. p. 99—100° and 114—115°; the former undergoes transformation into the latter above its m. p. (cf. A., 1926, 1033). The trans-*hydrogen succinate* has m. p. 84—84·5°, the *phenylurethane*, m. p. 98—98·5°.

The *trans*-2-*iso*propyl*cyclo*hexanol is esterified much more rapidly than the *cis*-isomeride, especially at a low temperature and in presence of a catalyst. Similarly, the *trans*-hydrogen phthalate is hydrolysed much more rapidly than the *cis*-phthalate, the ratio of the velocity constants in 75% alcohol at 69° being 18 : 1, and 34 : 1 in water at 69°. Similarly, with the hydrogen succinates, the ratio of the velocity constants for the *trans*- and *cis*-forms is 28 : 1 in water at 68°, 40 : 1 at 39°, and 67 : 1 at 0°. *p*-Nitro-*iso*propylbenzene has b. p. 124—125°/11 mm., n_D^{13} 1·5400, d^{13} 1·096. R. Brightman.

Condensation products of phenols and aldehydes. V. Substance, $C_{14}H_{15}O_2N$, isolated from the condensation products of phenol and formaldehyde, using ammonia as catalyst. VI. Decolorisation of the insoluble and infusible condensation product of phenol and formaldehyde. T. Shono (J. Soc. Chem. Ind. Japan, 1927, 30, 136—143, 143—145; cf. B., 1926, 595).—V. The principal constituent, $C_{14}H_{15}O_2N$ (*A*), of the condensation product of phenol and formaldehyde, when heated with nitrous acid, yields a brownish-yellow diazo-compound which at about 100° evolves nitrogen, decomposing to a tar and a brownish-yellow powder suspended in the liquid. The percentage of nitrogen evolved is exactly equal to that in *A*. *A* gives colour reactions in a neutral or an alkaline alcoholic solution with many metallic salts, mostly chlorides, but not in an acid solution. It shows, in alcoholic solution, a wide absorption band, centre about 281 μμ.

VI. The condensation product of phenol and formaldehyde formed by using ammonia and potassium hydroxide simultaneously as condensing agents under the ordinary pressure (B., 1926, 680) is markedly decolorised in proportion to the amount of ultra-violet light to which it is exposed. K. Kashima.

Nitration of *m*-iodophenol. H. H. Hodgson and F. H. Moore (J.C.S., 1927, 630—635).—*m*-Iodophenol is nitrated by sodium nitrate and concentrated sulphuric acid, giving 3-*iodo*-6-*nitrophenol*, m. p. 96° (*sodium* and *silver* salts; *methyl ether*, m. p. 92°; *acetate*, m. p. 95°; *benzoate*, m. p. 122°), and 3-iodo-4-nitrophenol (*sodium* salt; *methyl ether*, m. p. 69—70°; *acetate*, m. p. 73·7°; *benzoate*, m. p. 119°). Nitration of *m*-iodophenol in fuming sulphuric acid solution gives poor yields of 3-*iodo*-2-*nitrophenol*, m. p. 73·5° (*sodium*, *ammonium*, and *silver* salts; *methyl ether*, m. p. 82—83°; *acetate*, m. p. 102·5°). 3-*Iodo*-4 : 6-*dinitrophenol*, m. p. 98° (*silver* salt), is obtained from *m*-iodophenol, 3-iodo-4- and -6-nitrophenols by the method previously described (A., 1926, 281), as is 3-*iodo*-2 : 6-*dinitrophenol*, m. p. 151—152° (*silver* salt), from 3-iodo-2- and -6-nitrophenols. The 2 : 6-dinitro-compound is also obtained by nitration of *m*-iodophenol in oleum solution. 3-*Iodo*-2 : 4 : 6-*trinitrophenol*, m. p. 197° (*silver* salt), sublimes slowly from boiling concentrated sulphuric acid. 3-Iodobenzoquinone-4-oxime is oxidised by potassium ferricyanide to 3-iodo-4-nitrophenol, thus proving that nitrosation of *m*-iodophenol takes place in the 4-position (A., 1925, i, 1408). H. Burton.

Separation of *p*-cresol from its isomerides. H. D. Gibbs (J. Amer. Chem. Soc., 1927, 49, 839—844).—Technical *p*-cresol (1 kg.) is mixed with 2 : 6-dichlorobenzoquinonechloroimide (100 g.) with cooling, the mixture brought to p_H 10 by addition of aqueous 10% sodium hydroxide at 5—10°, and kept at this temperature for 1 hr. The resulting blue solution, the colour of which is due to the indophenols formed from the *o*- and *m*-cresols, is acidified with sulphuric acid and steam distilled. After four similar treatments, the *p*-cresol still gives a trace of blue colour with the chloroimide, probably owing to slight decomposition of the indophenols during steam distillation. The *p*-cresol thus purified, which is very hygroscopic, has b. p. 202·3°/760 mm. F. G. Willson.

Influence of nitro-groups on the reactivity of substituents in the benzene nucleus. IX. 2 : 3- and 2 : 5-Dinitro-4-methoxytoluenes. H. E. Dadswell and J. Kenner (J.C.S., 1927, 580—588; cf. A., 1926, 58).—Nitration of 2-nitro-4-methoxytoluene in sulphuric–acetic acid solution gives 2 : 3-dinitro-4-methoxytoluene, m. p. 132—133° (Kaufler and Wenzel, A., 1901, i, 590, give m. p. 126—128°), and 2 : 5-dinitro-4-methoxytoluene. Reduction of the former dinitro-compound gives the *o*-diamine, m. p. 75—76° (Kaufler and Wenzel, *loc. cit.*, give m. p. 72—73°), which condenses with benzil, yielding 8-*methoxy*-2 : 3-*diphenyl*-5-*methylquinoxaline*, m. p. 196—197°. Nitration of 2-nitro-*p*-cresol in glacial acetic acid furnishes 2 : 3-*dinitro*-p-*cresol* (66%), m. p. 157—158°, and 2 : 5-*dinitro*-p-*cresol* (33%), m. p. 112—113°, each of which on methylation gives the corresponding methoxy-compound.

Boiling methyl-alcoholic sodium methoxide solution converts 2 : 5-dinitromethoxytoluene into 5-*nitro*-2 : 4-*dimethoxytoluene* (72%), m. p. 117—118°, characterised by its preparation from 2 : 4-*dichloro*-5-*nitrotoluene*, m. p. 49—50°, by the action of sodium methoxide, and 6-nitro-3 : 4-dimethoxytoluene (28%), m. p. 119—120° (de Vries, A., 1910, i, 29, gives m. p. 94°). Sodium methoxide converts 3-*chloro*-6-*nitro*-4-*methoxytoluene*, m. p. 94—95°, 4-chloro-5-nitro-*o*-toluidine, and 4-chloro-3-nitro-*o*-toluidine into 6-nitro-3 : 4-dimethoxytoluene, 5-*nitro*-4-*methoxy*-*o*-*toluidine*, m. p. 158—159° (*acetyl* derivative, m. p. 154—155°, also obtained by nitration of 4-methoxyacet-*o*-toluidide), and 3-*nitro*-4-*methoxy*-*o*-*toluidine*, m. p. 61—62° (*acetyl* derivative, m. p. 176—176·5°), respectively. The last compound is converted by nitrous acid into 7-*nitro*-6-*methoxyindazole*, m. p. 173—174°.

Methyl-alcoholic ammonia at 145—150° converts 2 : 3-dinitro-4-methoxytoluene into 3-nitro-4-methoxy-*o*-toluidine (30% isolated as the above indazole)

and 2-*nitro*-4-*methoxy*-m-*toluidine*, m. p. 49—50° (*acetyl* derivative, m. p. 170—171°). The 2 : 5-dinitro-compound is decomposed by similar treatment.

2 : 3-Dinitro-4-methoxytoluene is oxidised by potassium permanganate to 2 : 3-*dinitro*-4-*methoxybenzoic acid*, m. p. 248—250° (decomp.) (*methyl* ester, m. p. 156°), which is converted by sodium methoxide into 3-*nitro*-2 : 4-*dimethoxybenzoic acid*, m. p. 210—212° (*methyl* ester, m. p. 118—119°). Oxidation of the mixture of nitrodimethoxytoluenes obtained from the treatment of 2 : 3-dinitro-4-methoxytoluene with methyl-alcoholic sodium methoxide at 110—115°, gave a mixture of nitrodimethoxybenzoic acids in which 2-nitroveratric acid predominated, thus showing that the 3- rather than the 2-nitro-group is displaced in the 2 : 3-dinitro-compound, whereas the 2-position in the 2 : 5-isomeride is more easily attacked. 4-*Methoxy*-m-*oxalotoluidide* has m. p. 218°.

H. BURTON.

Aromatic thionyl and chlorothionyl derivatives. II. 1 : 2- and 2 : 3-Thionyldihydroxyanthracenes. A. GREEN (J.C.S., 1927, 554—558).—1 : 2-*Thionyldihydroxyanthracene*, $C_6H_4<\begin{matrix}CH\\CH\end{matrix}>C_6H_2<\begin{matrix}O\\O\end{matrix}>SO$, m. p. 138—139° (decomp.), and 2 : 3-*thionyldihydroxyanthracene*, m. p. 188° (decomp.), are obtained from the corresponding dihydroxyanthracenes and thionyl chloride in carbon disulphide–pyridine solution. These compounds are stable to moisture. Boiling acetic acid containing a trace of pyridine converts the latter into the original dihydroxy-compound, whilst acetic anhydride furnishes 2 : 3-diacetoxyanthracene, m. p. 175° (Lagodzinski, A., 1906, i, 82, gives m. p. 155—160°). 2 : 3-Dihydroxyanthracene, m. p. 282° (Lagodzinski, *loc. cit.*, gives m. p. 192°), is best obtained by reducing hystazarin with stannous chloride to 2 : 3-dihydroxyanthranol, m. p. 288—289° (Schrobsdorff, A., 1903, i, 840, gives m. p. 282°), and subsequent reduction of the anthranol by an aluminium–mercury couple (cf. Perkin, J.C.S., 1923, **123**, 2035). H. BURTON.

Tri*cyclo*hexylcarbinol. N. D. ZELINSKI and M. W. GAVERDOVSKAJA (Ber., 1927, **60**, [*B*], 713—715).—Di*cyclo*hexyl ketone, b. p. 140—141°/12 mm. (*oxime*, m. p. 157—160°), and *tricyclohexylcarbinol*, b. p. 208°/10 mm., m. p. 81·5°, are isolated in small amount from the neutral products of the successive action of magnesium and carbon dioxide on *cyclo*hexyl chloride, the main product being hexahydrobenzoic acid. The carbinol is reduced by hydriodic acid to a *hydrocarbon*, $C_{19}H_{34}$, b. p. 340—345°, in the production of which a *cyclo*hexyl group may have become isomerised to a methylpentamethylene ring. *Tricyclohexylmethyl bromide*, m. p. 61°, is obtained from the carbinol and hydrobromic acid or from tri*cyclo*hexylmethane and bromine. H. WREN.

Elimination of the amino-group of tertiary amino-alcohols. IV. Displacement of the amino- by the hydroxy-group. A. MCKENZIE and R. ROGER (J.C.S., 1927, 571—576).—Deamination of α-amino-α-phenyl-β-ethylbutan-β-ol with nitrous acid gives α-phenyl-β-ethylbutan-αβ-diol, whilst α-amino-αγ-diphenyl-β-benzyl*iso*propyl alcohol yields a mixture of αγ-diphenyl-β-benzylpropane-αβ-diol and benzyl αβ-diphenylethyl ketone. α-Amino-αβ-diphenylbutan-β-ol (*hydrochloride*, m. p. 224—226°) yields diphenylmethyl ethyl ketone, showing that a phenyl group has migrated.

The results show that the phenyl group migrates more easily than ethyl or benzyl groups, and it is suggested that the low saturation capacity of the ethyl and benzyl groups causes a retardation or prevention of the "semipinacolinic deamination" change (see A., 1926, 610). H. BURTON.

Reduction products of plant sterols. R. J. ANDERSON and R. L. SHRINER (J. Biol. Chem., 1927, **71**, 401—406).—Reduction of α- and β-sitosterol with hydrogen and platinum-black yielded identical sitostanols, m. p. 140°, $[\alpha]_D$ +24°; *acetyl* derivative, m. p. 137—138°, $[\alpha]_D$ +14°; similar treatment of γ-sitosterol gave a sitostanol having m. p. 144—145°, $[\alpha]_D$ +18°, *acetyl* derivative, m. p. 143—144°, $[\alpha]_D$ +9—10°. C. R. HARINGTON.

Properties of cholesterol from different sources. R. J. ANDERSON (J. Biol. Chem., 1927, **71**, 407—418).—Preparations of cholesterol from various sources show small differences in m. p. and specific rotation which cannot be eliminated by the ordinary methods of purification; further, the acetyl derivatives of such preparations can be separated by crystallisation into fractions possessing markedly different physical properties. This indicates that ordinary cholesterol may be a mixture of isomeric substances corresponding with the mixture of phytosterols from which it is presumably synthesised in the animal body. C. R. HARINGTON.

Hydrogenation of triphenylcarbinol and phenylfluorenylcarbinol under pressure. V. N. IPATIEV and B. N. DOLGOV (J. Russ. Phys. Chem. Soc., 1926, **58**, 1023—1027).—See A., 1926, 949.

Thymolbenzein, 4-hydroxy-3-*iso*propyl-6-methylbenzophenone, and some of their derivatives. W. R. ORNDORFF and H. T. LACEY (J. Amer. Chem. Soc., 1927, **49**, 818—826).—Gradual addition of molten thymol to 0·515 mol. of benzotrichloride in presence of stannic chloride (1 mol.) yields 4-*hydroxy*-6-*methyl*-3-iso*propylbenzophenone* (I), m. p. 150—150·5° (*acetate*, m. p. 73°), and *thymolbenzein* (II), bright red, m. p. 184° [*hydrochloride*, decomp. 225—235° (open tube) or 235—250° (sealed tube); *sulphate*, m. p. 242—243°; *perchlorate*, decomp. 265—272°; *sodium* salt ($2H_2O$), dark blue with bronze reflex, softening at 235—245°, m. p. not below 310°; *methyl ether*, orange, m. p. 132—133°; *methyl ether hydrochloride*, m. p. 85—95° (sealed tube); *monoacetate*, orange, m. p. 143—144°]. The constitution of (I) was established by synthesis from benzoyl chloride, thymol, and aluminium chloride, and by fusion with alkali, which yielded *p*-thymotic acid. Bromination of (II) in glacial acetic and formic acids affords *dibromothymolbenzein*, red, m. p. 89—90°, as the *additive compound* with formic acid (1 mol.), m. p. 96—97°, whilst nitration in acetic acid yields *dinitrothymolbenzein*, yellow, m. p. not below 310° after darkening at 100—110° and carbonisation at 150—160°. Reduction of (II) with zinc dust and glacial acetic acid affords 4 : 4′-

dihydroxy-6 : 6′-*dimethyl*-3 : 3′-*di*isopropyltriphenylmethane, m. p. 158—159° (*dimethyl ether*, m. p. 105°; *diacetate*, m. p. 121°), which is also obtained by boiling (II) with phenylhydrazine. In 50% ethyl-alcoholic solution, thymolbenzein changes from red to yellow at p_H 1·5—2·5, and from yellow to red at p_H 7·6—9·0, whilst the dibromo-derivative changes from yellow to blue at p_H 5·6—7·2. Carbinol forms of thymolbenzein and the dibromo-derivative could not be obtained.

F. G. WILLSON.

Thymoltetrachlorophthalein and some of its derivatives. R. T. K. CORNWELL and A. J. ESSELSTYN (J. Amer. Chem. Soc., 1927, **49**, 826—830).—Condensation of thymol with tetrachlorophthalic anhydride in presence of stannic chloride yields *thymoltetrachlorophthalein* (I), colourless, m. p. 266° [*monosodium* salt, dark grey; *disodium* salt, black; *barium* salt, black; *lead* salt, tan coloured; *diacetate*, m. p. 184—185°; *dibenzoate*, m. p. 177—178°; *di*-(*phenylcarbamate*), m. p. 234—235°; *dimethyl ether*, yellow, m. p. 208—210°]. Bromination of (I) in glacial acetic acid affords *dibromothymoltetrachlorophthalein*, m. p. 223—225°. At p_H 9·2—10·0, (I) becomes blue, whilst the dibromo-derivative changes similarly at p_H 8·4—8·8. A lactoid structure is ascribed to (I) and to the dibromo-derivative, the above coloured derivatives being derived from the tautomeric quinonoid form.

F. G. WILLSON.

***cyclo*Butylacetic acid.** N. D. ZELINSKI and B. A. KASANSKI (Ber., 1927, **60**, [*B*], 711—713).—*cyclo*Butylmethyl alcohol is converted by phosphorus and iodine into *cyclo*butylmethyl iodide, and thence by magnesium and carbon dioxide into *cyclo*butylacetic acid, the properties of which indicate the presence of *cyclo*pentanecarboxylic acid. Partial isomerisation occurs during the conversion of the alcohol into the iodide, since the action of magnesium and air on the latter affords a mixture of alcohols giving a phenylurethane, m. p. 129°; the phenylurethanes of *cyclo*pentanol and *cyclo*butylmethyl alcohol have m. p. 136·5° and 68·5°, respectively.

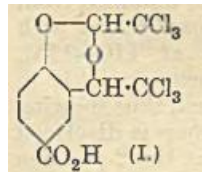
H. WREN.

Anilides and toluidides of chaulmoogric acid. P. HERRERA-BATTEKE (Philippine J. Sci., 1927, **32**, 35—40).—The following derivatives of chaulmoogric acid were prepared by heating chaulmoogramide with the theoretical quantity of the requisite amine at the boiling temperature: *anilide*, m. p. 89°; p-*bromoanilide*, m. p. 100°; o-*toluidide*, m. p. 95°; m-*toluidide*, m. p. 88°, and p-*toluidide*, m. p. 100°. S. I. LEVY.

Action of iodine in alkaline media on phenyl-*iso*crotonic acid: some new mixed anhydride derivatives of benzoylacrylic acid. E. CATTELAIN (Bull. Soc. chim., 1927, [iv], **41**, 352—356).—The following *mixed anhydride* derivatives of benzoylacrylic acid have been prepared from phenyl*iso*crotonic acid by Bougault's method (A., 1908, i, 791, 983): *hydrocinnamic*, m. p. 103°; p-*methoxybenzoic*, m. p. 132°; o-*toluic*, m. p. 141°; m-*toluic*, m. p. 107°; p-*toluic*, m. p. 127—128°; *piperonylic*, m. p. 135—136°; *hexahydrobenzoic*, m. p. 103—104°; o-*benzoylbenzoic*, m. p. 114—115°; p-*chlorobenzoic*, m. p. 122°, and m-*bromobenzoic*, m. p. 116—117°. On hydrolysis with dilute sodium hydroxide, they afford acetophenone from the benzoylacrylic acid first liberated.

R. BRIGHTMAN.

Condensation of *p*-hydroxybenzoic acid with chloral. F. D. CHATTAWAY and F. C. Y PRATS (J.C.S., 1927, 685—692).—*p*-Hydroxybenzoic acid condenses with chloral (2 mols.) in presence of a large excess of concentrated sulphuric acid, forming *anhydro*-5-*carboxy*-2-ββ*β*-*trichloro*-α-*hydroxyethoxy*-1-ββ*β*-*trichloro*-α-*hydroxyethylbenzene*, (I), m. p. 225·5—226·5° (*acid chloride*, m. p. 98—102°; *amide*, m. p. 195·5—197°; *ethyl* ester, m. p. 100·5—101·5°). *Anhydro*-5-*cyano*-2-ββ*β*-*trichloro*-α-*hydroxyethoxy*-1-ββ*β*-*trichloro*-α-*hydroxyethylbenzene*, m. p. 159·5—160·5°, obtained from the 5-amino-derivative (A., 1926, 1242), on hydrolysis with dilute sulphuric acid yields (I). Alcoholic potassium hydroxide converts (I) into a mixture of 5-*carboxy*-2-*ethoxy*-1-ββ*β*-*trichloro*-α-*hydroxyethylbenzene*, (II), m. p. 124—126°, 6-hydroxy*iso*phthalic acid (*ethyl* ester, m. p. 52·5°), and a small amount of o-carboxy-2-ethoxyphenylglycollic acid, identified by hydrolysis to 5-carboxy-2-hydroxybenzaldehyde [*phenylhydrazone*, m. p. 257—258° (decomp.)], and also by oxidation with alkaline potassium permanganate to 6-hydroxy*iso*phthalic acid. Hot concentrated sulphuric acid converts (II) into ωω-*dichloro*-5-*carboxy*-2-*hydroxyacetophenone*, m. p. 163—166°. This substance yields a *diacetyl* derivative, m. p. 194—196°; an *osazone*, $OH{\cdot}C_6H_3(CO_2H){\cdot}C(N_2HPh){\cdot}CH{:}N_2HPh$, m. p. 243·5°, and is reduced by hydriodic acid to o-*carboxy*-2-*hydroxyacetophenone*, m. p. 246—247°, (*phenylhydrazone*, m. p. 286°), which is also produced by the action of hydriodic acid on (II).



H. BURTON.

3-Nitro-4-aminobenzoyl-o-benzoic acid and derivatives. R. ADAMS, J. M. DAVIDSON, and I. GUBELMANN, Assrs. to NEWPORT CO.—See B., 1927, 212.

Action of magnesium organo-derivatives on *N*-tetraethylphthalamides. N. MAXIM (Compt. rend., 1927, **184**, 689—691).—The action of magnesium ethyl bromide on N-*tetraethyliso*phthalamide, m. p. 85°, and N-*tetraethylterephthalamide*, m. p. 127°, affords 15—20% of the ketone-amide, $Et{\cdot}CO{\cdot}C_6H_4{\cdot}CO{\cdot}NEt_2$, and 25—30% of the diketone, $C_6H_4(CO{\cdot}Et)_2$. N-*Tetraethyl*-o-*phthalamide*, m. p. 36°, b. p. 204°/10 mm., affords 10% of the ketone-amide and 15% of diethylphthalide. The structure $C_6H_4(CO{\cdot}NR_2)_2$ is assigned to these diamides (cf. Piutti, Annalen, 1885, **227**, 193), since this structure admits of ready interpretation of the formation of the ketone-amide. The formation of the diethylphthalide is attributed to intermediate formation of the tertiary alcohol, $NEt_2{\cdot}CO{\cdot}C_6H_4{\cdot}CEt_2{\cdot}OH$. m-*Propionylbenzdiethylamide*, b. p. 205°/10 mm. (*semicarbazone*, m. p. 145°); m-*dipropionylbenzene*, m. p. 34° (*di-semicarbazone*, m. p. 222°); p-*propionylbenzdiethylamide*, m. p. 82° (*semicarbazone*, m. p. 175°, *oxime*, 105°); p-*dipropionylbenzene*, m. p. 100° (*di-semicarbazone*, m. p. 226°), and o-*propionylbenzdiethylamide*, b. p. 186°/15 mm. (*semicarbazone*, m. p. 195°, *oxime*, m. p. 110°), are described. Magnesium phenyl

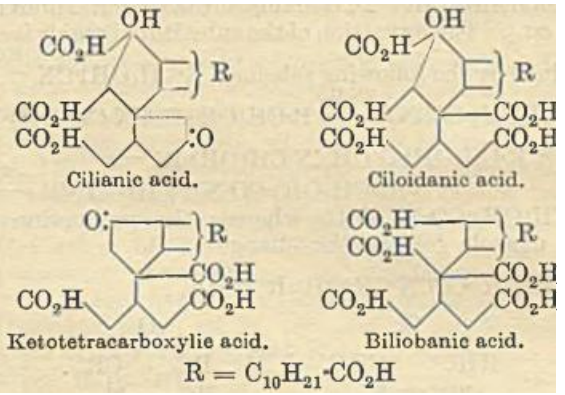
bromide does not react with the *N*-tetraethylphthalamides (cf. A., 1926, 837). R. BRIGHTMAN.

2 : 5-Diaminobenzene-1 : 4-dicarboxylic acid. G. SCHROETER.—See B., 1927, 212.

[New diarylamides of 2-naphthol-3 : 6-dicarboxylic acid] and manufacture of water-insoluble azo-dyes. CHEM. FABR. GRIESHEIM-ELEKTRON.—See B., 1927, 212.

Substitution derivatives of indigotin. II. Ethyl 2-nitro-3 : 4 : 5-trimethoxybenzoylacetate and related compounds. C. J. OVERMYER (J. Amer. Chem. Soc., 1927, 49, 499—509; cf. A., 1926, 415).—Modifications are described of Hamburg's method (A., 1899, i, 364) for the preparation of methyl 2-nitro-3 : 4 : 5-trimethoxybenzoate, m. p. 67°, and 2-nitro-3 : 4 : 5-trimethoxybenzoic acid, m. p. 166°. The acid chloride, m. p. 94°, was used for preparing the corresponding *amide*, m. p. 186°, and *anilide*, m. p. 158°, and was converted, by the action of ethyl sodioacetoacetate, into *ethyl* 2-*nitro*-3 : 4 : 5-*trimethoxybenzoylacetoacetate*, a reddish-yellow oil (*sodium* and *potassium* salts). The sodium salt of the latter, on treatment with aqueous ammoniacal ammonium chloride, yields *ethyl* 2-*nitro*-3 : 4 : 5-*trimethoxybenzoylacetate*, m. p. 85° (*potassium* salt), whilst hydrolysis with dilute sulphuric acid affords 2-*nitro*-3 : 4 : 5-*trimethoxyacetophenone*, m. p. 118°. Treatment of the potassium salt of ethyl 2-nitro-3 : 4 : 5-trimethoxybenzoylacetate with alcoholic methyl iodide yields *ethyl* α-2-*nitro*-3 : 4 : 5-*trimethoxybenzoylpropionate*, a red oil, which, on hydrolysis with dilute sulphuric acid, affords 2-*nitro*-3 : 4 : 5-*trimethoxypropiophenone*, a brown oil. *Ethyl* 2-*nitro*-3 : 4 : 5-*trimethoxybenzoylmalonate*, m. p. 96°, and *ethyl* 2-*nitro*-3 : 4 : 5-*trimethoxybenzoylcyanoacetate*, m. p. 110°, are obtained analogously from the above acid chloride. The cyano-derivative yields, on hydrolysis, 2-*nitro*-3 : 4 : 5-*trimethoxybenzoylacetonitrile*, m. p. 180°. Reduction of ethyl 2-nitro-3 : 4 : 5-trimethoxybenzoylacetate with zinc dust and glacial acetic acid affords 4-*hydroxy*-6 : 7 : 8-*trimethoxy*-2-*ethoxyquinoline oxide*, m. p. 61°, whilst ethyl 2-nitro-3 : 4 : 5-trimethoxybenzoylacetoacetate yields similarly *ethyl* 4-*hydroxy*-6 : 7 : 8-*trimethoxy*-2-*methylquinoline*-3-*carboxylate*, m. p. 183°. Hydrolysis of the latter yields the corresponding *acid*, m. p. 202°, at which temperature it loses carbon dioxide with formation of 4-*hydroxy*-6 : 7 : 8-*trimethoxy*-2-*methylquinoline*, m. p. 182°. Reduction of 2-nitro-3 : 4 : 5-trimethoxybenzoic acid with ammoniacal ferrous sulphate yields 2-*amino*-3 : 4 : 5-*trimethoxybenzoic acid*, m. p. 137°. Ethyl 2-nitro-3 : 4 : 5-trimethoxybenzoylacetate could not be hydrolysed to the corresponding acid, nor could the latter obtained from the corresponding malonate. Ethyl 2-nitro-3 : 4 : 5-trimethoxybenzoylacetonitrile could not be converted into the corresponding amide or acid. The synthesis of a hexamethoxyindigotin by the method previously described could not therefore be accomplished. F. G. WILLSON.

Constitution of the bile acids. X. Constitution of cilianic acid and certain other polycarboxylic acids of the cholic acid group. W. BORSCHE and R. FRANK (Ber., 1927, 60, [*B*], 723—732; cf. A., 1926, 1140).—Contrary to the observations of Wieland and Schlichting (A., 1922, i, 838), ciloidanic acid loses only 1 mol. of carbon monoxide when warmed with concentrated sulphuric acid at 60°. Evolution of carbon dioxide is appreciable only at about 100°, and is accompanied by further loss of 1 mol. of carbon monoxide. These results, considered in conjunction with the author's observation (*loc. cit.*) that cholic acid contains the hydroxyl group attached to the carbon atom 12 instead of 13 in ring III, render the annexed constitutions probable :



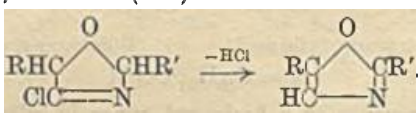
The presence of a hydroxyl group in cilianic acid is established by the evolution of 1 mol. of methane when its tetramethyl ester is treated with magnesium methyl iodide. Bilianic, *iso*bilianic, biloidanic acid, or its hydrate do not evolve carbon monoxide or dioxide to a considerable extent when treated for a protracted period with concentrated sulphuric acid at 100°. Under similar conditions, biliobanic acid slowly gives off oxides of carbon, probably owing to the oxidising action of sulphuric acid. *iso*-Cilianic acid evolves almost 1 mol. of carbon monoxide with varying and not very considerable quantities of carbon dioxide. H. WREN.

Action of aldehydes on azo-compounds. D. BIGIAVI (Gazzetta, 1927, 57, 160—162).—Bamberger's results (Ber., 1924, 57, 2085) are confirmed : the substance, m. p. 161—163°, obtained by the action of benzaldehyde on azobenzene (Barsilowski, A., 1892, 854) is benzanilide. It is suggested that the benzaldehyde condenses with a dissociated radical, PhN·; intermediate compounds in which oxygen is attached to nitrogen are considered improbable. E. W. WIGNALL.

Mechanism of reactions induced by hydrogen chloride between aromatic aldehydes and aldehydecyanohydrins in solution. B. H. INGHAM (J.C.S., 1927, 692—700).—The formation of oxazoles (cf. Fischer, A., 1896, i, 262), arylidenemandelamides, and 3-keto-2 : 5-diaryl-3 : 4-dihydro-1 : 4-diazines (cf. Minovici, A., 1899, i, 890; 1896, i, 703) by the condensation of aromatic aldehydes and aldehydecyanohydrins in presence of moist and dry hydrogen chloride has been studied. It is found that (*a*) iminochlorides are produced as intermediates, (*b*) exclusion of moisture favours oxazole formation, whereas presence of moisture favours the production of arylidenemandelamides, (*c*) no oxazole is formed when the hydroxy-group in the cyanohydrin is benzoylated or replaced by chlorine, (*d*) diazines are formed

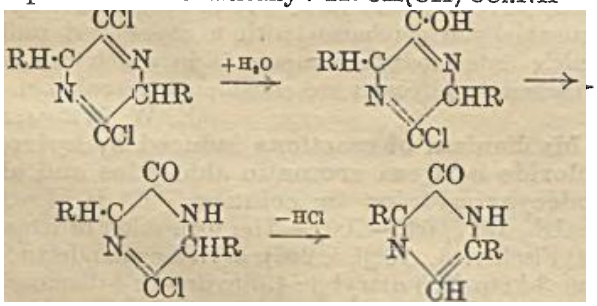
in best yield when there is not a large excess of aldehyde. Thus benzaldehyde and mandelonitrile in ethereal solution, saturated at 0° with hydrogen chloride, condense, giving benzylidenemandelamide, $C_6H_5\cdot CH(OH)\cdot CO\cdot N{:}CH\cdot C_6H_5$, unless moisture is rigidly excluded. In a perfectly dry medium, 2 : 5-diphenyloxazole is the predominant product. α-Chlorophenylacetonitrile and benzaldehyde do not react. Benzaldehyde and lactonitrile yield benzylidenelactamide, and anisaldehyde and anisaldehydecyanohydrin give 2 : 5-dianisyloxazole (cf. Minovici, *loc. cit.*). The formation of the substituted amide is explained by the following scheme: $R\cdot CH(OH)\cdot CN \xrightarrow{HCl} R\cdot CH(OH)\cdot CCl{:}NH \xrightarrow{R'\cdot CHO} R\cdot CH(OH)\cdot CCl{:}N\cdot CH(OH)\cdot R' \xrightarrow{H_2O} R\cdot CH(OH)\cdot C(OH){:}N\cdot CH(OH)\cdot R' \longrightarrow R\cdot CH(OH)\cdot CO\cdot NH\cdot CH(OH)\cdot R' \xrightarrow{-H_2O} R\cdot CH(OH)\cdot CO\cdot N{:}CHR'$, whereas the production of the oxazole follows the change

$R\cdot CH(OH)\cdot CCl{:}N\cdot CH(OH)\cdot R' \longrightarrow$



Benzoylmandelonitrile and benzaldehyde yield two isomeric *benzylidenebisbenzoylmandelamides*, $(BzO\cdot CHPh\cdot CO\cdot NH)_2CHPh$, having m. p. 250—251° and 223—224°.

m-Nitrobenzaldehydecyanohydrin condenses with *m*-nitrobenzaldehyde, giving two isomeric 2 : 5-*di*-m-*nitrophenyloxazoles*, m. p. 225—227° and 238°, together with 3-*keto*-2 : 5-*di*-m-*nitrophenyl*-3 : 4-*dihydro*-1 : 4-*diazine*, m. p. 277—278°; with benzaldehyde yielding 2-*phenyl*-5-m-*nitrophenyloxazole*, m. p. 156—157°, and the above diazine; hydrogen chloride converts the original cyanohydrin into the diazine and the di-*m*-nitrophenyloxazole. This production of the diazine is most probably explained by the change $NO_2\cdot C_6H_4\cdot CH(OH)\cdot CCl{:}NH,HCl \xrightarrow{O} C_{16}H_{10}O_5N_4 + HCl + H_2O$. The general formation of diazines is represented schematically: $2R\cdot CH(OH)\cdot CCl{:}NH \xrightarrow{-2H_2O}$



3-*Keto*-2 : 5-*di*-p-*nitrophenyl*-3 : 4-*dihydro*-1 : 4-*diazine*, m. p. 332—334°, and 2 : 5-*di*-p-*nitrophenyloxazole*, m. p. 228—232°, are obtained from *p*-nitrobenzaldehyde and *p*-nitrobenzaldehydecyanohydrin.

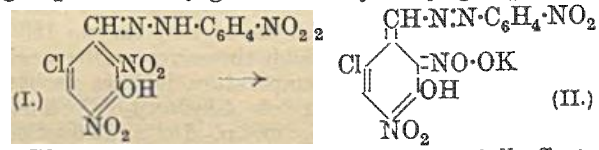
H. Burton.

Isomerisation of diphenylacetaldehyde into deoxybenzoin. S. Danilov and E. Venus-Danilova (J. Russ. Phys. Chem. Soc., 1926, **58**, 957—965).—See A., 1926, 726.

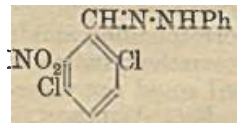
Alkyl lactolides of salicylaldehyde [α-2-oxidobenzyl ethers]. M. Bergmann and E. von Lippmann (Annalen, 1927, **452**, 135—140).—When salicylaldehyde dimethyl acetal (which need not be isolated in the pure condition) is heated at 130° under 0·5—1 mm. for 0·5 hr., methyl alcohol is eliminated with the formation, in small yield, of α-2-*oxidobenzyl methyl ether*, $C_6H_4<\begin{matrix}O\\ CH\cdot OMe\end{matrix}$, m. p. 217—218° (corr.). The corresponding *ethyl ether*, m. p. 156° (corr.), is obtained similarly from the diethyl acetal. Both are bimolecular in benzene solution, but unimolecular in phenol solution and in the form of vapour at 234°. Heating with dilute acids or alkali readily splits the oxide ring.

J. W. Baker.

Positional influence of substituents on chemical reactivity and colour. H. H. Hodgson (J. Soc. Dyers and Col., 1927, **43**, 72—76).—Mainly a discussion of results already published (A., 1925, i, 674, 1144; 1926, 281, 292, 1039). Chattaway and Clemo's generalisations on the relation between colour and constitution in the hydrazones of nitrobenzaldehydes (J.C.S., 1923, **123**, 3043) have been confirmed by the foregoing work (*loc. cit.*) on *p*-nitrophenylhydrazones of chloronitro-substituted *m*-hydroxybenzaldehydes. Chlorine produces a similar effect, which is more pronounced with 6-chloro- than with 2-chloro-substitution. Methylation of the hydroxyl group diminishes the colour except in the case of the 2 : 4 : 6-trichloro-3-methoxybenzaldehyde derivative. A *p*-amino-group has a marked influence, 3-nitro-4-aminobenzaldehyde affording a more intensely coloured *p*-nitrophenylhydrazone than the corresponding 4-halogen-3-nitrobenzaldehydes. The vivid royal-blue colour developed by 6-chloro-2 : 4-dinitro-3-hydroxybenzaldehyde-*p*-nitrophenylhydrazone in alcoholic solution with alkalis, in contrast with the behaviour of the corresponding hydrazone from 2-chloro-4 : 6-dinitro-3-hydroxybenzaldehyde, which gives no colour in the cold and only a claret colour on warming, is attributed to the position of the chlorine as a terminal member of a chain of five adjacent groups, and conjugate to the hydroxyl group:



The 2-nitro-group therefore exerts its full effect on the methine carbon atom, promoting mobility of the imino-hydrogen atom to give the configuration (II). The intermediate colour of the *p*-nitrophenylhydrazones of 4-chloro-2 : 6-dinitro- and 2 : 4-dichloro-6-nitro-3-hydroxybenzaldehyde is attributed to variations of valency distribution in the conjugate chains. Similarly, the exceptional behaviour of 2 : 5-dichloro-6-nitrobenzaldehydephenylhydrazone (Chattaway and Clemo, *loc. cit.*) is explained by the annexed structure, indicating repression of the effect of the nitro-group on the imino-hydrogen.



R. Brightman.

Action of trichloroacetic acid on phenols. J. van Alphen (Rec. trav. chim., 1927, **46**, 144—

149).—The replacement by trichloroacetic acid of the chloroform in the Reimer–Tiemann reaction yields the corresponding aldehydes and carbon dioxide in place of the expected α-keto-acids. Phenol yields small quantities of *o*- and *p*-hydroxybenzaldehydes; guaiacol gives a very little vanillin; *p*-cresol yields a small amount of 2-hydroxy-5-methylbenzaldehyde; and *p*-hydroxybenzoic acid gives a rather better yield of 4-hydroxy-3-aldehydobenzoic acid. The following substances yield small quantities of aldehydes (isolated as the *p*-nitrophenylhydrazones only): *p*-chlorophenol, pyrocatechol, resorcinol, quinol, phloroglucinol, thymol, *p*-aminophenol, salicylic acid, phenolphthalein, gallic acid, α- and β-naphthols, and alizarin. The presence of nitro-groups or the replacement of the hydroxyl by an alkyloxy-group inhibits the reaction; picric acid, *p*-nitrophenol, anisole, phenetole, veratrole, anisic acid, and menthol give negative results. The smallness of the yields is due to the production of triphenylmethane dyes, and in the case of guaiacol this reaction takes place almost exclusively. The dyes must be formed from the intermediate substances, $Ar{\cdot}CHCl_2$, not from an aldehyde, because vanillin itself when heated with guaiacol and sodium hydroxide does not yield a dye, whereas a dye is formed when vanillin, guaiacol, and zinc chloride are heated together.

The mechanism of these reactions probably involves the migration of the group $-CCl_2{\cdot}CO_2H$ from the oxygen atom of the phenol to a nuclear carbon atom. When, however, mono- and di-chloroacetic acids act on phenol or resorcinol, the resulting mono- and di-phenoxyacetic and resorcinol-*OO*-diacetic acids are recovered unchanged after heating with zinc chloride; no migration from oxygen to carbon takes place. J. M. Gulland.

Stereoisomerism and isomorphism of the phenyl styryl ketones. C. Dufraisse and A. Gillet (Ann. Chim., 1926, [x], **6**, 295—312).—A more detailed account of work already published (this vol., 58). J. W. Baker.

Hydrogenation of distyryl ketone and di-β-phenylethyl ketone. W. N. Ipatiev and N. A. Orlov (Compt. rend., 1927, **184**, 751—753).—Hydrogenation of distyryl ketone cannot be effected with copper oxide as catalyst or in *cyclo*hexane solution; in the latter case, an unstable amorphous product, C, 84·91%, H, 10·38%, which affords unsaturated products on warming, is formed. In benzene solution and in presence of nickel oxide (cf. Borsche and others, A., 1912, i, 194, 703; 1913, i, 171), the yield of di-β-phenylethyl ketone depends on the concentration, varying from 60% in 15% solution to 10% in 50% solution. In 20% alcoholic solution, the yield is 20%. Hydrogenation of di-β-phenylethyl ketone in *cyclo*hexane at 240° affords αε-di-*cyclo*hexylpentane, b. p. 315°. R. Brightman.

Comparative migratory tendencies of phenyl and diphenylyl radicals. M. Delaville (Compt. rend., 1927, **184**, 462—463).—By the dehydration of the corresponding tertiary alcohol, *α-diphenylylstyrene*, m. p. 93° (*dibromide*, m. p. 156°; *nitrosite*, m. p. 136°), was prepared. Silver nitrate acted on the iodohydrin of this compound, forming *phenyl diphenylylmethyl ketone*, m. p. 140° (*oxime*, m. p. 151°). The migration of the diphenylyl radical was confirmed by the preparation of the isomeric *diphenylyl benzyl ketone*, m. p. 149° (*oxime*, m. p. 156°), and *phenyldiphenylylacetaldehyde*, m. p. 96° (*oxime*, m. p. 160°).

B. W. Anderson.

Acenaphthene derivatives. P. Ruggli and A. Jenny (Helv. Chim. Acta, 1927, **10**, 228—242).—3-Acenaphthyl benzyl ketone prepared in 65—68% yield by a modification of the method of von Papcke (A., 1888, 701) (*oxime*, m. p. 138°; *phenylhydrazone*, m. p. 138—139°; *picrate*, m. p. 113—116°), treated with phosphorus pentachloride in chloroform solution, yields *ββ-dichloro-α-phenyl-β-3-acenaphthylethane*, which when heated in methyl-alcoholic solution with potassium hydroxide, or for 0·75 hr. in a vacuum at 140°, is converted into *β-chloro-α-phenyl-β-3-acenaphthylethylene*, m. p. 77·5°, which cannot be converted into the corresponding acetylene derivative. Oxidation of benzyl 3-acenaphthyl ketone with potassium permanganate in pyridine solution converts it into *phenyl-3-acenaphthylglyoxal*, m. p. 148·5° (*monohydrazone*, m. p. 199—200°), which does not yield a dihydrazone, but yields a *quinoxaline* derivative, m. p. 162°. The *monoxime*, m. p. 204—205° (decomp.), is obtained by the action of either hydroxylamine on the diketone, or amyl nitrite on the original ketone. The latter, on bromination in chloroform solution, yields *3-acenaphthyl ω-bromobenzyl ketone*, m. p. 118°, which on treatment with methyl-alcoholic potassium hydroxide solution yields *3-acenaphthyl ω-hydroxybenzyl ketone*, m. p. 138° (*benzoyl* derivative, m. p. 156°), which on oxidation with potassium permanganate yields phenylacenaphthylglyoxal (above). Nitration of 3-acenaphthyl benzyl ketone in acetic acid and acetic anhydride with nitric acid, *d* 1·4, yields *nitroacenaphthyl benzyl ketone*, m. p. 189°, which when treated with phosphorus pentachloride yields *ββ-dichloro-α-phenyl-β-nitroacenaphthylethane*, m. p. 136° (decomp.), which when heated at 140° yields *β-chloro-β-nitro-α-phenylacenaphthylethylene*, m. p. 160—161°. When treated with hydroxylamine, nitroacenaphthyl benzyl ketone does not yield an oxime, but an isomeric *substance*, m. p. 136—137°; and on reduction with sodium hydrogen sulphite yields a *substance*, m. p. 164°. Phenyl-β-naphthylglyoxal (Ruggli and Reinert, A., 1926, 391) yields a *monohydrazone*, m. p. 136°, and a *dihydrazone*, m. p. 163°, which when shaken with mercuric oxide in benzene suspension yields phenyl-β-naphthylacetylene (Ruggli and Reinert, *loc. cit.*). The corresponding phenyl-α-naphthylglyoxal similarly yields a *monohydrazone*, m. p. 152°, and a *dihydrazone*, m. p. 217—218° (decomp.), but the latter cannot be converted into the acetylene derivative.

J. W. Baker.

Nitration of benzil. 3 : 5 : 3′ : 5′-Tetranitrobenzil. F. D. Chattaway and E. A. Coulson (J.C.S., 1927, 577—579; cf. A., 1926, 728).—3 : 3′-Dinitrobenzil (*monophenylhydrazone*, m. p. 171°; *osazone*, m. p. 269°; *quinoxaline* derivative, m. p. 213°), on further nitration yields 3 : 5 : 3′ : 5′-tetranitrobenzil, m. p. 179° (Christie and Kenner, A., 1926, 408, give m. p. 168°) [*monophenylhydrazone*, m. p. 236°; quinoxaline derivative, m. p. 285° (Christie

and Kenner, *loc. cit.*, give m. p. 274°)], together with 3 : 5-dinitrobenzoic acid. This acid is produced by oxidation of the tetranitro-compound with chromic acid. H. BURTON.

Dioximes. XLI. G. PONZIO (Gazzetta, 1927, **57**, 117—124).—The "α-form of benzoylformhydroxamic acid oxime," m. p. 177° or 174° (Gastaldi, A., 1924, i, 733; Gazzetta, 1924, **54**, 588), is impure phenylhydroxyglyoxime, m. p. 191° [*hydrazine* salt, $CPh(N{\cdot}OH){\cdot}C(N{\cdot}OH){\cdot}OH,N_2H_4$, m. p. 165°, decomp.], mixed with phenyloximinoacetic acid when prepared from ethyl phenylglyoxylate. The "β-form," m. p. 183°, of *p*-methylbenzoylformhydroxamic acid oxime (*p*-tolylhydroxyglyoxime) (cf. Gastaldi, A., 1924, i, 1209; Baiardo, A., 1926, 1262) is identical with the α-form, m. p. 186°; the supposed isomerisation of the nickel salt is a gel formation. The single form, m. p. 186°, is also obtained by the hydrolysis of *p*-tolylchloroglyoxime; the single triacetyl derivative has m. p. 122—123°.

3-Hydroxy-5-phenyl-1 : 2 : 4-oxadiazole (cf. A., 1926. 1159) is decomposed by nitric acid into benzonitrile, ammonia, and carbon dioxide; heated with aniline in a sealed tube, it gives *s*-diphenylcarbamide; *sodium* and *silver* salts, the *salt* $Ph{\cdot}C_2N_2O{\cdot}OAg$,$Ph{\cdot}C_2N_2O{\cdot}OH$, m. p. 212° (decomp.), a *copper* salt, and a *basic copper* salt, $Ph{\cdot}C_2N_2O{\cdot}CuOH$, are described. The 3-*methoxy*-derivative, m. p. 26°, is obtained by methylation of the sodium salt, or by the action of sodium methoxide on the 3-chloro- or 3-bromo-compound (see this vol., 470), and, similarly, the 3-*ethoxy*-derivative, m. p. 64°; these compounds are very stable towards alkali. E. W. WIGNALL.

New resacetophenone. F. MAUTHNER (J. pr. Chem., 1927, [ii], **115**, 274—278).—The third isomeric resacetophenone (cf. Nencki and Sieber, A., 1881, 591; Claus, A., 1896, i, 227), 3 : 5-*dihydroxyacetophenone*, m. p. 147—148° (*semicarbazone*, m. p. 205—206°; *p-nitrophenylhydrazone*, m. p. 236—237°; *diacetyl* derivative, m. p. 91—92°), may be obtained by demethylating 3 : 5-dimethoxyacetophenone (A., 1924, i, 524) with aluminium chloride in chlorobenzene solution. H. E. F. NOTTON.

Derivatives of methyl α-piperonylidene-ethyl ketone. B. O'DONOGHUE, H. RYAN, and J. KEANE (Proc. Roy. Irish Acad., 1926, **37**, [*B*], 141—148).—Piperonal condenses with methyl ethyl ketone in presence of dry hydrogen chloride at 0° to yield *methyl α-piperonylidene-ethyl ketone*, $MeCO{\cdot}CMe{:}CH{\cdot}C_6H_3{:}O_2CH_2$, m. p. 97—98° (*oxime*, m. p. 130°). In presence of alkali, this condenses with benzaldehyde, anisaldehyde, and piperonal to yield, respectively, 3-*phenyl*-4-*piperonyl*-5-*methyl*-, 3-*anisyl*-4-*piperonyl*-5-*methyl*-, and 3 : 4-*dipiperonyl*-5-*methyl*-Δ^2-cyclo*penten*-1-*one*, m. p. 88·6—89·4°, 112—113°, and 127—128°, respectively [*tetrabromide* of the last-named, m. p. 136° (decomp.)]. In presence of dry hydrogen chloride at 0°, however, the condensation products obtained are, respectively, 3-*phenyl*-4-*piperonyl*-2-*benzylidene*-5-*methyl*-Δ^3-cyclo*penten*-1-*one*, m. p. 140—141°, 3-*anisyl*-4-*piperonyl*-2-*anisylidene*-5-*meihyl*-Δ^3-cyclo*penten*-1-*one*, m. p. 150—151°, and 3 : 4-dipiperonyl-2-piperonylidene-5-methyl-Δ^3-*cyclo*penten-1-one (I), m. p. 220—222° (cf. Ryan and Devine, A., 1916, i, 654; Ryan and Lennon, A., 1925, i, 1282), which are also obtained by the action of a further molecule of the aldehyde in presence of dry hydrogen chloride at 0° on the products (above) obtained in presence of alkali. By the action of a concentrated solution of dry hydrogen chloride in alcohol at 40° on 3 : 4-dipiperonyl-5-methyl-Δ^2-*cyclo*penten-1-one, it is converted into the isomeric 3 : 4-*dipiperonyl*-5-*methyl*-Δ^3-cyclo*penten*-1-*one*, m. p. 133·5—134·5°, which condenses with another mol. of piperonal in presence of alkali to yield (I). All these condensation products give colours with concentrated sulphuric acid. J. W. BAKER.

Derivatives of piperonylidenemethyl ethyl ketone. B. O'DONOGHUE, H. RYAN, and J. KEANE (Proc. Roy. Irish Acad., 1926, **37** [*B*], 149—153).—Piperonal condenses with methyl ethyl ketone in presence of alkali to yield *piperonylidenemethyl ethyl ketone*, m. p. 146—147° (*phenylhydrazone*, m. p. 82—83°), which condenses with another molecule of piperonal in presence of alkali to yield the *piperonylidenemethyl* α-*piperonylidene-ethyl ketone*, m. p. 186—187° [*tetrabromide*, m. p. 126—128° (decomp.)]. In presence of dry hydrogen chloride, however, the condensation product is 3 : 4-dipiperonyl-5-methyl-Δ^3-*cyclo*penten-1-one (cf. preceding abstract), whilst with anisaldehyde the product is 4-*anisyl*-3-*piperonyl*-2-*anisylidene*-5-*methyl*-Δ^3-cyclo*penten*-1-*one*, m. p. 220—222°. J. W. BAKER.

Derivatives of veratrole and of methylvanillin. I. B. L. VANZETTI (Gazzetta, 1927, **57**, 162—172).—Veratroin is not obtained solid, even when prepared by reduction of veratril (3 : 4 : 3′ : 4′-tetramethoxybenzil) (new m. p. 223°). The latter condenses with *o*-phenylenediamine to give a *quinoxaline*, m. p. 198·5—199°; with hydroxylamine to give a *substance*, m. p. 110—113°. Veratrilic acid is not obtained by heating veratroin with potassium hydroxide solution in a current of air, nor by heating veratril with aqueous potassium hydroxide, and only in small quantity, with some veratric acid, when alcohol is present. Fusion of veratril with potassium hydroxide above 234° gives veratrilic acid, which has two forms, m. p., respectively, about 85° and below 68° (decomp.). Veratrilic acid in solution exposed to air resinifies.

Attempts to obtain di-3 : 4-dimethoxyphenyl ketone by the action of carbonyl chloride, or of veratric acid and zinc chloride, on veratrole, were not very successful. Action of magnesium methyl iodide on the ketone yields αα-*di*-3 : 4-*dimethoxyphenylethyl alcohol*, m. p. 95—96°.

Benzilic acid is obtained in 95% yield by the action of sodium hydroxide dissolved in ethyl alcohol on an ethereal solution of benzil. E. W. WIGNALL.

Alkylation of hydroxynaphthaquinone. III. Synthesis of lapachol. L. F. FIESER (J. Amer. Chem. Soc., 1927, **49**, 857—864; cf. this vol., 155).—Treatment of the silver salt of hydroxynaphthaquinone with α-bromo-γ-methyl-Δ^β-butene (isoprene hydrobromide) in cold ethereal suspension yields 2-γ-*methyl*-Δ^β-*butenoxy*-α-*naphthaquinone*, pale yellow, m. p. 149—150°, together with 3-hydroxy-2-γ-methyl-Δ^β-butenyl-α-naphthaquinone, yellow, m. p. 139—140°, identical with lapachol (cf. Hooker, J.C.S.,

1896, **65**, 1355). Crotyl bromide yields similarly 2-*crotyl*-α-*naphthaquinone*, (I), yellow, m. p. 137°, 4-*crotyl*-β-*naphthaquinone*, (II), orange-yellow, m. p. 120°, and 3-*hydroxy*-2-*crotyl*-α-*naphthaquinone*, yellow, m. p. 132—133°. When treated with cold, concentrated sulphuric acid, the last affords 2-*methyl*-7 : 8-*benzochroman*-5 : 6-*quinone*, orange, m. p. 164°, and 2-*methyl*-6 : 7-*benzochroman*-5 : 8-*quinone*, yellow, m. p. 122·5°. When heated above the m. p., both (I) and (II) are converted into 3-*hydroxy*-2-α-*methyl*-Δ^{β}-*propenyl*-α-*naphthaquinone*, m. p. 69°, and this, when treated with cold, concentrated sulphuric acid, yields 1 : 2-*dimethyl*-5 : 6-*benzocoumaran*-3 : 4-*quinone*, m. p. 109—110°. F. G. WILLSON.

Sulphonation of anthraquinone in presence of mercury. A. MEYER (Compt. rend., 1927, **184**, 609—611).—Potassium anthraquinone-α-sulphonate when heated with 80% sulphuric acid at 190° in presence of mercuric sulphate affords about 33% of the theoretical amount of anthraquinone. The liquors obtained on dilution contain the α- and β-anthraquinonesulphonic acids in the ratio 65 : 35. The theory previously advanced (A., 1926, 1146) regarding the mechanism of the conversion of the α- into the β-sulphonic acid is thus confirmed. Under similar conditions, anthraquinone-β-sulphonic acid is stable. Sulphonation of anthraquinone at 160° in presence of mercuric sulphate (cf. Martinet and Roux, A., 1921, i, 257, 732) affords chiefly anthraquinone-α-sulphonic acid, together with the 1 : 5- and 1 : 8-disulphonic acids and a little trisulphonic acid. The presence of the β-monosulphonic acid could not be established. R. BRIGHTMAN.

Anthraquinonesulphonic acids. H. E. FIERZ-DAVID [with A. KREBSER and W. ANDERAU] (Helv. Chim. Acta, 1927, **10**, 197—227).—A summary of an extensive re-examination of the preparation and properties of anthraquinone-mono- and -di-sulphonic acids, their salts and derivatives, in accordance with methods previously described in the literature. A large amount of solubility data for metallic salts in water at 18° and 100° is given, for which the original must be consulted. In presence of mercury salts, monosulphonation of anthraquinone yields 97% of the α-acid (*chloride*, m. p. 216—218°) and 3% of the β-acid. The sodium (+H_2O), potassium, ammonium, calcium (+$3H_2O$), strontium (+$3H_2O$), barium (+H_2O), magnesium (+$16H_2O$), ferrous (+$8H_2O$), nickel (+$8H_2O$), zinc (+$8H_2O$), cadmium (+$16H_2O$), copper (+$8H_2O$), manganous (+$16H_2O$), and lead (+$6H_2O$) salts of anthraquinone-α-sulphonic acid are described. Disulphonation in presence of mercury salts yields 40—45% of the 1 : 5-acid, 23% of the 1 : 8-acid, the remaining 20—25% consisting of 1 : 5-, 4·5%; 1 : 8, trace; 1 : 6-, about 5%; and 1 : 7-, 12—15%. The pure 1 : 5-acid (+$4H_2O$), m. p. 310—311° (decomp.), yields a *disulphonyl chloride*, m. p. 265—270° (decomp.); *dianilide*, m. p. 269—270°; *diamide*, m. p. above 350°. The *pyridine*, m. p. 245—246°, *aniline*, *sodium* (+$4H_2O$), *potassium*, *ammonium*, *calcium* (+$3H_2O$), *strontium* (+$3H_2O$), *barium* (+$2H_2O$), *lead* (+$4H_2O$), *magnesium* (+$8H_2O$), *zinc* (+$8H_2O$), *ferrous* (+$8H_2O$), *cobalt* (+$8H_2O$), *nickel* (+$8H_2O$), *copper* (+$8H_2O$), *cadmium* (+$7H_2O$), and *manganese* (+$7H_2O$) salts are described. The 1 : 8-acid (+$5H_2O$), m. p. 293—294° (decomp.), yields a *disulphonyl chloride*, m. p. 222—223°; *dianilide*, m. p. 237—238° (decomp.); *diamide*, m. p. above 340°. The *aniline*, *sodium* (+$4H_2O$), *potassium* (+$2H_2O$), *ammonium* (+$2H_2O$), *calcium* (+$5·5H_2O$), *strontium* (+$3·5H_2O$), *barium* (+$3·5H_2O$), *lead* (+H_2O), *magnesium* (+$6H_2O$), *zinc* (+$6H_2O$), *ferrous* (+$6H_2O$), *cobalt* (+$6H_2O$), *nickel* (+$6H_2O$), *copper* (+$7H_2O$), *cadmium* (+$5H_2O$), and *manganese* (+$4H_2O$) salts are described. The 1 : 6-acid (+$5H_2O$), m. p. 215—217° (decomp.) (2·5H_2O lost in a vacuum desiccator) yields a *disulphonyl chloride*, m. p. 197—198° (decomp.); *dianilide*, m. p. 227—228° (decomp.); additive *compound* of the dianilide with nitrobenzene, m. p. 142—143°. The *sodium* (+$3H_2O$), *potassium* (+1·5H_2O), *ammonium*, *calcium* (+$5H_2O$), *barium* (+$2H_2O$), *magnesium* (+$8H_2O$), and *nickel* (+$8H_2O$) salts are described. The 1 : 7-acid (+$4H_2O$), m. p. 120° (? dissolves in its water of crystallisation), yields a *disulphonyl chloride*, m. p. 231—232° (decomp.); *dianilide*, m. p. 237—238° (decomp.); and the *sodium* (+$2H_2O$), *potassium* (+$2H_2O$), *ammonium* (+$2H_2O$), *calcium* (+$6H_2O$), *barium* (+2·5H_2O), *magnesium* (+$10H_2O$), and *nickel* (+$10H_2O$) salts are described. The chlorination and bromination of the anthraquinonedisulphonic acids were repeated and the following derivatives are described: 1 : 5-chlorosulphonic acid (+$4H_2O$), m. p. 236—237° (decomp.) [*sodium* (+0·5H_2O), *potassium* (+$2H_2O$), *calcium* (+$2H_2O$), *magnesium* (+$8H_2O$), and *nickel* (+$8H_2O$) salts]; 1 : 8-chlorosulphonic acid (+$3H_2O$), m. p. 183—184° (decomp.) [*sodium* (+H_2O), *potassium* (+$2H_2O$), *calcium* (+$4H_2O$), *barium* (+$3H_2O$), *magnesium* (+$6H_2O$), and *nickel* (+$6H_2O$) salts]: 1 : 6-chlorosulphonic acid (+$3H_2O$), m. p. 248—249° (decomp.) [potassium and calcium (+$2H_2O$) salts]: 1 : 5-bromosulphonic acid (+2·5H_2O), m. p. 265—266° [potassium salt, (+$2H_2O$)]: 1 : 6-bromosulphonic acid (+$4H_2O$), m. p. 268—269°. Attempts to prepare the 6- and 7-chloroanthraquinone-1-sulphonic acids from the corresponding 6-halogen-1-nitro-compounds by means of sodium sulphite were unsuccessful, but the various nitro-, amino-, and acetamido-halogeno- and dihalogeno-anthraquinones were prepared and their properties are summarised. Sulphonation of anthraquinone in absence of mercury salts yields the β-sulphonic acid, of which the *sodium* (+H_2O), *potassium*, *ammonium*, *magnesium* (+$2H_2O$), *calcium* (+$2H_2O$), *strontium* (+H_2O), *barium* (+H_2O), *ferrous* (+$6H_2O$), *cobalt* (+$6H_2O$), *nickel* (+$6H_2O$), *manganese* (+$2H_2O$), *zinc* (+$2H_2O$), *cadmium* (+$2H_2O$), *copper* (+H_2O), and *lead* (+$3H_2O$) salts are described. Disulphonation at 140° yields anthraquinone-2 : 6- and -2 : 7-disulphonic acids in the ratio 2 : 3; at 150° the ratio is 9 : 11, and with a vanadium catalyst it is 1 : 1. The 2 : 6-disulphonic acid yields a *disulphonyl chloride*, m. p. 186° [*sodium* (+$2H_2O$), *potassium*, *ammonium*, *magnesium* (+$3H_2O$), *calcium* (+$5H_2O$), *barium* (+$5H_2O$), *ferrous* (+$8H_2O$), *cobalt* (+$8H_2O$), *nickel* (+$8H_2O$), *zinc* (+$6H_2O$), *copper* (+$4H_2O$), and *lead* (+$5H_2O$) salts]. The following salts of the 2 : 7-disulphonic acid are described: *sodium* (+$4H_2O$), *potassium* (+H_2O), *ammonium* (+H_2O), *magnesium* (+$5H_2O$), *calcium* (+$2H_2O$), *strontium* (+$2H_2O$), *barium* (+H_2O),

ferrous (+6H_2O), *cobalt* (+6H_2O), *nickel* (+6H_2O), *zinc* (+4H_2O), *copper* (+6H_2O), and *lead* (+2H_2O). When anthraquinonesulphonic acids are heated with concentrated sulphuric acid in chlorobenzene or nitrobenzene solution for 8 hrs., no elimination of the sulphonic acid groups occurs up to a temperature of 180°, but at 210° in presence of mercury as a catalyst the 1-, 1 : 5-, and 1 : 8-acids yield, respectively, 80, 74, and 78% of anthraquinone. At the most, only traces of anthraquinone are produced with the other isomerides or when a vanadium catalyst is used. Sodium anthraquinone-2 : 6-disulphonate heated with sodium chlorate and hydrochloric acid yields first *2-chloroanthraquinone-6-sulphonic acid* [*sodium* and *barium* (+H_2O) salts; *acid chloride*, m. p. 202°] and finally 2 : 6-*dichloroanthraquinone*, m. p. 282°. Similarly, *2-chloroanthraquinone-7-sulphonic acid* [*barium* (+H_2O) salt; acid *chloride*, m. p. 176°] and 2 : 7-dichloroanthraquinone are obtained.

J. W. Baker.

Production of anthraquinone derivatives. H. A. E. Drescher, W. Smith, J. Thomas, and Scottish Dyes, Ltd.—See B., 1927, 246.

[Bz-2′-]Hydroxybenzanthrones. K. Schirmacher, K. Zahn, K. Wilke, and P. Ochwat, Assrs. to Grasselli Dyestuff Corp.—See B., 1927, 275.

Tannins. XXIV. Chebulic acid. III. K. Freudenberg and T. Frank (Annalen, 1927, **452**, 303—315; cf. Freudenberg and Fick, A., 1920, i, 849).—Specially purified chebulic acid has the formula $C_{41}H_{34}O_{27}$ (*M* 958), $[\alpha]_{578}$+65·1° in aqueous alcohol. The mol. wt. averages 962 by alkalimetric, 977 by electrometric titration, 875 ebulliometrically in glacial acetic acid or methyl succinate. Fission experiments with 5% sulphuric acid at 100°, with 0·2*N*-sodium hydroxide at 32°, with boiling water, with tannase, and with boiling water followed by tannase, lead to the equation: $C_{41}H_{34}O_{27}+5H_2O$=3 mols. of gallic acid + 1 mol. of dextrose + 1 mol. of acid $C_{14}H_{14}O_{11}$.

C. Hollins.

Constitution of α-kirondrin. Volmar and Samdahl (Compt. rend., 1927, **184**, 535—537; cf. this vol., 387).—α-Kirondrin has the formula $C_{24}H_{37}O_{10}$, and is believed to be a saturated, non-phenolic lactone containing one or more aldehydo-groups. The ready reduction of cold Fehling's solution, Nessler's reagent, and ammoniacal silver nitrate point to the presence of aldehydo-groups, but α-kirondrin gives no osazone either before or after attempted hydrolysis with dilute acid or emulsin, and is therefore not a glucoside. It dissolves in water to a neutral solution which becomes acid on boiling, or in alkali to a yellow solution which becomes colourless on acidification; a lactonic structure is suggested to explain these reactions. It does not decolorise bromine in the cold, or give a colour with ferric chloride. The general properties, and especially the intense greenish-yellow fluorescence in ultra-violet light, are reminiscent of quassine and other substances obtained from the natural order *Simarubaceæ*, and therefore an anthracene complex is probably present.

J. M. Gulland.

Catalytic hydrogenation of carone. S. N. Iyer and J. L. Simonsen (J. Indian Inst. Sci., 1927, **9A**, 169—172).—See A., 1926, 1042.

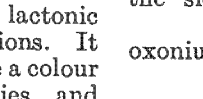
Enolisation of camphor. II. Camphor-enol ethyl ether (2-ethoxybornylene). M. Bredt-Savelsberg and C. Rumscheidt (J. pr. Chem., 1927, [ii], **115**, 235—255; cf. A., 1924, i, 530).—Attempts to prepare an ether of enolic camphor by thermal decomposition of 2-methoxycamphane-3-trimethylammonium hydroxide gave only camphor, methyl alcohol, and trimethylamine. Camphoracetal was prepared by Arbusov's method (A., 1908, i, 555); the second compound, b. p. 82—83°/15 mm., obtained by this author was probably a mixture of camphor and ethyl orthoformate. The acetal does not react with sodium or sodium ethoxide; with acetyl chloride and pyridine, camphor is obtained. Treatment with phosphoric oxide and pyridine at 110—130° for 8 hrs. converts it into an unsaturated substance, b. p. 73·9—75·1°/12 mm., $d_4^{10\cdot8}$ 0·9356, $n^{10\cdot3}$ 1·46795, which must consist mainly of *2-ethoxybornylene*, since it is oxidised by potassium permanganate to 3-carbethoxy-2 : 2 : 3-trimethyl*cyclo*pentane-1-carboxylic acid (*allo*ethyl hydrogen camphorate, Brühl, A., 1892, 1100) and camphor. It rapidly absorbs atmospheric oxygen, and is hydrolysed to camphor by water or dilute acids. Catalytic hydrogenation in presence of platinum-black gives camphor and bornyl ethyl ether, b. p. 73—74°/10 mm.

H. E. F. Notton.

Essence of camphor. VII. Catalytic action of Japanese acid earth on *l*-linalool. K. Ono and Z. Takeda (Bull. Chem. Soc. Japan, 1927, **2**, 16—19; cf. this vol., 156).—*l*-Linalool was heated with 10% of Japanese acid earth at 159°. The product volatile in steam contained (?) myrcene, *d*-limonene, *d*-terpineol, and geraniol, whilst the non-volatile residue contained an olefinic sesquiterpene alcohol, $C_{15}H_{26}O$, b. p. 187—190°/20 mm., $d_4^{21\cdot5}$ 0·90197, n_D^{22} 1·4942, and a diterpene oxide, $C_{20}H_{34}O$, b. p. 196—200°/20 mm., $d_4^{21\cdot5}$ 0·9186, n_D^1 1·4946 (cf. Semmler and Jonas, A., 1915, i, 63).

H. E. F. Notton.

Hydrogenation of xanthone and xanthen. V. N. Ipatiev and N. A. Orlov (J. Russ. Phys. Chem. Soc., 1926, **58**, 1034—1038).—See this vol., 251.

Action of bromine on furylacrylic acid. C. Moureu, C. Dufraisse, and J. R. Johnson (Ann. Chim., 1927, [x], **7**, 5—13).—Addition of 4 atoms of bromine to a suspension of furylacrylic acid in chloroform at −15°, in an atmosphere of dry carbon dioxide, yields a crystalline *tetrabromide*, m. p. 110—111° (decomp.), which decomposes immediately on exposure to air with evolution of hydrogen bromide. It is suggested that two of the bromine atoms enter the side-chain, the other two going to form an oxonium dibromide,  , the compound being an intermediate product in the formation of the tribromo-acid, $C_4H_2OBr\cdot[CHBr]_2\cdot CO_2H$, obtained by Gibson and Kahnweiler (A., 1890, 959). On treatment of the chloroform solution with mercury, the original furylacrylic acid is regenerated. Similarly, αβ-dibromo-β-phenylpropionic acid, on treatment with mercury, yields cinnamic acid. Successive treatment of the tetrabromide with sodium sulphate and sodium

carbonate in an attempt to prepare furylbromoethylene (cf. following abstract) probably yielded this substance in solution, but it could not be isolated. Bromofurylbromoethylene prepared by the method of Gibson and Kahnweiler (*loc. cit.*) has the following constants: b. p. 98—99°/10 mm., n_D^{18} 1·6174, d_4^0 1·9643, d_4^{18} 1·9373. J. W. Baker.

Furylacetylene. C. Moureu, C. Dufraisse, and J. R. Johnson (Ann. Chim., 1927, **7**, 14—42).—Furylethylene, m. p. about —96°, b. p. 99—100°/760 mm., 49—50°/130 mm., 32—33°/57 mm., 25°/27 mm., and 19°/17 mm., $d_4^{18\cdot5}$ 0·9445, $n_D^{18\cdot5}$ 1·4992, is obtained as a by-product in the preparation of furylacrylic acid by Gibson and Kahnweiler's method (A., 1890, 959), but is best obtained by heating the latter at 270—280°, rising gradually to 300—320° (yield 40%). It rapidly polymerises in presence of air and light, but is stabilised by the addition of about 0·5% of quinol or pyrocatechol. Under minutely prescribed conditions, which must be closely followed, treatment of furylethylene with bromine in anhydrous ether at —17° yields the *dibromide* (pale green leaflets, m. p. about 20°, which readily decomposes and was not isolated in the pure state); this on treatment with a 50% excess of alcoholic potassium hydroxide solution at 0° (added in one portion because alcohol itself decomposes the dibromide) yields *furylbromoethylene* (probably mainly the α-bromo-compound), b. p. 61—62°/17 mm., 42—43°/3 mm., which in air undergoes spontaneous oxidation to a lachrymatory *substance*, probably furacyl bromide, $C_4H_3O\cdot CO\cdot CH_2Br$. On treatment with a 10% excess of an 18% alcoholic solution of potassium hydroxide at 100° and subsequent exact neutralisation, furylbromoethylene yields *furylacetylene*, b. p. 105—106°/760 mm., 54—55°/120 mm., d_4^0 1·0127, d_4^{20} 0·9919, 1·5055, which is purified by conversion into its *copper* compound, which gives acetylene when treated with aqueous sodium cyanide. The *mono-* and *di-silver* and *mercury*, m. p. 118—119°, compounds are described. Furylacetylene reacts slowly with sodium but vigorously with potassium to give the *potassium* derivative, which absorbs carbon dioxide to form potassium furylpropiolate(?). Magnesium ethyl bromide converts furylacetylene quantitatively into magnesium furylethinyl bromide (and ethane), which with carbon dioxide yields *furylpropiolic acid*, m. p. 113—114° (decomp. on Maquenne block), 108—110° (decomp. in a capillary tube). With alcohol, furylacetylene forms an azeotropic mixture, b. p. 77—78°/760 mm., 37—38°/124 mm., 32—33°/95 mm., d_4^{18} 0·8610, n_D^{18} 1·409, containing 38% of the acetylene. J. W. Baker.

Preparation and reactions of pyrylium perchlorates. O. Diels and K. Alder (Ber., 1927, [*B*], 716—723).—4 : 6-*Di*-p-*tolyl*-2-*methylpyrylium perchlorate*, m. p. 275° (decomp.) after softening, is obtained by warming toluene with a mixture of acetic anhydride and perchloric acid; its constitution is established by its conversion by means of ammonia into 4 . 6-di-*p*-tolyl-2-methylpyridine, m. p. 96° (cf. Thomae, A., 1907, i, 138). It is assumed that the anhydride and perchloric acid yield initially a mixed anhydride, $Ac\cdot O\cdot ClO_3$, which with toluene affords perchloric acid and *p*-tolyl methyl ketone. From the latter compounds (2 mols.), an unsaturated ketone is derived, converted by the mixed anhydride into a pyrylium perchlorate. In confirmation, 4 : 6-diphenyl- and 4 : 6-di-*p*-tolyl-2-methylpyrylium perchlorates are obtained from acetophenone and *p*-tolyl methyl ketone, respectively. 4 : 6-Di-*p*-tolyl-2-methylpyrylium perchlorate is converted by aniline into 1-*phenyl*-4 : 6-*di*-p-*tolyl*-2-*methylpyridinium perchlorate*, m. p. 217°, and by *as*-phenylmethylhydrazine into 1-*methylanilino*-4 : 6-*di*-p-*tolyl*-2-*methylpyridinium perchlorate*, m. p. 177°; benzylamine behaves similarly. With phenylhydrazine in ethereal solution, it gives primarily the *compound* $(CH<^{C(C_6H_4Me)\cdot O}_{C(C_6H_4Me):CH}>CMe\cdot NH\cdot NHPh$, m. p. 129—130°, and ultimately a mixture of 2-*phenylhydrazino*-1-*anilino*-4 : 6-*di*-p-*tolyl*-2-*methyl*-1 : 2-*dihydropyridine*, m. p. 141°, and the *phenylhydrazone* of δ-*phenylhydrazino*-β-p-*tolyl*-$\Delta^{\alpha\gamma}$-*pentadienyl* p-*tolyl ketone*, m. p. 241°. Piperidine and dimethylamine transform the perchlorate respectively into 1 : 3′ : 5′-*di*-p-*tolylphenylpiperidine*, m. p. 146°, and 3 : 5-*di*-p-*tolyldimethylaniline*, m. p. 106°. Similarly, 2 : 4 : 6-trimethylpyrylium perchlorate, obtained from mesityl oxide or acetone and acetic anhydride and perchloric acid, is converted by dimethylamine into *N*-dimethyl-*as*-*m*-xylidine. 4 : 6-*Di*-o-*xylyl*-2-*methylpyrylium perchlorate*, m. p. 282° (decomp.), is formed from *o*-xylene and the "mixed anhydride," with which benzene does not appear to react. H. Wren.

β-[4-]Phenylcoumarins. G. Bargellini and A. Grippa (Gazzetta, 1927, **57**, 138—145).—2 : 4-*Dihydroxy*-3′ : 4′ : 5′-*trimethoxybenzophenone*, yellow, m. p. 165°, obtained by heating resorcinol with 3 : 4 : 5-trimethoxybenzoic acid and zinc chloride, condenses with sodium acetate and acetic anhydride to give 7-*acetoxy*-4-(3′ : 4′ : 5′-*trimethoxyphenyl*)-*coumarin*, m. p. 118—120°, which hydrolyses to the corresponding 7-hydroxy-compound [4-(3 : 4′ : 5′-trimethoxyphenyl)umbelliferone, cf. Bogert and Isham, A., 1914, i, 532]. This with diazomethane gives the 7-*methoxy*-compound, m. p. 172—175°, but with methyl sulphate and sodium hydroxide, β-(2′ : 4′-*dimethoxyphenyl*)-3 : 4 : 5-*trimethoxycinnamic acid*, m. p. 156—158°; by demethylation, 7-*hydroxy*-4-(3′ : 4′ : 5′-*trihydroxyphenyl*)*coumarin*, m. p. 315—317° (*tetra-acetyl* derivative, m. p. 146—148°), is obtained.

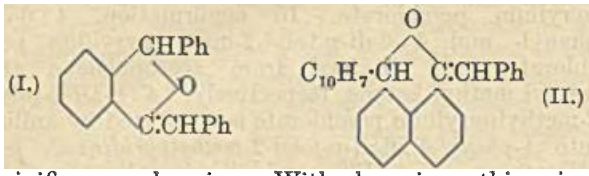
By the method of Bogert and Isham (*loc. cit.*), condensing ethyl 3 : 4 : 5-trimethoxybenzoylacetate with phloroglucinol, 5 : 7-*dihydroxy*-4-(3′ : 4′ : 5′-*trimethoxyphenyl*)*coumarin*, m. p. 245—247° (*diacetyl* derivative, m. p. 190—191°), is prepared; this is methylated by diazomethane to the 5 : 7 : 3′ : 4′ : 5′-*pentamethoxy*-compound, m. p. 204—206°, and demethylated to impure 5 : 7-*dihydroxy*-4-(3′ : 4′ : 5′-*trihydroxyphenyl*)-*coumarin* (*penta-acetyl* derivative, m. p. 170—171°).

Using pyrogallol, 7 : 8-*dihydroxy*-4-(3′ : 4 : 5′-*trimethoxyphenyl*)*coumarin*, m. p. 274—276°, is obtained (*diacetyl* derivative, m. p. 161—162°).

E. W. Wignall.

Arylbenzylidenephthalans and naphthalans; disubstituted indones. R. Weiss and P. Fastmann (Monatsh., 1926, **47**, 727—732; cf. A., 1926, 294, 401).—Phenylphthalide is converted by mag-

nesium benzyl chloride in ether–benzene solution into *phenylbenzylidenephthalan* (I), m. p. 128—131°, which



resinifies on keeping. With bromine, this gives 2 : 3-diphenylindone. *p-Tolylbenzylidenephthalan*, m. p. 150—155°, and *2-phenyl-3-p-tolylindone*, m. p. 136—137°, are obtained in a similar way from *p*-tolylphthalide. Magnesium α-naphthyl bromide and naphthalic anhydride in warm toluene solution form *8-α-naphthoyl-1-naphthoic acid*, m. p. 208—212°, which is reduced by hydriodic acid and red phosphorus in boiling glacial acetic acid to *α-naphthylnaphthalide*, m. p. 192—194°. The latter is reduced by sodium amalgam and alcohol to *8-α-naphthylmethyl-1-naphthoic acid*, m. p. 160—162°, whilst with magnesium benzyl chloride it gives *α-naphthylbenzylidenenaphthalan* (II), m. p. 173—177°. *8-o-Toluoyl-1-naphthoic acid*, m. p. 183—184°; *o-tolylnaphthalide*, m. p. 146—150°, and *o-tolylbenzylidenenaphthalan*, m. p. 125—127°, are prepared by analogous methods. H. E. F. Notton.

Derivatives of 2-phenyl-1 : 3-benzdithiole. W. R. H. Hurtley and S. Smiles (J.C.S., 1927, 534—537).—Nitric acid oxidises 2-phenyl-1 : 3-benzdithiole to the sulphonium nitrate, from which the ψ-base is liberated by alkali (cf. A., 1926, 948). *2-o-Nitrophenyl-1 : 3-benzdithiole* does not undergo this oxidation, but *2-p-methoxyphenyl-1 : 3-benzdithiole*, m. p. 72°, readily gave the *nitrate*, which, with sodium hydroxide, yielded *2-p-methoxyphenyl-1 : 3-benzdithiole 2-oxide*, m. p. 158° (*chloride*), and *2-p-hydroxy-1 : 3-benzdithiole*, m. p. 118°, is even more easily oxidised to the *nitrate*. The foregoing nitrate, treated with potassium carbonate, forms *1 : 3-benzdithiole-2-p-benzoquinone*, $C_6H_4S_2C{:}C_6H_4{:}O$, scarlet, m. p. 212—213° (*hydrochloride*). *1 : 3-Benzdithiole-2-β-naphthaquinone*, is similarly obtained, the normal mercaptol not being formed. *2-Styryl-1 : 3-benzdithiole*, m. p. 80° (*nitrate*), is also described. B. W. Anderson.

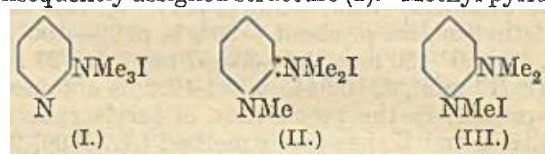
Vat dyes [of the thioindigo series]. H. Wagner and others.—See B., 1927, 212.

Production of derivatives of oxindole-3-acetic acid and its homologues containing halogens substituted in the aromatic nucleus. Chem. Fabr. vorm. Schering.—See B., 1927, 286.

[Compounds of the pyrrole and indole series and isomerisations in these series.] L. Alessandri and M. Passerini (Ber., 1927, **60**, [*B*], 807; cf. A., 1926, 1151).—A claim for priority against Putochin (A., 1926, 1151). A plea is entered for the application of the term "formyl" to the aldehydie group when attached to nitrogen. H. Wren.

Oxidation of pyridine and the pyridine nucleus by permanganate. M. Delépine (Bull. Soc. chim., 1927, [iv], **41**, 390—393).—See this vol., 254.

Alkyl halides of 2-aminopyridine. A. E. Tschitschibabin and R. A. Konovalova (J. Russ. Phys. Chem. Soc., 1926, **58**, 1170—1174).—The possibility of isomerism in the methiodides of dimethylaminopyridine and methylpyridonemethylamine, both of which are mono-acid bases, is discussed. Dimethylaminopyridine and methyl iodide give a *methiodide*, m. p. 183—184°, the solution of which with picric acid gives a *picrate*, m. p. 113°. Moist silver oxide affords a soluble *quaternary base*. On distillation, dimethylaminopyridine was obtained. The methiodide is consequently assigned structure (I). Methyl pyridone-



methylamine and methyl iodide give a *methiodide* decomposing in air. Moist silver oxide gives a silver mirror, together with dimethylamine and methylpyridone. Sodium hydroxide gives dimethylamine. The methiodide is assigned the tautomeric structures (II) and (III). M. Zvegintzov.

Derivatives and oxidation products of 2-aminopyridine. A. Kirpal and E. Reiter (Ber., 1927, **60**, [*B*], 664—666).—2-Aminopyridine is oxidised by sodium hypochlorite in aqueous solution to *2 : 2′-azopyridine*, m. p. 81° [*nitrate*, m. p. 158° (decomp.); *picrate*, m. p. 180° (decomp.)], which is reduced by stannous chloride to *2 : 2′-hydrazopyridine*, m. p. 168° (decomp.). Benzaldehyde and 2-aminopyridine afford *benzylidene-2 : 2′-dipyridylamine*, $(C_5H_4N{\cdot}NH)_2CHPh$, m. p. 109°, which passes above its m. p. into 2-aminopyridine and *benzylidene-2-aminopyridine*, b. p. 200°/18 mm.; the latter compound is converted by water into benzaldehyde and benzylidene-2 : 2′-dipyridylamine. *Benzylidene-3-aminopyridine* has b. p. 315°/atm. pressure.

H. Wren.

2 : 5-Diaminopyridine and 2 : 3-diaminopyridine. A. E. Tschitschibabin and A. W. Kirsanov (Ber., 1927, **60**, [*B*], 766—776).—2 : 5-Diaminopyridine is conveniently prepared by the action of tin and hydrochloric acid on 5-nitro-2-aminopyridine; when pure, it is reasonably stable towards light and air. The *dihydrochloride*, *chlorostannite*, m. p. 208° after incipient decomposition at 190°, and *diacetyl* derivative, m. p. 289—290°, are described. When suitably treated with nitrous acid, the diamine gives diazonium salts containing an intact amino-group in position 2, from which, by the customary reactions, 5-chloro-2-aminopyridine, m. p. 134—135°, 5-iodo-2-aminopyridine, m. p. 128·5°, and *2-aminopyridyl-5-arsinic acid*, m. p. 137—140° when rapidly heated, are obtained; the *sodium* (+$6H_2O$), *cupric*, *ferric*, and *silver* salts of the acid are described.

Reduction of 3-nitro-2-aminopyridine with tin and hydrochloric acid affords *2 : 3-diaminopyridine*, m. p. 112—113°, and *4(or 6)-chloro-2 : 3-diaminopyridine*, m. p. 131—132°. 2 : 3-Diaminopyridine behaves as a typical *o*-diamine, yielding dicyclic *derivatives*, $C_5H_4N_4$, m. p. 195°, with nitrous acid; $C_7H_7N_3$, m. p. 189·5—190·5° with acetic anhydride; $C_{19}H_{13}N_3$, m. p. 136—138°, with benzil, and $C_{19}H_{11}N_3$, m. p. 217—218° (decomp.), with phenanthraquinone. *4(or 6)-Chloro-2 : 3-diaminopyridine* similarly affords the *compounds*, $C_5H_3N_4Cl$, m. p. 211—212° after

darkening at 195°, with nitrous acid, $C_7H_6N_3Cl$, m. p. 176—177°, with acetic anhydride, and $C_{19}H_{10}N_3Cl$ with phenanthraquinone.

Reduction of 5-chloro-3-nitro-2-aminopyridine (to be described later) with tin and hydrochloric acid yields 5-*chloro*-2 : 3-*diaminopyridine*, m.p. 164·5—165°, and 5 : 6(or 4 : 5)-*dichloro*-2 : 3-*diaminopyridine*, m. p. 165—166° [condensation *product* with phenanthraquinone, $C_{19}H_9N_3Cl_2$, m. p. 252—254° (decomp.)].

H. Wren.

Indole condensation of phenylhydrazones. A. Korczynski, W. Brydowna, and L. Kierzek (Bull. Acad. Polonaise, 1926, A, 149—158).—See this vol., 255.

Synthesis of quinoline and acridine compounds. K. Matsumura (J. Amer. Chem. Soc., 1927, 49, 810—818).—Sulphonation of 8-hydroxyquinoline affords the 5-sulphonic acid, which forms a hydrate and has m. p. (anhydrous) 322—323° (cf. Claus and Posselt, A., 1890, 522). An alkaline solution with benzenediazonium chloride gives 8-*hydroxyquinoline*-7-*azobenzene*-5-*sulphonic acid*, dark red, m. p. 310° after darkening at 267° (*sodium* salt, orange), and this, on reduction with stannous chloride and hydrochloric acid, affords 7-*amino*-8-*hydroxyquinoline*-5-*sulphonic acid*, ($+1H_2O$), orange, m. p. (anhydrous) not below 310° [N-*acetyl* derivative, yellow, m. p. 277° (decomp.); N-p-*nitrobenzoyl* derivative, yellow, m. p. 297° (decomp.)]. Diazotisation of the latter affords the corresponding *diazonium* derivative, yellow, decomp. above 187°, which, when heated with concentrated sulphuric acid at 120—150°, yields 7 : 8-*dihydroxyquinoline*-5-*sulphonic acid*, yellow, m. p. 302° (decomp.) (cf. Claus and Baumann, A., 1897, i, 580). When heated with hydrochloric acid at 170°, 7-amino-8-hydroxyquinoline-5-sulphonic acid is converted into 7-*amino*-8-*hydroxyquinoline*, decomp. above 117°, m. p. 124° [*hydrochloride*, m. p. 256°; *picrate*, m. p. 205° (decomp.); N-*acetyl* derivative, m. p. 177° (*methiodide*, yellow, m. p. 195°)]. Treatment of an alkaline solution of 8-hydroxyquinoline with iodine in aqueous potassium iodide yields 5-*iodo*-8-*hydroxyquinoline*, m. p. 127—128° (*methiodide*, m. p. 142°), together with 5 : 7-di-iodo-8-hydroxyquinoline, decomp. above 195°, m. p. 210° (cf. Claus, G.P. 78,880). 5-Nitro-8-hydroxyquinoline yields, similarly, 7-*iodo*-5-*nitro*-8-*hydroxyquinoline*, orange, m. p. 249° (decomp.), which, on reduction with stannous chloride, affords 7-*iodo*-5-*amino*-8-*hydroxyquinoline*, m. p. 157° after softening at 147° [*hydrochloride*, m. p. 255° (decomp.); *picrate*, decomp. 159°].

When heated in amyl-alcoholic solution with copper-bronze, *o*-chlorobenzoic acid and *o*-phenetidine yield 2-*ethoxydiphenylamine*-2′-*carboxylic acid*, yellow, m. p. 160—161°, and this, when treated with concentrated sulphuric acid at 100°, yields 4-hydroxyacridone, yellow, m. p. 300° (cf. Ullmann, A., 1907, 842), together with 4-*ethoxyacridone*, yellow, m. p. 299° (decomp.). Reduction of the latter with sodium and amyl alcohol yields 4-*ethoxyacridine*, yellow, m. p. 80° [*hydrochloride*, yellow, m. p. 220° (decomp.); *sulphate*, yellow, m. p. 250°; *picrate*, yellow, m. p. 255°; *methosulphate*, orange-yellow, m. p. 189°]. 4-Hydroxyacridone yields similarly 4-*hydroxyacridine*, yellow, m. p. 117° [*hydrochloride*, orange, m. p. 252° (decomp.); *sulphate*, orange, m. p. 240°; *picrate*, orange, m. p. 215°]. Sulphonation of the latter affords 4-*hydroxyacridine*-1-*sulphonic acid*, yellow, m. p. 301° (decomp.), and the potassium salt of this, when treated in aqueous solution with potassium iodide and bleaching powder, yields 3-*iodo*-4-*hydroxyacridine*-1-*sulphonic acid*, yellow, decomp. above 240°, m. p. 264°.

F. G. Willson.

Quinoline derivatives. III. 2-Phenylquinoline-4-carboxylic acid. H. John [with F. Kahl] (J. pr. Chem., 1927, [ii], 115, 279—280).—Dry distillation of manganese, cobalt, and nickel 2-phenylquinoline-4-carboxylates yields only 2-phenylquinoline, but the beryllium, vanadium, chromium, zirconium, mercury, thorium, and uranium salts give, in addition, the compound of m. p. 303° (cf. this vol., 159).

H. E. F. Notton.

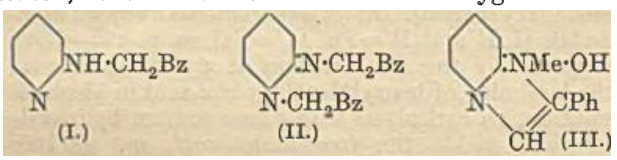
Glyoxalone and glyoxalidone as anhydrides of amino-acid derivatives. C. Granacher and M. Mahler (Helv. Chim. Acta, 1927, 10, 246—262).—Tripeptide derivatives of the type

$R{\cdot}CO{\cdot}NH{\cdot}C(:CHR'){\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}CO_2R''$ (I) are smoothly converted into glyoxaline derivatives of the type $CO_2R''{\cdot}CH_2{\cdot}N<\begin{matrix}CO\ C{\cdot}CHR\\ CR{:}N\end{matrix}$ by simply heating above their m. p. in a vacuum, providing the asterisked carbon atom is primary. When it is secondary, fission occurs, yielding the lactimide (lactimone, cf. Mohr and Geis, A., 1908, i, 339), $O<\begin{matrix}CO{\cdot}C{:}CHR''\\ CR{:}N\end{matrix}$, and the amino-ester, $CHR'''{\cdot}NH_2{\cdot}CO_2R''$ (R‴=group attached to the secondary carbon). *Ethyl* α-*benzamidocinnamylaminoacetate* (I, R and R′=Ph, R″=Et), m. p. 135—136°, prepared by the condensation of glycine ester with the lactimide of benzylidenehippuric acid in alcoholic solution, on hydrolysis with dilute sodium hydroxide solution, yields the free amino-*acid*, m. p. 165° (decomp.), and when heated at 170° under 12 mm. for 2 hrs. yields *ethyl* 2-*phenyl*-4-*benzylideneglyoxal*-5-*one*-1-*acetate*, m. p. 108—110°. This on hydrolysis with sodium carbonate in aqueous-alcoholic solution yields the free *acid*, m. p. 200—202° (decomp.) (*sodium* salt), which on reduction either with sodium amalgam and acetic acid or catalytically yields the fully reduced 2-*phenyl*-4-*benzylglyoxalid*-ɔ-*one*-1-*acetic acid*, $CO_2H{\cdot}CH_2{\cdot}NH<\begin{matrix}CO\text{——}C{\cdot}CH{\cdot}CH_2Ph\\ CHPh{\cdot}NH\end{matrix}$, m. p. 158—160°, which is stable to hot, dilute alkali, but is readily hydrolysed to benzaldehyde and phenylalanylglycine (or its anhydride) by heating with 0·1*N*-hydrochloric acid, or with alcohol in a sealed tube for 3 hrs. at 170—180°. Reduction of α-benzamidocinnamylglycine with 2·5% sodium amalgam yields α-benzoyl-β-phenylpropionylglycine (benzoylphenylalanylglycine; cf. Mohr and Stroschein, A., 1909, i, 581). By the application of similar methods are obtained α-*acetamidocinnamylglycine*, m. p. 185—188° (decomp.) (*ethyl* ester, I, R=Me, R′=Ph, R″=Et, m. p. 155°); *ethyl* 2-*methyl*-4-*benzylideneiminazol*-ɔ-

one-1-*acetate* (hydrolysed to the *sodium* salt of the corresponding acid), which on reduction probably yields the iminazolidone derivative, since on preparing the oily *amide* of the product, fission into phenylalanylglycine and acetaldehyde occurs, the same products being obtained by the action of hydrochloric acid. Condensation of leucine ester hydrochloride with the lactimide of hippuric acid in presence of sodium ethoxide yields the *ethyl* ester, m. p. 173°, of the amorphous α-*benzamidocinnamyl-leucine*, which is obtained on hydrolysis. By a similar method is obtained the amorphous α-*benzamidocinnamylalanine* (*ethyl* ester, m. p. 116—117°). α-Benzamido*iso*butyryl-lactimide condensed with glycine ester hydrochloride yields α-*benzamido*iso*butyrylglycine ester*, m. p. 123—124°, and with alcoholic methylamine yields α-*benzamido*iso*butyrylmethylamide*, m. p. 140—142°. J. W. BAKER.

Manufacture of barbituric acid derivatives. J. D. RIEDEL.—See B., 1927, 237.

Tautomerism of 2-aminopyridine. V. 2-Phenylpyriminazole and the preparation of the homologues of pyriminazole. A. E. TSCHITSCHIBABIN (J. Russ. Phys. Chem. Soc., 1926, **58**, 1159—1169; cf. A., 1921, i, 450; 1924, i, 987; 1925, i, 158, 1328).—The preparation and properties of the products of interaction of phenacyl bromide and 2-aminopyridine are described and discussed from the point of view of ring-chain tautomerism in heterocyclic compounds. This interaction readily yields a bromide, m. p. 129°, which, on treatment with alkali, gives a base, m. p. 140°, which contains no oxygen, so cannot have the structure (I) suggested by Palazzo and Marogna. Both the bromide and the free base give chloroplatinates, which lose water when heated, but otherwise contain no oxygen. The



bromide cannot be benzoylated, so that the interaction of phenacyl bromide and α-aminopyridine must result in ring closure with the formation of 2-phenylpyriminazole. Further action of alkali on the mother-liquor after the separation of the bromide gives a second *base*, m. p. 120° (*chloroplatinate*, m. p. 242°). The corresponding *bromide* is obtained by the action of phenacyl bromide on 2-phenylpyriminazole. The insolubility, stability, and precipitation with alkalis of the free base suggest the open-chain structure (II) which gives the pyriminazole ring on treatment with acids. 2-*Phenylpyriminazole methiodide*, m. p. 220—221°, does not give a base on treatment with alkali, but gives with moist silver oxide a strongly alkaline, very soluble *quaternary ammonium base*, which must therefore have the ring structure (III). M. ZVEGINTZOV.

Reaction of nicotinuric acid with picric and picrolonic (?) acids. Y. SENDJU (J. Biochem. [Japan], 1926, **6**, 161—162).—Nicotinuric acid (obtained by condensation of glycine with nicotinic acid) with picric acid yields the yellow *compound*, $C_8H_8O_3N_2,C_5H_3O_7N_3$, m. p. 167°; with picrolonic (?) acid, the *compound* $C_8H_8O_3N_2,C_{10}H_8O_5N_4$, m. p. 196°, is obtained. CHEMICAL ABSTRACTS.

Constitution of thiasine. E. B. NEWTON, S. R. BENEDICT, and H. D. DAKIN (Science, 1926, **64**, 602).—Thiasine (Benedict, Newton, and Behre, A., 1926, 421) is identical with ergothioneine (Tanret, A., 1909, i, 671), the betaine of thiolhistidine (Barger and Ewins, J.C.S., 1911, **99**, 2336). A. A. ELDRIDGE.

Triazoles. IV. Mechanism of Brunner's triazole synthesis. K. BRUNNER and J. MEDWETH (Monatsh., 1926, **47**, 741—746).—Evidence in favour of the mechanism suggested (A., 1915, i, 1007) for the synthesis of dimethyltriazole from diacetamide and semicarbazide has now been obtained by the synthesis of the hypothetical intermediate product. Cyanic acid does not react with dimethyltriazole in cold ethereal solution, but when potassium cyanate is added to an acetic acid solution of this substance at −5°, 84% of 3 : 5-*dimethyl*-1 : 2 : 4-*triazole*-1-*carboxylamide*, m. p., when freshly prepared, 130° (decomp.), is precipitated. The latter does not show the reactions of the cyanate ion; it is quantitatively decomposed by (*a*) warm water, (*b*) alcohol, and (*c*) aniline, forming in each case 3 : 5-dimethyl-1 : 2 : 4-triazole, with (*a*) carbon dioxide and ammonia, (*b*) ethyl allophanate, and (*c*) *s*-diphenylcarbamide. The corresponding thiocarbamide was not formed from thiocyanic acid and dimethyltriazole. As was expected, a carboxylamide could not be obtained thus from 1-phenyl-3 : 5-dimethyl-1 : 2 : 4-triazole and cyanic acid, and thiocyanic acid gave only a *thiocyanate*, m. p. 116—117°. H. E. F. NOTTON.

Triazoles. V. Phenyldimethyltriazole derivatives. W. GABEL and O. SCHMIDEGG (Monatsh., 1926, **47**, 747—753).—1-Phenyl-3 : 5-dimethyl-1 : 2 : 4-triazole, prepared by an improved method, gives a *methiodide*, m. p. 158—159°; *methochloride* (*chloroplatinate*; *mercurichloride*, $C_{11}H_{14}N_3Cl,3HgCl_2$); *methohydroxide*; *ethiodide*, m. p. 194°, decomposed into free base and ethyl iodide at 300°; *ethochloride*, m. p. 54° (*chloroplatinate*), and *ethohydroxide*. When heated at 100° with fuming sulphuric acid containing 31% of sulphur trioxide, phenyldimethyltriazole gives a *monosulphonic acid* (+H_2O); the *barium*, *copper*, *potassium*, and *sodium* salts are described. H. E. F. NOTTON.

Triazoles. VI. Nitration of phenyl- and naphthyl-1 : 2 : 4-triazoles. F. HERNLER and F. MATTHES (Monatsh., 1926, **47**, 791—802).—1-*Nitrophenyl*-3 : 5-*dimethyl*-1 : 2 : 4-*triazole* (75%), m. p. 149° (*picrate*, m. p. 141—142°, *chloroplatinate*, decomp. 270°), is obtained from phenyldimethyltriazole and nitric–sulphuric acids at 65°. It is reduced by alkaline stannous chloride to an *azo*-derivative, m. p. 158°, and by tin and hydrochloric acid to *aminophenyldimethyltriazole*, m. p. 183° [*picrate*, m. p. 177°; *chloroplatinate*, decomp. 250°; impure *acetyl* derivatives, m. p. 91—93°, and 109—116° (mixtures (?) of mono- and di-acetyl derivatives), from which pure *acetamidophenyldimethyltriazole picrate*, m. p. 196°, was isolated; *benzoyl* derivative, m. p. 88—90°]. The amino-group in this substance could be diazotised

and coupled with β-naphthol-3 : 6-disulphonic acid (red *dye*), but attempts to replace it by bromine in order to compare the product with 1-p-*bromophenyl*-3 : 5-*dimethyl*-1 : 2 : 4-*triazole*, m. p. 92—93° (*picrate*, m. p. 163—165°), prepared from *p*-bromophenylhydrazine and diacetamide, were unsuccessful. *o*-, *m*-, and *p*-Nitrophenylhydrazines and diacetamide give principally the corresponding acetylnitrophenylhydrazines; only in the case of the *m*-derivative could a triazole, 1-m-*nitrophenyl*-3 : 5-*dimethyl*-1 : 2 : 4-*triazole*, m. p. 128°, be isolated. This is not identical with the product of direct nitration. Attempts to establish the constitution of the latter by synthesis from *p*-acetamidophenylhydrazine or by reductive or oxidative fission were also fruitless. The following were obtained by direct nitration: 1-*nitro*-α-*naphthyl*-, m. p. 75—76°; 1-*nitro*-β-*naphthyl*-, m. p. 85°, and 1-*nitrosulphophenyl*-3 : 5-*dimethyl*-1 : 2 : 4-*triazole* (cf. preceding abstract); also 1-*nitrophenyl*-3 : 5-*diethyl*-1 : 2 : 4-*triazole*, m. p. 105—106°, which is reduced by tin and hydrochloric acid to 1-*aminophenyldiethyltriazole*, m. p. 119—120° (*hydrochloride*, m. p. 66—69°; *chloroplatinate*; *benzoyl* derivative, m. p. 161—162°). H. E. F. Notton.

7-Amino-derivatives of benztriazole and benziminazole. H. Lindemann and H. Krause (J. pr. Chem., 1927, [ii], **115**, 256—273).—The 7-aminobenztriazoles and -benziminazoles here described, like the 1-aminocarbazoles (A., 1926, 75), do not undergo ring closure in the 1 : 7-position when treated with nitrous acid or acetic anhydride. Instead, with the former they give diazonium salts which couple in the normal manner with amines or phenols, forming, for example, 2 : 5-*dimethyl*-7-*benziminazoleazo*-β-*naphthylamine*, red, m. p. 281°, and 2 : 5-*dimethyl*-7-*benziminazolcazo*-β-*naphthol*, bluish-red, m. p. 210°. 3-Nitro-4 : 5-diaminobenzoic acid (*monohydrochloride*; *monoacetyl* derivative, m. p. 270°) is conveniently prepared by heating 4-chloro-3 : 5-dinitrobenzoic acid with excess of aqueous ammonia and reducing directly with hydrogen sulphide. It is converted by acetic anhydride in presence of sulphuric acid into 7-*nitro*-2-*methylbenziminazole*-5-*carboxylic acid*, m. p. 305°, which is reduced by tin and hydrochloric acid to the 7-*amino*-derivative, m. p. 310° (*hydrochloride*; *acetyl* derivative, m. p. above 375°); and by nitrous acid into 7-*nitrobenztriazole*-5-*carboxylic acid*, m. p. 300° (decomp.), which is reduced similarly to 7-*aminobenztriazole*-5-*carboxylic acid*, m. p. 310° (*hydrochloride*; *acetyl* derivative, m. p. 315°). 3 : 5-Dinitro-*p*-toluidine is reduced by sodium sulphide to 3-*nitro*-4 : 5-*diaminotoluene* (I), m. p. 158° (*monoacetyl* derivative, m. p. 211°), which gives 7-*nitro*-2 : 5-*dimethylbenziminazole*, m. p. 248°, with acetic anhydride; (I) is further reduced by stannous chloride and hydrochloric acid to 3 : 4 : 5-*triaminotoluene*, m. p. 105°. When the *triacetyl* derivative, m. p. 249°, of this is boiled with hydrochloric acid, or 3 : 5-dinitro-4-acetamidotoluene is reduced with stannous chloride and hydrochloric acid, 7-*amino*-2 : 5-*dimethylbenziminazole* ($+H_2O$), m. p. 100°, is formed. Its *diacetyl* derivative, m. p. 169°, is easily hydrolysed by acids to a *monoacetyl* derivative, m. p. 160° (*hydrochloride*, m. p. 235°; *acetate*, m. p. 125°). On treatment with nitrous acid, (I) affords 7-*nitro*-5-*methylbenztriazole*, m. p. 277° (decomp.), which is reduced to 7-*amino*-5-*methylbenztriazole*, m. p. 155° (*diacetyl* derivative, m. p. 226°, hydrolysed by ammonia to a *monoacetyl* derivative, m. p. 230°). H. E. F. Notton.

Azo-dyes [naphthatriazoles]. I. G. Farbenind. etc.—See B., 1927, 275.

Synthesis of 8-methyl-7-ethylxanthine from a glyoxaline derivative. F. M. Diaz de Plaza (Anal. Fis. Quím., 1926, **24**, 731—737).—From 5-chloro-4-nitro-2-methyl-1-ethylglyoxaline, prepared by the method of Sarasin and Wegmann (A., 1924, i, 1115), 4-*nitro*-2-*methyl*-1-*ethylglyoxaline*-5-*carboxylamide*, m. p. 272° (decomp.), was obtained by way of 5-*chloro*-4-*nitro*-2-*methyl*-1-*ethylglyoxaline*, m. p. 77°. By reduction of the above amide, 4-*amino*-2-*methyl*-1-*ethylglyoxaline*-5-*carboxylamide*, m. p. 166°, was obtained; the *hydrochloride* has m. p. 195°. By heating the free base with ethyl carbonate, 8-*methyl*-7-*ethylxanthine*, m. p. 340° (decomp.), was obtained. G. W. Robinson.

Porphyrin syntheses. IX. New porphyrin synthesis. Oxidation of porphyrins. H. Fischer, P. Halbig, and B. Walach (Annalen, 1927, **452**, 268—302; cf. A., 1926, 1261).—Porphins are obtained by condensing a dibromobispyrrylmethene salt with an αα-dimethylbispyrrylmethene salt in glacial acetic acid at about 200°. Thus, bis-(2-bromo-3 : 4-dimethylpyrryl)methene hydrobromide and bis-(3 : 4 : 5-trimethylpyrryl)methene hydrochloride yield *octamethylporphin*, together with 5-acetyl-3 : 4 : 5-trimethylpyrrole, whilst a *hexamethyldiethylporphin* (unmelted at 360°) is obtained from the dibromomethene and biscryptopyrrylmethene [bis-(2 : 3-dimethyl-4-ethylpyrryl)methene]. These porphins and *iso*ætioporphyrin show no observable spectroscopic difference in nitrobenzene solution. Cautious oxidation of octamethylporphin with hydrogen peroxide in concentrated sulphuric acid solution at 10° gives a red, crystalline *substance*, $C_{28}H_{28}ON_4$; at 15—20° the product is dimethylmaleinimide, m. p. 118°.

*iso*Ætioporphyrins are obtained (i) by air oxidation of bis-(2-carboxy-3-methyl-4-ethyl-5-pyrryl)methane in formic acid; (ii) by condensing bis-(2-bromo-3-methyl-4-ethyl-5-pyrryl)methene with bis-(2 : 3-dimethyl-4-ethyl-5-pyrryl)methene in glacial acetic acid at 180—190°; (iii) by condensing the dibromomethene with bis-(2 : 4-dimethyl-3-ethyl-5-pyrryl)-methene; (iv) by heating bis-(2-carboxy-3-methyl-4-ethyl-5-pyrryl)methane with 20% sodium hydroxide and silver at 180°. All four products give identical spectra, as do their respective copper and iron salts. Crystallographic measurements by Steinmetz show that (iii) differs from (i) and (ii), which are identical; (iv) is probably different from the other two. Oxidation with hydrogen peroxide in concentrated sulphuric acid gives a *substance*, $C_{32}H_{36\text{ or }38}ON_4$, m. p. 236°. *iso*Ætioporphyrin is oxidised by air in bright sunshine to methylethylmaleinimide.

*iso*Mesoporphyrin (methyl ester, m. p. 275°) is obtained by condensing together (i) bis-(2-carboxy-3-methyl-4-ethyl-5-pyrryl)methane and bis-(2-carboxy-3-methyl-4-β-carboxyethyl-5-pyrryl)methane in

formic acid in a current of air, or (ii) bis-(2-bromo-3-methyl-4-ethyl-5-pyrryl)methene and bis-(2 : 3-dimethyl-4-β-carboxyethyl-5-pyrryl)methene in glacial acetic acid at 190°. Crystallographic data by STEINMETZ confirm the identity.

4-Carbethoxy-3 : 5-dimethylpyrryl-2 : 4-dimethylpyrrolenylmethene, m. p. 120°, from ethyl 2-aldehydo-3 : 5-dimethylpyrrole-4-carboxylate and 2 : 4-dimethylpyrrole; *3 : 5-dimethyl-4-ethylpyrryl-(3-carbethoxy-2 : 4-dimethylpyrrolenyl)methene*, m. p. 132°, from cryptopyrrolealdehyde and ethyl 2 : 4-dimethylpyrrole-3-carboxylate; *bis-(2-bromo-3-methyl-4-ethyl-5-pyrryl)methene*, m. p. 182° (*hydrobromide*, unmelted at 270°), from the methane by bromination, and *bis-(2 : 3-dimethyl-4-β-carboxyethyl-5-pyrryl)methene hydrochloride*, m. p. 212° (decomp.), by condensation of 2 : 3-dimethyl-4-β-carbomethoxyethylpyrrole with formic–hydrochloric acid, are described.

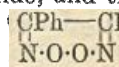
[With M. SCHUBERT and A. OSSENBRUNNER].—Cryptopyrrole, condensed with hydrogen cyanide in chloroform saturated with hydrogen chloride, gives cryptopyrrolealdehyde (azine, m. p. 172°) in 90% yield without isolation of the aldimine. The "amine," formerly (Fischer and Schubert, A., 1924, i, 544) considered to be bis-(2 : 4-dimethyl-3-ethylpyrryl)-methylamine, formed as a by-product in the aldehyde preparation, melts at 148° (not 142°) and has the composition $C_{18}H_{25}N_3$.

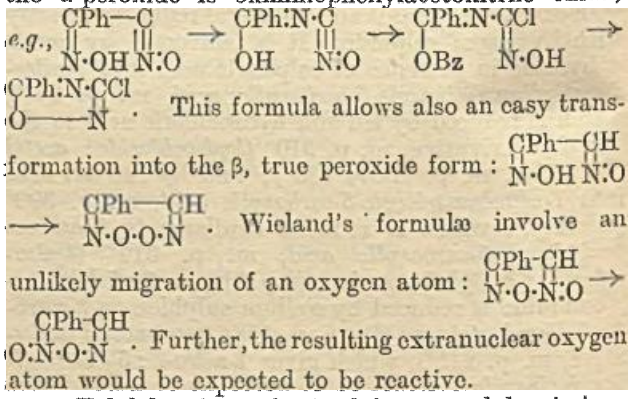
Ethyl 2 : 4-dimethyl-3-ethyl-5-pyrrylglyoxylate, m. p. 80°, obtained by way of its *imine* from cryptopyrrole and ethyl cyanoformate, is hydrolysed to the free *acid* (darkens at 150° and decomposes). Cryptopyrrolealdehyde condenses with hippuric acid to give the *azlactone*, m. p. 172°, with ethyl cyanoacetate to form the *compound* $C_{14}H_{18}O_2N_2$, m. p. 122°, and with oxindole to give the *compound* $C_{17}H_{18}ON_2$, m. p. 227° (darkens at 196°). Cryptopyrrolealdoxime is converted by acetic anhydride into *α-cyanocryptopyrrole*, m. p. 134°. Dicryptopyrrylmethene, m. p. 151° [perchlorate; hydrobromide; sulphate; *arsenate* (decomp. 211°); *picrate* (decomp. 174°)], is prepared by condensing cryptopyrrole with hydrogen cyanide or with formic acid, and also results from the action of arsenic acid on cryptopyrrole. It forms complex salts with *nickel*, m. p. 200—203°; *cobalt*, m.p. 198°; *copper*, 185—187°; *zinc*, m. p. 197°; ferrous *iron*, decomp. 215°, and *mercury*, m. p. 160° (decomp.). By reduction with zinc dust and acetic acid, it regenerates cryptopyrrole; oxidation with nitric acid or chromic acid gives methylethylmaleinimide, m. p. 69°.

C. HOLLINS.

Disulphoisatide. A. WAHL and FERICEAN (Compt. rend., 1927, **184**, 826—828).—By the action of hydrogen sulphide on a cold suspension of isatin in 10 parts of alcohol, 90% of the theoretical yield of disulphoisatide is obtained. The amount of sulphur eliminated is in agreement with Laurent's formula, $2C_8H_5O_2N+3H_2S=C_{16}H_{12}O_2N_2S_2+2H_2O+S$ (cf. A., 1924, i, 322), and not with that recently proposed by Sander (cf. A., 1925, i, 977). Mol. wt. determinations in phenol give 320—324 for disulphoisatide.

R. BRIGHTMAN.

Dioximes. XLII. G. PONZIO and L. AVOGADRO (Gazzetta, 1927, **57**, 124—138).—The arylglyoxime peroxides, regarded by Wieland (A., 1908, i, 108; 1921, i, 605) as 4-aryl-1 : 2 : 5-oxadiazole 2- and 4-oxides, or as 2 : 3-cyclic oxides, have different constitutions. Whilst Wieland's formula is accepted for dibenzoylglyoxime peroxide, α-phenylglyoxime peroxide, m. p. 108—112°, is now regarded as oximinophenylacetonitrile oxide, and the β-form, m. p. 108°, as a true peroxide,  . A mixture of the α- and β-forms melts at 65—90°. Whilst the α-peroxide is hydrolysed by sodium hydroxide to phenylmetazonic acid and 3-hydroxy-5-phenyl- and 5-hydroxy-3-phenyl-1 : 2 : 4-oxadiazoles, the β-peroxide gives ω-nitrophenylacetonitrile. Whilst benzoyl chloride converts the α-peroxide into *3-chloro-5-phenyl-1 : 2 : 4-oxadiazole*, m. p. 5·5°, b. p. 171°/134 mm., the β-peroxide does not react. (The diphenyl-, phenylmethyl-, and benzoylmethyl-glyoxime peroxides similarly do not react, in contrast with diacylglyoxime peroxides.) 3-Chloro-5-phenyloxadiazole is also obtained by the action of phosphorus pentachloride, in which process 5-phenyloxadiazole is not formed (cf. Wieland and Semper, A., 1908, i, 108); it is stable to alkali, but reacts with sodium ethoxide or methoxide to give the 3-alkoxy-derivatives (see this vol., 462). Benzoyl bromide does not react with the β-peroxide, but converts the α-peroxide into *3-bromo-5-phenyl-1 : 2 : 4-oxadiazole*, m. p. 68°, stable to alkali, but reacting with sodium alkoxide to give an alkoxy- and ultimately the hydroxy-derivative, for which this is a convenient method of preparation; the bromo-compound is also obtained by the action of phosphorus pentabromide. By the action of hydriodic acid on either peroxide, but more readily with the α-form, 5-phenyloxadiazole is formed, with ω-aminoacetophenone (phenylhydrazone, new m. p. 163°).

These reactions, with those previously described (A., 1923, i, 472, 855, 1019, 1137; 1926, 1159; this vol., 134, 135), are best explained by assuming that the α-peroxide is oximinophenylacetonitrile oxide; 
e.g., CPh(N·OH)—C(N:O) → CPh(OH):N·C(N:O) → CPh(OBz):N·CCl(N·OH) → CPh(O——N):N·CCl. This formula allows also an easy transformation into the β, true peroxide form: CPh(N·OH)—CH(N:O) → CPh(N·O·O·N)—CH. Wieland's formulæ involve an unlikely migration of an oxygen atom: CPh(N·O·N:O)—CH → CPh(O:N·O·N)—CH. Further, the resulting extranuclear oxygen atom would be expected to be reactive.

β-*p*-Tolylglyoxime, obtained from *p*-tolyl oximinomethyl ketone (new m. p. 107—108°; $+H_2O$, 83—84°), gives in nitric acid the corresponding β-peroxide, m. p. 100—101°. This is reduced by zinc and acetic acid, and is converted by sodium hydroxide into the compound $C_6H_4Me\cdot C(CN):NO_2Na$.

E. W. WIGNALL.

Anthraquinone vat dyes [thiazines]. I. G. FARBENIND.—See B., 1927, 211.

Conessine. D. D. KANGA, P. R. AYYAR, and J. L. SIMONSEN (J. Indian Inst. Sci., 1927, **9A**, 173—177).—See A., 1926, 1047.

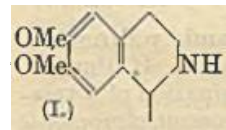
Yohimba alkaloids. II and III. G. HAHN and W. BRANDENBURG (Ber., 1927, **60**, [*B*], 669—679, 707—711; cf. A., 1926, 1263).—II. A solution of the residues from the technical isolation of yohimbine is rendered just alkaline with ammonia and the precipitate (*A*) is removed; the filtrate is evaporated to dryness, giving a residue *B*. The solution of the latter substance in the requisite quantity of ammonia is placed under diminished pressure at a temperature not exceeding 30°, whereby yohimbenic and *allo*yohimboaic acids are successively deposited. Complete separation of the two acids from one another is achieved by taking advantage of (*a*) the sparing solubility of yohimbenic acid hydrochloride in dilute, aqueous hydrochloric acid, (*b*) the behaviour of yohimbenic acid towards methyl or ethyl alcohol (*loc. cit.*), or (*c*) the sparing solubility of *allo*yohimboaic acid hydrochloride in methyl alcohol. Isolation of yohimboaic and *iso*yohimboaic acids from the residues is effected by esterification with ethyl alcohol and hydrogen chloride, removal of the sparingly soluble ethyl yohimboate hydrochloride, and separation of ethyl *iso*yohimboate from the filtrate. The precipitate *A* (see above) is treated with benzene and hydrogen chloride is passed into the solution. The bases are liberated from the precipitated hydrochlorides and hydrolysed with alcoholic potassium hydroxide. Yohimbenic acid and the ethyl esters of yohimboaic and *iso*yohimboaic acids are obtained from the solution by the methods just described. The following compounds are described in detail: allo*yohimbine*, $C_{21}H_{26}O_3N_2$ or $C_{22}H_{28}O_3N_2$, $[\alpha]_D^{20}$ −72·7° in pyridine (also *trihydrate*, m. p. 98—99°, and *monohydrate*, m. p. 135—140°), which is considered identical with the dihydroyohimbine of Warnat (A., 1926, 1263) [Warnat's nomenclature is criticised, since the relationship of the substance to yohimbine rests solely on a somewhat indefinite analysis]; allo*yohimbine hydrochloride*, decomp. 278—279°; allo*yohimboaic acid*, $C_{20}H_{24}O_3N_2,H_2O$, m. p. 248—250°, $[\alpha]_D^{20}$ −79·5° in pyridine (Warnat's dihydroyohimboaic acid), and its *hydrochloride*, $C_{20}H_{24}O_3N_2,HCl,H_2O$, m. p. 288—290° (decomp.); *ethyl* allo*yohimboate hydrochloride*; *iso*yohimboaic acid, $C_{20}H_{24}O_3N_2,H_2O$, decomp. 268—269°, $[\alpha]_D^{20}$ +147° in pyridine (also $+1{\cdot}5H_2O$); *iso*yohimbine, m. p. 239—240°, $[\alpha]^{20}$ +57·6° in pyridine, and its *hydrochloride*, m. p. 298—299° (decomp.); ethyl *iso*yohimboate, m. p. 243°.

III. Further analyses of "methylyohimbenic acid methylbetaine" (A., 1926, 1263) indicate the formula, $C_{21}H_{26}O_3N_2,4H_2O$, whence the substance must be regarded as *yohimbenic acid methylbetaine*. To yohimbenic acid and yohimbene the formulæ $C_{20}H_{24}O_3N_2,2H_2O$ and $C_{21}H_{26}O_3N_2$ are assigned. The compounds are thus isomeric with yohimbine, *allo*- and *iso*-yohimbine, and yohimboaic acid, respectively. The identity of Spiegel's *meso*yohimbine (A., 1916, i, 286) with *iso*yohimbine is confirmed (cf. Warnat, A., 1926, 1263), but the supposed identity of *iso*yohimbine with corynanthine (cf. Fourneau and Fiore, A., 1912, i, 49) cannot be maintained.

iso*Yohimbine hydrochloride* has $[\alpha]_D^{20}$ +103·8° in water. Yohimbine and *iso*yohimbine have $[\alpha]_D^{23}$ +84·11° and +57·6° in pyridine, whereas the corresponding acids have $[\alpha]^{20}$ +79° and +147° in the same solvent. Yohimbene has $[\alpha]_I^{18}$ +43·7° in pyridine [a negative value was previously (*loc. cit.*) reported erroneously]. The following compounds are new: *silver yohimbenate*; *yohimbenic acid hydrochloride*, m. p. 299—300°; the *perchlorate* of yohimbenic acid methylbetaine; *ethyl yohimbenate*, m. p. 250—251°, and its *hydrochloride*, decomp. 223—225°.

H. WREN.

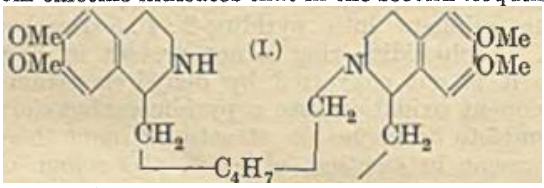
Ipecacuanha alkaloids. I. Constitution of emetine and cephæline. E. SPATH and W. LEITHE (Ber., 1927, **60**, [*B*], 688—702).—The possibility that emetine resembles palmatine in structure is discounted by the observation that it fails to yield hemipinic acid in addition to *m*-hemipinic acid when oxidised. The presence of a berberine-like complex is improbable, since it is oxidised to oxalic acid under conditions which cause the transformation of berberine sulphate into pyridine-2 : 4 : 5-tricarboxylic acid. A piperidine ring is not present in emetine, since it is not converted by dehydrogenation and subsequent oxidation into a pyridinecarboxylic acid. A complete berberine-like structure cannot therefore be present in emetine, although the colour of its dehydro-derivative indicates a close relationship. Since oxidation of emetine in faintly alkaline solution affords 1-keto-6 : 7-dimethoxy-1 : 2 : 3 : 4-tetrahydro-*iso*quinoline, the complex (I) must be present in the alkaloid. Since *N*-benzoylemetine is oxidised to 3 : 4-*dimethoxy*-6-β-*benzamidoethylbenzoic acid*, m. p. 172—173° (decomp.), the imino-group is present as such in the alkaloid. Since Carr and Pyman (J.C.S., 1914, **105**, 1591) obtained 6 : 7-dimethoxy*iso*quinoline-1-carboxylic acid by the oxidation of emetine, it appears either that an unusual instance of dehydrogenation of a dimethoxytetrahydro*iso*quinoline has been encountered or that the acid originates from a second nitrogenous complex. Evidence of the presence of a second tetrahydro*iso*quinoline group is obtained by the production of *m*-hemipinic acid from emetine in 65% of the amount derivable theoretically on the supposition of the presence of only one such nucleus, whereas, under similar conditions, palmatine and papaverine, which actually contain only one dimethoxy*iso*quinoline nucleus, give 34 and 28% of *m*-hemipinic and hemipinic acids and 25% of *m*-hemipinic acid, respectively. Further confirmation is obtained by treatment with permanganate of the residues left after the conversion of emetine into 1-keto-6 : 7-dimethoxy-1 : 2 : 3 : 4-tetrahydro*iso*quinoline (see above); the yield of *m*-hemipinic acid attains 96% (after allowance for the ketonic base). Contrary to the observations of Carr and Pyman (*loc. cit.*) and of Windaus and Herman (A., 1914, i, 721), emetine yields *m*-hemipinic acid in addition to 1-keto-6 : 7-dimethoxy-1 : 2 : 3 : 4-tetrahydro*iso*quinoline when oxidised.



Cephæline (of which emetine is the methyl ether)

is converted into cephæline *O*-ethyl ether, which appears to be oxidised by permanganate to a mixture of 1-keto-6 : 7-dimethoxy- and -7-methoxy-6-ethoxy-1 : 2 : 3 : 4-tetrahydro*iso*quinoline; the mixture could not be separated into its components, but its m. p. is raised by the addition of either of them. Further evidence in favour of this view is found in the production of *m*-hemipinic acid and the methyl ethyl ether of nor-*m*-hemipinic acid by more drastic oxidation.

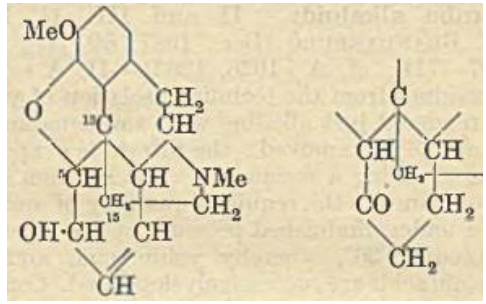
In the second phase of the Emde degradation of emetine, trimethylamine is produced, whereby the presence of a secondary, monocyclic nitrogen atom appears confirmed. In the third stage of the degradation, the second tertiary nitrogen atom is not completely eliminated, hydrocarbons being obtained in poor yield. Since emetine under these conditions is not separated into two approximately similar components, the second tertiary nitrogen atom cannot represent the sole point of union of the two *iso*quinoline complexes, and the production of 2 mols. of 1-keto-6 : 7-dimethoxy-1 : 2 : 3 : 4-tetrahydro*iso*quinoline from emetine indicates that in the second *iso*quinoline



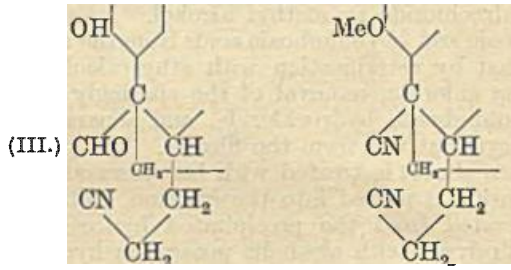
complex also a carbon chain is attached in position 1. The partial formula (I) is therefore suggested. Probably the tertiary nitrogen atom forms a portion of a piperidine ring. H. WREN.

Synthesis of oxyberberine and palmatine. R. D. HAWORTH, J. B. KOEPFLI, and W. H. PERKIN, jun. (J.C.S., 1927, 548—554).—Bromination of β-veratrylpropionic acid yielded β-6-*bromoveratrylpropionic acid*, m. p. 118—119°, which, when treated with sulphuric acid, formed 4-*bromo*-6 : 7-*dimethoxy*-1-*hydrindone*, m. p. 120—121°. From the iso*nitroso*-derivative, m. p. 236° (decomp.), of this hydrindone, 6-*bromo*-2-*carboxy*-3 : 4-*dimethoxyphenylacetonitrile*, m. p. (+H_2O) 98—100°, was obtained, and the *anhydride*, m. p. 151°, of this hydrolysed to 6-*bromo*-3 : 4-*dimethoxyhomophthalic acid*, m. p. 166—167°. This acid, debrominated (sodium amalgam) and treated with acetyl chloride, yielded the required 3 : 4-*dimethoxyhomophthalic anhydride* (I), m. p. 104—105°. The anhydride was condensed with β-piperonylethylamine, and the methyl ester of the resulting crude amic acid boiled with phosphorus oxychloride, forming oxyberberine. Similarly, palmatine was synthesised by condensing (I) with β-veratrylethylamine, forming N-β-*veratryl*-3 : 4-*dimethoxyhomophthalamic acid*, the methyl ester of which, when treated with phosphorus oxychloride, yielded *oxypalmatine*, m. p. 183°. Oxypalmatine was reduced electrolytically to tetrahydropalmatine, and this was oxidised by iodine to palmatine iodide. B. W. ANDERSON.

Morphine alkaloids. C. SCHOPF (Annalen, 1927, **452**, 211 267). **I. Constitution of morphine and codeïne.**—For the linking of the C^{15} atom, Gulland and Robinson's suggestion (J.C.S., 1923, **123**, 980, 989; A., 1926, 83) is confirmed as against the Knorr–Wieland formula (A., 1925, i, 1090, 1448), and the formula (I) for codeine is considered to be definitely proved. The oxime of dihydrocodeinone



(II) undergoes a Beckmann change when treated with cold thionyl chloride, giving an *iso*oxime (III), m. p. 196—198° [*picrate*, m. p. 207—208°; *acetyl* derivative, m. p. 225° (decomp.); *oxime*, m. p. 218—219°]. This is shown to be a cyano-aldehyde

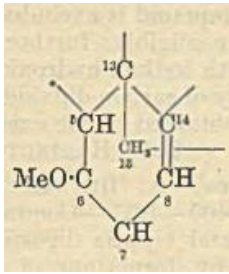
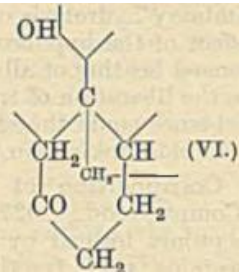


(Robinson structure), and not a cyano-ketone (Knorr–Wieland structure); the oxime of the methyl ether undergoes dehydration to a dinitrile which still contains intact the nitrogen ring, since by Hofmann degradation no loss of carbon atoms occurs. Any dehydration of the cyano-ketone (*cf.* dehydration of camphoroxime) would lead to fission of the nitrogen ring.

The *iso*oxime (III) is methylated by Rodionov's method with phenyltrimethylammonium hydroxide (A., 1926, 532) to form the *methyl ether*, $C_{19}H_{24}O_3N_2$ [base, amorphous; *hydriodide*, m. p. 249—250°; *picrate*, m. p. 221° (decomp.); *oxime*, amorphous]. The oxime of the methyl ether is converted by cold thionyl chloride or hot acetic anhydride into a *dinitrile* (IV) (*methiodide* sinters at 200°, melts partly at 203—204°, decomposes at 207°). By heating the methiodide with sodium hydroxide, there is obtained an oily *base*, $C_{20}H_{25}O_2N_3$ (*perchlorate*, m. p. 203—204°; *methiodide* non-crystalline), which is reduced by hydrogen and palladium to a *dihydro*-derivative (*perchlorate*, m. p. 197—198°; *methiodide*, m. p. 190°).

II. Constitution of thebaine [with L. WINTERHALDER].—Thebaine, the methyl ether of an enolic codeinone, gives on reduction a mixture of products from which for the first time a pure crystalline tetrahydrothebaine is now isolated. This is found to be identical with Mannich's dihydromorphine dimethyl ether (A., 1917, i, 473). The presence of two double linkings in thebaine is thus demonstrated, since a cyclic bridge linking (cf. Wieland and Kotake, A., 1925, i, 1090, 1448) would not be reduced under the mild conditions employed, and the Knorr–Robinson

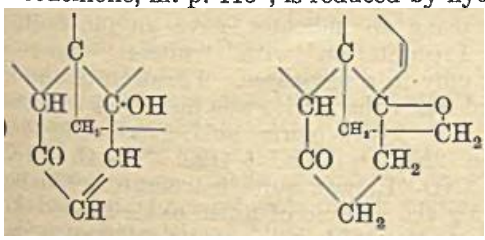
formula for thebaine (V) is established. The mechanism of the reduction is discussed. Dihydrothebaine,

(V.)   (VI.)

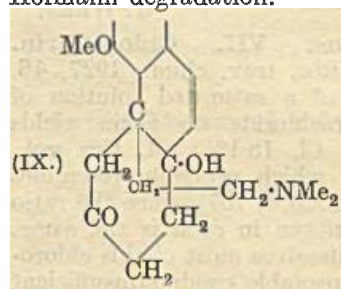
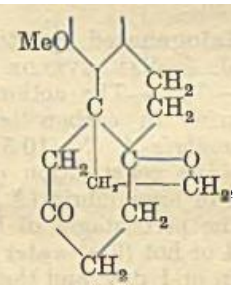
first formed by reduction of $\Delta^{8(14)}$, is further reduced only under energetic conditions, giving dihydrothebaine (VI), the chain $-O\cdot CH\cdot CH{:}CH-$ being analogous with a system of conjugated double linkings. Dihydrothebainone also results directly from thebaine, 1 : 6-reduction in the conjugated system $C^{14}-C^{6}-O-$ being followed by 1 : 4-hydrogenation in the system $C^{5}-C^{8}$ and hydrolysis of the methoxyl. Tetrahydrothebaine is formed by 1 : 4-reduction in the system $C^{14}-C^{6}$, followed by reduction of the resulting $\Delta^{7(8)}$. In every case hydrogenation of C^{14} occurs, and indications of the production of stereoisomeric ketones are obtained when palladium–calcium carbonate is the catalyst.

For the isolation of the reduction products, the ethereal solution of the mixed bases is shaken with alkali to remove some dihydrothebainone, m. p. 130—140°, and then deposits dihydrothebaine, m. p. 160—162° (picrate, m. p. 238°). The ether residue with hydroxylamine yields dihydrothebainoneoxime hydrochloride, m. p. 305°, and the ketone-free bases are treated with hydrochloric acid to convert dihydrothebaine into dihydrocodeinone, removed as oxime, m. p. 259°. The ether-soluble residues contain in 20% yield tetrahydrothebaine, m. p. 83°, after purification as picrate, m. p. 222°, or as hydrochloride, m. p. 115—116° ($+H_2O$). Tetrahydrothebaine methiodide melts at 135—140° ($+H_2O$) or 212° (anhyd.), and is probably a stereoisomeride of Freund and Speyer's product, m. p. 244—246° (A., 1921, i, 125).

III. Constitution and configuration of hydroxycodeinone [with F. Borkowsky].—The structure (VII) assigned by Gulland and Robinson (*loc. cit.*) to hydroxycodeinone is supported by known data and by further experimental evidence. Hydroxydihydrocodeone (VIII) (Freund and Speyer, A., 1917, i, 217), obtained in 33% yield by Hofmann degradation of hydroxydihydrocodeinone, gives a *phenylhydrazone*, m. p. 228°. The intermediate hydroxyde-*N*-methyldihydrocodeinone, m. p. 115°, is reduced by hydrogen

(VII.)  (VIII.)

and palladium to the corresponding *dihydro*-compound, m. p. 136—137° (*methiodide*, m. p. 280°), which by Hofmann degradation yields *hydroxytetrahydrocodeone* (as VIII, without double linking), m. p. 150—153°, obtained also by palladium–hydrogen reduction of hydroxydihydrocodeone. Reduction of hydroxydihydrocodeinone with aluminium amalgam, followed by methylation with diazomethane, methyl sulphate, or phenyltrimethylammonium hydroxide, gives hydroxydihydrothebainone methyl ether (Freund and Speyer, *loc. cit.*), m. p. 151—153° (*methiodide*, m. p. 206—208°), which by successive Hofmann degradations yields first a *base*, $C_{20}H_{27}O_4N$ (IX), m. p. 133—135° (*methiodide*, m. p. 209°; *di* compound, m. p. 83—85°), and then *hydroxydihydrothebaone methyl ether*, m. p. 87—89° (obtainable also by methylation of hydroxydihydrothebaone with methyl sulphate), converted by means of hydrogen and palladium into the *tetrahydromethyl ether* (X), m. p. 74—76°. The latter is also obtained by reduction of the base (IX) to its *dihydro*-compound, m. p. 83—85° (*methiodide*, amorphous, m. p. 95—100°), followed by Hofmann degradation.

(IX.)   (X.)

Hydroxyde-*N*-methyldihydrothebainone (Freund and Speyer, *loc. cit.*), m. p. 239—240°, is converted by dehydration with cold hydrobromic acid into the *hydrobromide*, m. p. 230—231°, of a base, $C_{19}H_{23}O_3N$, which is reduced by hydrogen and palladium to a *tetrahydro*-derivative, m. p. 135—137° (as base). The results of the determination of reactive (hydroxylic) hydrogen in a number of ketones and "desbases" of the hydroxycodeinone series by Zerewitinov's method with magnesium methyl iodide are in accord with the formulæ assigned. C. Hollins.

Colour reactions of *apo*morphine and its detection in presence of morphine. J. von Miko (Pharm. Zentr., 1927, 68, 193—195).—One drop of aqueous ammonia added to 5 c.c. of aqueous *apo*morphine produces a green colour; subsequent shaking with chloroform gives a violet lower layer. A distinct pink tinge in the chloroform is given by 0·00002 g. of *apo*morphine in 1 c.c. of 1% aqueous morphine. *apo*Morphine is said to be formed during the sterilisation of morphine on the water-bath; this is not the case. B. W. Anderson.

Opium alkaloids. VII. Synthesis of laudanine and laudanidine. E. Spath and A. Burger (Monatsh., 1926, 47, 733—740).—A second synthesis of laudanine (cf. A., 1922, i, 568) has now been based on Pictet's synthesis of laudanosine (A., 1900, i, 685; 1909, i, 323). The latter is prepared in 70% yield by electrolytic reduction of a solution of crude papaverine methosulphate in dilute sulphuric acid, using a lead cathode. The racemic laudanosine is partly hydrolysed by heating in a sealed tube with

10 times its weight of hydrochloric acid (*d* 1·19) for exactly 20 min. at 100°. The product is extracted with sodium hydroxide, when laudanosine (50%) remains undissolved, whilst the solution contains a mixture of phenolic bases from which laudanine (12%) may be isolated. *d*- and *l*-Laudanosine are converted in the same way into *d*-laudanine, $[\alpha]_D^{15}$ +93·5°, and *l*-laudanine, $[\alpha]_D^{15}$ −94·8°, the latter being identical with laudanidine. Attempts to resolve laudanine directly were unsuccessful.

H. E. F. NOTTON.

Opium alkaloids. VIII. Synthesis of papaverine. E. SPATH and A. BURGER (Ber., 1927, **60**, [*B*], 704—706).—The final step in Pictet and Gams' synthesis of papaverine (cf. A., 1909, i, 671) is accomplished by the conversion of dihydropapaverine into papaverine by the action of palladised asbestos (40%) at 200° in presence of air. Under similar conditions, tetrahydropapaverine also yields papaverine which is only slightly affected by the reagent at 225°.

H. WREN.

Halogenated proteins. VII. Chlorofibrin. A. J. J. VANDEVELDE (Rec. trav. chim., 1927, **46**, 133—136).—The action of a saturated solution of chlorine in carbon tetrachloride on fibrin yields *chlorofibrin*-A (N, 10·5; Cl, 18·1%) (cf. this vol., 65), the constitution of which probably resembles that of bromofibrin (A., 1925, i, 707), since the ratio of the percentages of halogen in each is the same. Cold or hot (61°) water dissolves most of this chlorofibrin in 1 day, and the insoluble residue (insufficient amount obtained for analysis) is scarcely acted on in 15 days. This hydrolysis is due to the conversion of about 90% of the chlorine into an ionised condition, the strong acid converting the fibrin into soluble products. Chlorofibrin-*A* is not decomposed by ether, but when left in contact for 1 day with 0·5*N*-potassium hydroxide it dissolves, and acetic acid precipitates *chlorofibrin*-Ac in small quantity (N, 12·2; Cl, 10·5%). The filtrate contains ionised chlorine to the extent of 83·2% of the total original chlorine, together with a little un-ionised chlorine. Alcohol converts chlorofibrin-*A* into *chlorofibrin*-Ad (N, 11·4; Cl, 16·6%), and the filtrate contains ionised chlorine to the extent of 60·4% of the total original chlorine, but no un-ionised chlorine.

J. M. GULLAND.

Unsaturated dipeptide-anhydrides, and dehydration of amino-acid derivatives. M. BERGMANN (Z. physiol. Chem., 1927, **165**, 167—169).—A question of priority.

C. R. HARINGTON.

Tetrapeptide from gliadin. R. NAKASHIMA (J. Biochem. [Japan], 1926, **6**, 55—60).—A substance, m. p. 283—285°, obtained as colourless needles (1 g.) in a peptic digestion of gliadin (16 g.) contains 4·3 mols. of water to 1 mol. of a tetrapeptide apparently consisting of 1 mol. of tyrosine, 2 mols. of glutamine, and 1 mol. of glutamic acid. Of the total nitrogen content of 14·58%, 4·93% is ammonia-nitrogen, and 9·94% is amino-nitrogen.

CHEMICAL ABSTRACTS.

Constitution of the proteins. III. S. GOLDSCHMIDT (Z. physiol. Chem., 1927, **165**, 149—154).—Under no conditions could the results of Brigl and Held (A., 1926, 630) regarding the oxidation of carbonyldiglycylglycine by hypobromite be confirmed, and, if the experiment be so conducted that preliminary hydrolysis of the compound is excluded, the effect of the hypobromite is negligible; further, prolonged heating of albumin with sodium hydroxide led to the liberation of traces only of carbon dioxide. No evidence could therefore be obtained of the existence of ureide linkings in protein.

C. R. HARINGTON.

Composition of peptones. A. BLANCHETIERE (Compt. rend., 1927, **184**, 405—407).—Commercial peptones formed by peptic and tryptic digestion of proteins were fractionated by formation of carbamates, and 14—33% of the total nitrogen content of the peptones is considered to be present as diketopiperazines.

L. F. HEWITT.

Decomposition of soya-bean protein. III. Decomposition with sodium hydroxide. IV. M. MASHINO (J. Soc. Chem. Ind. Japan, 1926, **29**, 248—251, 252—254).—III. Soya-bean protein obtained from four different sources was decomposed by treating with 19·65% sodium hydroxide at 100° for 0·5—12 hrs. and the amounts of ammoniacal and amino-nitrogen liberated were determined. The amount of ammonia liberated increases during the first 4 hrs., but then remains almost constant. Ammoniacal nitrogen (4—12 hrs.) is 16·5, 18·6, 19·5, and 17% in the four cases, respectively, of the total nitrogen. The rate of decomposition of the protein is nearly the same for the four samples. Amino-nitrogen (12 hrs.) is 65·6, 68, 68·6, and 67·6% in the four cases, respectively, of the total nitrogen.

IV. A discussion of the above and previous work (A., 1926, 1048). The violet colour of the biuret reaction for soya-bean protein is apparently related to ammonia in protein. When all the ammonia is evolved, no violet colour is observed. The free carboxyl group in the protein molecule may be present in combination with an amino-group. The rate of decomposition of soya-bean protein is little affected by pre-treatment with superheated steam. Oil-extracted soya-bean cake is therefore used for producing amino-acids.

K. KASHIMA.

Determination of nitrite formed by replacement of nitro-groups in presence of highly-coloured reaction products. R. H. CLARK and N. M. CARTER (Trans. Roy. Soc. Canada, 1926, [iii], **20**, III, 429—438).—An attempt has been made to find a method of determining the amount of nitrite formed when nitro-groups in organic compounds are replaced by hydroxyl or ethoxyl groups. Reduction to nitric oxide with mercury and sulphuric acid or to ammonia always gave very low results. Direct titration of the excess of alkali, either conductometrically or using an indicator, gave an indefinite end-point. Precipitation with "nitron" was satisfactory only in a few cases. Titration of the iodine liberated when the nitrite was mixed with potassium iodide and hydrochloric acid, according to the equation $2NaNO_2 + 2KI + 4HCl = 2NaCl + 2KCl + 2H_2O + 2NO + I_2$, was quite inaccurate. Finally, by measuring the volume of nitric oxide formed in this reaction, fairly satisfactory results (94% and upwards of the theoretical values) were obtained.

R. CUTHILL.

Determination of formic acid. F. Oberhauser and W. Hensinger (Z. anorg. Chem., 1927, **160**, 366—372).—Formic acid may be determined bromometrically by treating the solution with sodium acetate or sodium hydrogen carbonate in excess, then with a standard solution of bromine in *N*-potassium bromide until a permanent yellow colour remains, adding a known excess of arsenious acid to discharge this colour, acidifying with hydrochloric acid, and titrating the excess of arsenious acid with the bromine solution, using indigo-carmine–styphnic acid as indicator. In absence of sodium acetate, the hydrobromic acid formed exerts a marked retarding effect on the reaction between bromine and formic acid, even in direct sunlight. Mineral acids also have a retarding influence on the reduction of mercuric chloride to mercurous chloride by formic acid, but this may be overcome as follows: The formic acid solution is treated with at least a 50% excess of mercuric chloride and sufficient to give a 0·5% solution of the mercury salt, followed by sodium hydroxide solution drop by drop until a faint opalescence persists; 10 c.c. of saturated sodium acetate solution are added and the mixture is boiled for 2 hrs. in a water-bath. The precipitated mercurous chloride is collected, washed, and dissolved in an excess of standard bromine solution, the excess being determined as described above. A. R. Powell.

Micro-determination of methoxyl. A. Friedrich (Z. physiol. Chem., 1927, **163**, 141—148).—A 3% thiosulphate solution is found preferable to the red phosphorus suspension, and may contain cadmium sulphate for the simultaneous absorption of hydrogen sulphide. The low results are due to incomplete reaction between alkyl iodide and silver nitrate, and it is recommended that for micro-determinations a constant volume (2 c.c.) of alcoholic silver nitrate be used and 0·12 mg. be added to the weight of silver iodide. Results within 0·1% of the theoretical are then obtained. Complete dissolution of the substance is advisable. C. Hollins.

Phenol tests. II. Nitrous acid tests. H. D. Gibbs (J. Biol. Chem., 1927, **71**, 445—459).—The colour produced by the action of nitrous acid on phenol is due to the secondary condensation of the *p*-nitrosophenol, which is the primary product of the reaction; the colour development is greatly accelerated by the presence of mercury salts (*e.g.*, with Millon's reagent). The optimum reaction for the colour development is p_H 4—5. Whilst *para*-substituted phenols give similar colour reactions, a somewhat longer time and higher temperature are required for the colour development. The dissociation value, pk_a, for *p*-nitrosophenol, determined spectrophotometrically, is 6·4. C. R. Harington.

Determination of uric acid. A. Boivin.—See this vol., 488.

Determination of sulphur in proteins. L. C. Maxwell, F. Bischoff, and N. R. Blatherwick.—See this vol., 486.

Biochemistry.

Gasometric determination of small amounts of carbon monoxide in blood and determination of blood volume. D. D. Van Slyke and F. S. Robscheit-Robbins (J. Biol. Chem., 1927, **72**, 39—50).—The method of Harington and Van Slyke (A., 1924, ii, 872) has been adapted to the determination of small amounts of carbon monoxide in blood; by the use of this technique, the determination of blood volume by the carbon monoxide method may be carried out after saturation of only 5—10% of the total hæmoglobin with carbon monoxide. Experiments on dogs, in which the carbon monoxide was introduced by intravenous injection of a small amount of blood saturated with the gas, indicate that the blood volume may be determined by this method with an error of 5%. C. R. Harington.

Physical chemistry of proteins. VI. Activity coefficients of the ions in certain oxyhæmoglobin solutions. E. J. Cohn and A. M. Prentiss (J. Gen. Physiol., 1927, **8**, 619—639).—The effect of a neutral salt such as magnesium sulphate on the solubility of oxyhæmoglobin is shown to be similar to its effect on a sparingly soluble salt (cf. Bronsted and Petersen, A., 1922, ii, 199), and hence the effect is presumably due to the change in the activity of the oxyhæmoglobin caused by the presence of the neutral salt. It is shown that the solubility of oxyhæmoglobin in phosphate solutions is given by $\log S/S_0 - 2\sqrt{\mu}/(1+1{\cdot}5\sqrt{\mu})$, where S is the solubility when the ionic strength is μ and S_0 is the solubility in absence of salt (calculated to be 12·2, 11·2, and 13·1 g. per litre at p_H 6·4, 6·6, and 6·8, respectively). W. O. Kermack.

Blood bilirubin. G. Förster and B. Förstner (Magyar Orvosi Arch., 1926, **27**, 455—465).—There is an individual, physiological variation in the bilirubin content of human blood of 0·2—1·0%. Bilirubin in the serum is oxidised in diffused light, hence the determination should be made soon after withdrawing the sample. Chemical Abstracts.

Relationship between chemical composition of blood and lymph in the dog. R. M. Arnold and L. B. Mendel (J. Biol. Chem., 1927, 72, 189—211).—In the normal dog, the protein content of the lymph is considerably lower than that of the blood-serum, but the diffusible constituents of the two fluids are closely similar in amount; changes induced in the composition of the blood-serum, by abnormal physiological conditions, are immediately reflected by parallel changes in the lymph; there must therefore exist free interchange of diffusible constituents between the two fluids. C. R. Harington.

Characterisation and determination of oxalate in the blood and in the cerebrospinal fluid. C. O. Guillaumin (Bull. Soc. Chim. biol., 1927, 9, 247—262).—Methods previously described for the

determination of oxalate in the blood and in the cerebrospinal fluid are shown to contain sources of error, and a modified method is described. The concentration of oxalate in the serum and cerebrospinal fluid of normal individuals is less than 2 mg. per litre, whilst in pathological cases the blood oxalate never exceeds 40 mg. per litre. It is doubtful whether the crystals described by Rodillon (Bull. Sci. Pharmacol., 1920, 249) in the cerebrospinal fluid really consist of calcium oxalate. W. O. KERMACK.

Action of blood on sulphides. W. DENIS and L. REED (J. Biol. Chem., 1927, **72**, 385—394).—Intravenous or parenteral injection of sodium sulphide is followed, in dogs, by a rise in the inorganic sulphate content of the blood, which is particularly marked in absence of renal function, but by no change in the neutral sulphur. Hydrogen sulphide is therefore presumably detoxicated in the animal organism by oxidation to sulphuric acid. C. R. HARINGTON.

Determination of carbamide in blood. H. CHABANIER, M. LEBERT, and R. WAHL (Bull. Soc. Chim. biol., 1927, **9**, 277—279).—The authors have been unable to confirm the findings of Pagel (A., 1924, ii, 575) and Pechon (A., 1926, 763) to the effect that the concentrations of carbamide may be markedly different in consecutive samples of blood drawn from the same individual. W. O. KERMACK.

Adrenaline content of blood. H. SCHLOSSMANN (Arch. exp. Path. Pharm., 1927, **121**, 160—203).—The hydrodynamic resistance of the vessels of the isolated dog's ear, perfused at a constant pressure of 20—30 cm. of water, is used as a very sensitive measure of the adrenaline content of the perfusing liquid. Results are given for the adrenaline content of arterial blood in the normal state and after excitation of the suprarenal in various ways. Asphyxia and injection of nicotine produce an adrenaline concentration as high as 1 part in 50×10^6 parts.
E. A. LUNT.

Effect of neutral salts on the acid charge of certain substances. L. AMBARD, F. SCHMID, and M. ARNOVLYEVITCH (Bull. Soc. Chim. biol., 1927, **9**, 236—246).—A theoretical discussion of the effects of neutral salts on the alkaline reserve in the blood, the rate of hydrolysis of sucrose by acid, the precipitation of protein, the colour assumed by an indicator in solution, the activity of enzymes, and on the rate of lung-ventilation leads to the conclusion that all these effects can be traced to the same cause, viz., an increased appropriation of acid by substances in solution after the addition of neutral salts.
W. O. KERMACK.

Gas and electrolyte equilibria in the blood. IX. Distribution of electrolytes between transudates and serum. A. B. HASTINGS, H. A. SALVESEN, J. SENDROY, and D. D. VAN SLYKE (J. Gen. Physiol., 1927, **8**, 701—711).—The electrolyte content of serum transudates differs from that of the serum itself in a manner explicable on the assumption of the existence of the Donnan membrane equilibrium between the two fluids. When serum and salt solutions approximating to œdema fluid in composition are equilibrated across a collodion membrane, the distribution of electrolytes becomes similar to that between serum and œdema fluid *in vivo*.
W. O. KERMACK.

Blood-sugar of cod, sculpin, and pollock during asphyxia. M. L. MENTEN (J. Biol. Chem., 1927, **72**, 249—253).—The normal fasting blood-sugar concentration of the above fish was from 0·014 to 0·04%; both under normal and asphyxial conditions, however, this value was greatly influenced by the previous feeding. C. R. HARINGTON.

Micro-determination of sugar and reducing substances in blood. V. LAPA (Bull. Soc. Chim. biol., 1927, **9**, 310—323).—Treatment of blood or plasma with mercuric acetate in presence of sodium hydrogen carbonate precipitates, not only proteins, but also all nitrogenous components. The reducing power may then be determined by any of the ordinary micro-methods. The reducing power after fermentation is independent of the method used and varies from 3 to 6 mg. (as dextrose) per litre.
W. O. KERMACK.

Determination of small quantities of sugar. Application to blood and to other body-fluids. A. BAUDOUIN and J. LEWIN (Bull. Soc. Chim. biol., 1927, **9**, 280—309).—To 15 c.c. of the neutral solution to be examined 1 c.c. of a solution containing 3·60 g. of mercuric iodide and 12 g. of sodium iodide per 100 c.c. and 1 c.c. of *N*-sodium hydroxide solution are added. The mixture is heated for 3 min. on the boiling water-bath and then cooled, and there is then added 1 c.c. of a solution containing 1·783 g. of potassium iodate dissolved in sufficient 5% sulphuric acid to make the volume to 1 litre. The iodine liberated converts the mercury formed during the heating into mercuric iodide, and the excess of iodine is then titrated with sodium thiosulphate.
W. O. KERMACK.

Blood-sugar. Fractionation of the reducing substances in blood-filtrates. B. SJOLLEMA (Biochem. Z., 1927, **182**, 453—459).—Blood-filtrates obtained by the method of Folin and Wu contain, besides dextrose, an amount of reducing substance much greater than the content of reducing non-sugar substances such as uric acid. A method is described for the determination of dextrose in presence of very small amounts of disaccharides (lactose, maltose). When such sugar solutions are shaken with animal charcoal and a little acetic acid is added, dextrose remains in solution, whereas the disaccharide is almost completely adsorbed. If, in place of acetic acid, the solution is shaken with ether, the disaccharide remains in solution. P. W. CLUTTERBUCK.

Analytical method of establishing the "nitrogen formula" for blood-serum. M. LAUDAT (Bull. Soc. Chim. biol., 1927, **9**, 137—148).—Detailed methods are described for establishing the "nitrogen formula" (cf. Widal and Laudat, Compt. rend. Soc. Biol., 1926, **95**, 1233), the determinations including those for total non-protein nitrogen, carbamide, uric acid, creatine, creatinine, ammonia, and amino-acids, and the undetermined nitrogen. Well-known methods, with certain modifications, are recommended, and this method of analysis has proved useful in studying the retention of nitrogenous sub-

stances in renal impermeability. The amount of serum required for the complete analysis is not greater than 15 c.c. A. WORMALL.

Thiasine ; its structure and identification with ergothioneine. E. B. NEWTON, S. R. BENEDICT, and H. D. DAKIN (J. Biol. Chem., 1927, **72**, 367—373). —Thiasine (A., 1926, 421) gives the Pauly reaction, yields trimethylamine on warming with potassium hydroxide, and reduces permanganate in the cold; the sulphur is readily removed by oxidation with ferric chloride, although it is stable towards alkali. Re-determination of the sulphur content indicated 13·4%; the substance was therefore suspected to be identical with ergothioneine (cf. Tanret, A., 1909, i, 671), and the identity was confirmed by direct comparison, and by the identity of the behaviour of the substance with that described by Barger and Ewins (J.C.S., 1911, **99**, 2336) for ergothioneine. The compound (which it is proposed to name thioneine) has been isolated also from human blood (cf. Eagles and Johnson, this vol., 369). C. R. HARINGTON.

Non-protein sulphur compounds of blood. I. Sympectothion. G. HUNTER and B. A. EAGLES (J. Biol. Chem., 1927, **72**, 123—132).—Modifications are described in the method of isolation of the compound previously obtained by the authors (A., 1926, 85) from blood; this compound is now shown to contain sulphur, and is named sympectothion, the formula suggested being $C_{18}H_{32}O_5N_6S_2$; it has $[\alpha]_D^{17\cdot5}$ +115°, the previously recorded value being in error. The possible relationship of the compound to the thiasine of Benedict and others (A., 1926, 421) is discussed (cf. preceding abstract). C. R. HARINGTON.

Non-protein sulphur compounds of blood. II. Glutathione. G. HUNTER and B. A. EAGLES (J. Biol. Chem., 1927, **72**, 133—146).—A substance apparently identical with glutathione has been isolated from blood-corpuscles by a modification of the original method of Hopkins (A., 1921, i, 635); colorimetric determinations indicate the presence of about 100 mg. of this substance per 100 c.c. of red corpuscles. C. R. HARINGTON.

Measurement of hæmolysin. C. B. COULTER (J. Gen. Physiol., 1927, **10**, 541—544).—A method is described for the measurement of hæmolysin concentration, the principle of which is to compare under standard conditions the percentage of hæmolysis produced by a given amount of the unknown with that produced by varying amounts of a standard hæmolysin solution. W. O. KERMACK.

Protein associated with hæmolysin in rabbit-serum and -plasma. C. B. COULTER (J. Gen. Physiol., 1927, **10**, 545—550).—The hæmolysin of immune serum is associated with the water-insoluble euglobulin. Its activity is retarded by the presence in the solution of fibrinogen. Hæmolysis and hæmagglutinin appear to be distinct entities, since the activity of the former is destroyed, and that of the latter apparently increased by extraction with alcohol. W. O. KERMACK.

Hæmolysis by the photo-sensitising action of hæmatoporphyrin. R. FABRE and H. SIMONNET (Compt. rend., 1927, **184**, 707—709).—Lecithin freed from cholesterol by the method previously described (A., 1926, 1283), when irradiated in presence of hæmatoporphyrin by means of a mercury-vapour lamp for 60 min., acquires hæmolytic powers towards the red cells of the dog. Partial separation of the hæmolysing product has been effected by alcohol–ether fractionation. R. BRIGHTMAN.

Unscaled fibres. A. T. KING (Biochem. J., 1927, **21**, 434—436).—A method has been devised for the mechanical removal of the scales or outer layer of wool fibres in such a way as to leave the cortex intact. It consists essentially in drawing the fibre across the edge of a suitable glass plate, or over a series of such plates. The effectiveness of the method is illustrated by photomicrographs of wool fibres in various stages of scale removal. S. S. ZILVA.

Distribution of unsaturated fatty acids in tissues. II. Voluntary muscle of the ox. W. R. BLOOR (J. Biol. Chem., 1927, **72**, 327—343).—Figures are given for the distribution of lipins in various voluntary muscles and in the heart-muscle of the ox. The content of phospholipins, unsaponifiable matter, and cholesterol was highest in the most active muscles; a similar relationship was not observed with respect to the glycerides. Cholesterol esters are often absent from muscle, and, when present, are found in small amounts only. Emphasis is laid on the relationship of the phospholipin content to the mitochondria of muscle-cells, and the probable role of the phospholipins as constant constituents of protoplasm is discussed. C. R. HARINGTON.

Ovary. XII. Fatty acids of lecithin from corpus luteum. M. C. HART and F. W. HEYL (J. Biol. Chem., 1927, **72**, 395—402; cf. this vol., 69, 168). —The lecithin–cadmium chloride compound obtained from the acetone extract of corpus luteum yielded, on hydrolysis, 49·4% of fatty acids, of which 17% was palmitic, 26% stearic, 22% oleic, 26% linoleic, and 7% arachidonic acid; there was also obtained 2% of an acid, $C_{20}H_{34}O_2$, the presence of which had been previously observed in the neutral fat fraction, and for which the name *ovarenic acid* is now proposed. The above figures are similar to those previously obtained for the neutral fat, which supports the hypothesis that a function of the corpus luteum is to maintain a supply of the labile phospholipins which are required during pregnancy. C. R. HARINGTON.

Structure of the histone of the thymus. III. Acid- and base-binding power after peptic digestion. K. FELIX and A. HARTENECK (Z. physiol. Chem., 1927, **165**, 103—120).—Peptic digestion of the histone of the thymus causes an equal increase in acidic and basic groups and an equal increase in free amino-nitrogen and in formaldehyde-titratable carboxyl groups. The acidic groups liberated appear to be entirely carboxyl groups; the basic non-amino-groups set free probably belong to the guanidine group of arginine; this hypothesis is supported by the low figure for the increase in the carboxyl groups titratable in alcohol compared with the increase in base-binding capacity. No ammonia could be detected. Pepsin, therefore, apparently splits acid–basic linkings. After preliminary digestion of the

histone with trypsin, pepsin caused no further increase in acid- or base-binding power, but the nitrogen which could be methylated increased in amount.

C. R. HARINGTON.

Crystals of Charcot, Leyden, Böttcher, and Neumann. F. WREDE, F. BOLT, and E. BUCH (Z. physiol. Chem., 1927, **165**, 155—166).—The crystals described by the above workers (Compt. rend., 1853, 3; Arch. Anat. und Physiol., 1872, 54, 324; *ibid.*, 1865, **32**, 525; Arch. mikr. Anat., 1866, **2**, 508) were almost certainly those of spermine phosphate.

C. R. HARINGTON.

Glutathione. G. HUNTER and B. A. EAGLES (J. Biol. Chem., 1927, **72**, 147—166).—By a method similar in principle to that of Hopkins (A., 1921, i, 635), there was isolated from yeast and from liver a sulphur-containing peptide which is regarded as glutathione; the product from liver was contaminated with cystine, but was otherwise similar to that from yeast and from blood (cf. this vol., 477). The material agreed with that of Hopkins (*loc. cit.*) and with the compound synthesised by Stewart and Tunnicliffe (A., 1925, i, 795) in its optical rotation, but differed from it in possessing a higher content of nitrogen and a lower content of sulphur. The preparations contained total N 11·5—12·0, amino-N 7·8—7·9, S 8·85—10·27%. On hydrolysis, the amino-nitrogen was increased by one half. The optical rotation after reduction was $[\alpha]_D$ −4·74°; it is thought that the completely reduced substance may be dextrorotatory. On the basis of the above results, the authors deduce the presence of a third amino-acid (? serine) in ester combination in the glutathione molecule; the direct evidence adduced by Hopkins (*loc. cit.*) for the constitution of glutathione is questioned on the ground of the present authors' inability to effect a sharp separation of glutamic acid hydrochloride from cystine dihydrochloride after hydrolysis of their products.

C. R. HARINGTON.

Isolation of glutathione. F. G. HOPKINS (J. Biol. Chem., 1927, **72**, 185—187).—Hunter and Eagles (cf. preceding abstract) have omitted to discuss the evidence in favour of the accepted constitution of glutathione which is afforded by the synthesis of the compound by Stewart and Tunnicliffe (A., 1925, i, 795); the sulphur in glutathione is very much more labile than that in cystine; loss of sulphur at some stage in the isolation may therefore explain the results of Hunter and Eagles.

C. R. HARINGTON.

Colorimetric determination of cystine and glutathione. G. HUNTER and B. A. EAGLES (J. Biol. Chem., 1927, **72**, 177—183).—The method of Folin and Looney (A., 1922, ii, 539) for the colorimetric determination of cystine has been modified by the substitution of sodium hydroxide for sodium carbonate as the necessary alkali; the modified method is applicable also to the determination of glutathione, which yields 0·464 times the depth of colour given by the same weight of cystine.

C. R. HARINGTON.

Cystine in liver. G. HUNTER and B. A. EAGLES (J. Biol. Chem., 1927, **72**, 167—175).—Preparations of glutathione obtained from liver showed a high content of sulphur and a high specific rotation; this was found to be due to contamination with free cystine, which must therefore occur as such in the liver. The possible relationship of this observation to the physiological synthesis of taurocholic acid, and to the occurrence of cystinuria, is discussed.

C. R. HARINGTON.

Micro-volumetric determination of sulphur in biological fluids. B. POHORECKA-LELESZ (Bull. Soc. Chim. biol., 1927, **9**, 263—276).—Sulphate is precipitated as benzidine sulphate which is titrated in boiling distilled water, in presence of phenol-red, with 0·02*N*-sodium hydroxide solution. The method may be applied for the determination of sulphate in body-fluids, only 0·5 c.c. of urine or 5 c.c. of serum being required, and also for the determination of total sulphur in such fluids if the sulphur is first oxidised to sulphate.

W. O. KERMACK.

Normal excretion of zinc in urine and fæces of man. K. R. DRINKER, J. W. FEHNEL, and M. MARSH (J. Biol. Chem., 1927, **72**, 375—383).—The average daily excretion of zinc by the adult human is 0·89 mg. in the urine and 9·8 mg. in the fæces. Ingestion of a single meal rich in zinc causes an immediate and great increase in the fæcal excretion of zinc, which may persist for 2—3 days; the urinary excretion of zinc is not perceptibly affected.

C. R. HARINGTON.

Micro-determination of ammonia in urine. J. WEBER and W. KRANE (Z. physiol. Chem., 1927, **165**, 45—52).—The ammonia is precipitated with Nessler's reagent or with sodium cobaltinitrite and alcohol; the ammonia is liberated from the precipitate, in the first case with sodium hydroxide and potassium sulphide, and in the second case with sodium hydroxide alone, steam-distilled into excess of standard acid, and determined by titration. The method is applicable to quantities of ammonia of 0·5 mg. and upwards.

C. R. HARINGTON.

Determination of oxalic acid in urine by means of the rocking-extraction method of Widmark. C. G. HOLMBERG (Biochem. Z., 1927, **182**, 463—469).—Widmark's method (Skand. Arch. Physiol., 1926, 84, 61) for the determination of urinary benzoic acid is adapted to the determination of oxalic acid in urine.

P. W. CLUTTERBUCK.

Effect of light on uroporphyrin. B. T. SQUIRES (Biochem. J., 1927, **21**, 437—440).—Over the p_H range 6·2—8·2, there is a differential fading which reaches a maximum at about p_H 7·3. The rate of the general fading of uroporphyrin solutions is greater in the case of those containing crude uroporphyrin than in those containing the purified compound. The fading of crude uroporphyrin is in part associated with the presence of oxygen; this is not the case with pure uroporphyrin. As uroporphyrin solutions fade, there is no change in the positions of the absorption bands, which simply fade away. Within the above range of p_H, the appearance of "Kalilichtreaktion" band described by Schumm at 461 $\mu\mu$ could not be detected. On exposure of crude or purified uroporphyrin solutions in quartz tubes to ultra-violet light, a general fading irrespective of p_H is obtained.

S. S. ZILVA.

Iron in nutrition. IV. Correction of nutritional anæmia with ash of plants and animal

tissues and with soluble iron salts. E. B. HART, C. A. ELVEJHEM, J. WADDELL, and R. C. HERRIN (J. Biol. Chem., 1927, 72, 299—320; cf. A., 1925, i, 1354).—The nutritional anæmia which occurs in young rats on a diet of whole milk and ferric oxide can be cured by the addition of the ash, or an alcoholic extract, of lettuce or cabbage; spleen marrow and an alcoholic extract of maize were efficient supplements, but the ash of these substances was not so. Pure ferrous sulphate had no effect, although a commercial sample of the salt cured the anæmia. The supplementing factor is thus apparently of an inorganic character, but is not connected with the solubility of the iron compounds administered (cf. Mitchell and Schmidt, A., 1926, 1269). C. R. HARINGTON.

Action of mineral waters on carbohydrate metabolism. Experiments [on diabetics]. O. KAUFFMANN-COSLA, R. ZORKENDORFER, and W. ZORKENDORFER (Bull. Soc. Chim. biol., 1927, 9, 174—202).—1000—1500 G. *per diem* of the natural mineral waters of Carlsbad and Marienbad, of which the principal constituent is sodium sulphate, bring about the recovery of mild and moderately severe diabetics. A. WORMALL.

Oxidative processes in the living cell. A. OPARIN (Biochem. Z., 1927, 182, 155—179).—An investigation of the aerobic oxidation of glycine under the influence of the plant respiratory chromogen chlorogenic acid, a didepside of caffeic and quinic acids (A., 1922, i, 309). It is concluded that in the living cell the chromogen is oxidised by molecular oxygen and phenoloxydase to a pigment, and that the pigment is then reduced by oxido-reductase to the original chromogen, the necessary hydrogen being derived from water, whilst the hydroxyl remains for the actual oxidation. The oxidation and reduction of the chromogen are normally in equilibrium. A high oxygen uptake by the living cell, following chemical or mechanical injury, leads to deep-seated oxidation of the respiratory chromogen, with the formation of an inactive pigment, and oxidation within the cell ceases. J. PRYDE.

Metabolism of tissues growing *in vitro*. I. Ammonia and urea production by kidney. B. E. HOLMES and E. WATCHORN (Biochem. J., 1927, 21, 325—334).—Growing embryonic rat kidney-tissue produces considerable amounts of ammonia and urea in contrast to "resting" embryonic kidney-tissue, *i.e.*, living but non-proliferating tissue, which produces neither ammonia nor urea. Preliminary experiments with brain-tissue indicate the probable existence of urease in the rat brain. S. S. ZILVA.

Brain metabolism. IV. Carbohydrate metabolism of brain-tissue of depancreatised cats. B. E. HOLMES and E. G. HOLMES (Biochem. J., 1927, 21, 412—418).—The lactic acid values of the brain fall and rise with the blood-sugar. Hyperglycæmia brought about by the administration of anæsthetics is also accompanied by an increased brain lactic acid content. Similarly, the hyperglycæmia of depancreatised cats is responsible for a correspondingly higher value of resting lactic acid in the brain of the cat. The brain-tissue of diabetics, like that of normal animals, is capable of converting dextrose into lactic acid and of removing lactic acid under aerobic conditions. The lactic acid of the brain is therefore formed from the dextrose supplied by the blood. S. S. ZILVA.

p_H of muscles of marine animals. K. FURUSAWA and P. M. T. KERRIDGE (J. Marine Biol. Assoc., 1927, 14, 657—659).—The average p_H of the muscles of various marine animals was 7·06 in the resting condition and 6·33 in rigor; these figures are in close agreement with those obtained for the muscles of the frog and the cat. C. R. HARINGTON.

***Post-mortem* changes in the free sugar, glycogen, phosphates, and lactic acid in mammalian muscle.** W. W. SIMPSON and J. J. R. MACLEOD (Trans. Roy. Soc. Canada, 1926, [iii], 20, V, 371—375).—Experiments have been carried out to determine the total reducing substances, the free sugar, and the glycogen content of extracts of the liver and muscle of standard white rats, previously starved for 24 hrs. The free sugar, which accounts for a small percentage only of the total reducing value, is much lower in the liver extracts of insulin-treated rats than with the normals. Insulin treatment causes little, if any, change in the glycogen content or total reducing value. With muscle-extract, on the contrary, there is no reduction in free sugar following insulin. Changes taking place in the glycogen, free sugar, lactic acid, and soluble phosphorus of frozen rabbit muscle, after various short periods of thawing, indicate that some polymerised carbohydrate (perhaps a lower dextrin) must be formed from the disappearing glycogen. A. WORMALL.

Acid formation in thiocyanate rigor in frog's muscle. G. E. SELTER (Z. physiol. Chem., 1927, 165, 18—27).—In thiocyanate rigor in frog's muscle there is a marked increase in lactic acid and no constant change in the phosphoric acid. The phenomenon is therefore probably due to increased acidity. C. R. HARINGTON.

Significance of ions in muscular function. IX. Influence of different anions on lactic acid formation and phosphoric acid exchange in minced muscle. G. E. SELTER (Z. physiol. Chem., 1927, 165, 1—17).—The effects of additions of various sodium salts to minced muscle on the formation of lactic acid and the amount of free phosphoric acid vary greatly (they may, indeed, be in the reverse direction) according to the concentration of salt employed. A salt which increases the rate of disappearance of phosphoric acid does not necessarily diminish the formation of lactic acid. Complete inhibition of lactic acid formation is obtained only in presence of those anions (fluoride and oxalate) which entirely suppress the degradation of lactacidogen. In view of these results, it is unsafe to deduce the behaviour of the lactic acid, under any given conditions, from the observed behaviour of the phosphoric acid. C. R. HARINGTON.

Degradation of glycogen in muscle. H. VON EULER, R. NILSSON, and B. JANSSON (Z. physiol. Chem., 1927, 165, 121—129).—The decolorisation of methylene-blue by muscle is influenced to an equal extent by sodium and potassium phosphates. The

rate of decolorisation was not definitely affected by the state of nutrition of the animal; the process of reduction is accelerated to a slight extent by addition of small concentrations of glycogen; it is inhibited by high concentrations of glycogen and by all concentrations of dextrose; in the case of yeast, the reduction is not accelerated by glycogen.

C. R. HARINGTON.

Carbohydrate utilisation. II. Rate of disappearance of carbohydrates from the blood. J. G. REINHOLD and W. G. KARR (J. Biol. Chem., 1927, **72**, 345—365).—Oral administration to rabbits of galactose, maltose, sucrose, starch, lactose, and lævulose produced hyperglycæmia of descending orders of magnitude; in general, therefore, the magnitude of the effect varies directly with the rate of absorption of the carbohydrate and inversely with its capacity to form glycogen. The hyperglycæmia was increased by preliminary starvation, except in the case of starch, and was diminished by preliminary feeding with gelatin, except in that of maltose. Simultaneous administration of maltose, galactose, or lævulose together with dextrose produced less hyperglycæmia than dextrose alone; this effect was not observed with starch or lactose. The typical hyperglycæmia produced by lactose or sucrose could not be reproduced by administration of mixtures of dextrose and galactose or of dextrose and lævulose.

C. R. HARINGTON.

Action of glucosone on normal animals (mice) and its possible significance in metabolism. A. HYND (Proc. Roy. Soc., 1927, B, **101**, 244—261).—Glucosone produces similar symptoms in mice to those of insulin when injected subcutaneously. The effect is slightly modified by administration of dextrose, and appreciably by adrenaline, pituitrin, and acetoacetic acid injections. Glucosone does not produce hypoglycæmia. The possibility of the significance of glucosone in carbohydrate metabolism is thus confirmed (cf. Thannhauser and Jenke, A., 1926, 317).

L. F. HEWITT.

Effect of glycine on the metabolism of isolated perfused muscle. D. RAPPORT and L. N. KATZ (Amer. J. Physiol., 1927, **80**, 185—199).—A preparation is described for the study of the metabolism of the isolated hind limb of the dog perfused with blood. The oxygen consumption of the resting muscles was found to be 0·0024—0·0093 c.c. per g. per min. Addition of 5 g. of glycine to the perfusing blood caused a notable increase in the oxygen consumption which might be sustained for several hours. It is concluded that the specific dynamic action of glycine is a direct effect on the cells of the tissues stimulated. It is argued that the respiratory quotient in this type of experiment is totally untrustworthy as an index of the metabolism of different foodstuffs.

R. K. CANNAN.

Metabolism of women. III. Lipin content of blood in relation to menstrual cycle. R. OKEY and R. E. BOYDEN (J. Biol. Chem., 1927, **72**, 261—281).—During, and immediately after menstruation, there was observed a fall in the cholesterol content of the blood; the other lipins remained relatively unchanged in amount.

C. R. HARINGTON.

Influence of nutrition on synthesis and oxidation. A. PALLADIN and D. FERDMANN (Biochem. Z., 1927, **182**, 193—203).—Rabbits receiving phenol *per os* excrete more in a combined form when they are fed on an "acid" diet than when fed on a "basic" diet. Intravenously-injected phenol is recovered in greater amount in "basic" than in "acid"-fed rabbits, whilst the relative amount of combined phenol is higher in the latter animals. It is concluded that an acid diet favours the oxidation and conjugation of phenol.

J. PRYDE.

Effect of heat and oxidation on nutritive value of protein. H. GOLDBLATT and A. R. MORITZ (J. Biol. Chem., 1927, **72**, 321—326).—The nutritive value of caseinogen was not impaired by heating for 36 hrs. in a current of air at 110—130°.

C. R. HARINGTON.

Dietary value of potato protein. G. A. HARTWELL (Biochem. J., 1927, **21**, 282—288).—Potato protein given in a diet consisting mainly of mashed cooked potatoes was found insufficient to promote growth. Reproduction took place, but many of the young were born dead and few could be reared. If this diet was given during lactation only, the young rats were undersized and the mothers lost weight during lactation. The addition of bread to the potato diet during lactation improved the condition of the young, but not of the mother. The dietetic deficiency of the potato diet is due to the insufficient consumption of potato protein and not to its quality.

S. S. ZILVA.

Growth on diets rich in fat. H. LEVINE and A. H. SMITH (J. Biol. Chem., 1927, **72**, 223—238).—Normal growth in young rats was obtained on diets in which 86% of the caloric requirements were supplied in the form of fat and the remainder as protein, provided that adequate supplies of salt were maintained; on such diets, the fat was almost quantitatively absorbed, and the caloric intake per 100 g. body-weight was the same as that on an ordinary mixed diet. No abnormalities were observed in the liver after maintenance of the diet rich in fats for 83 days.

C. R. HARINGTON.

Effect of carbon monoxide inhalation on metabolism. F. M. WALTERS (Amer. J. Physiol., 1927, **80**, 140—149).—The body temperature and the metabolic rate of the rat were depressed by breathing carbon monoxide to a degree varying with the carbon monoxide saturation of the blood. There is a relation between the fall in metabolic rate and the symptoms of poisoning.

R. K. CANNAN.

Effect of the administration of excessive amounts of water. I. C. H. GREENE and L. G. ROWNTREE (Amer. J. Physiol., 1927, **80**, 209—229).—There are reported the effects on the volume and on the concentrations of proteins, electrolytes, and non-electrolytes of the blood of the forced administration of large amounts of water to the dog.

R. K. CANNAN.

Excitability of nervous centres in terms of their hydrochloric acid content. L. AMBARD and F. SCHMID (Compt. rend., 1927, **184**, 769—771).—Excess of hydrochloric acid above the normal gives rise to hyper-excitement symptoms, from vasomotor

reactions and high blood pressure to convulsions; deficiency of hydrochloric acid produces the converse symptoms. The concentration relation Protein HCl $\rightleftharpoons[NaCl \times H_2CO_3]/[HCl \times NaHCO_3]=K$ is proposed and its biological applications are discussed.

R. BRIGHTMAN.

Synthetic production of different flavours. E. BARYSCHEVA (Pflüger's Arch., 1926, **215**, 103—105)—By means of mixtures of four solutions of saline (sodium chloride), sweet (sucrose), acid (oxalic acid), and bitter (quinine hydrochloride) substances, it is claimed that the taste of any substance may be simulated by varying the proportions of each. The odour of many substances interferes with the experiments.

L. F. HEWITT.

Action of choline and histamine on the excretion of dyes from the blood. G. FARKAS and H. TANGL (Biochem. Z., 1927, **182**, 406—410).—Vasodilator substances (choline) increase, and vasoconstrictor substances (histamine) retard the excretion of dyes from the blood.

P. W. CLUTTERBUCK.

Potassium, sodium, and calcium content of blood after ingestion of calcium chloride. J. WEBER and W. KRANE (Z. physiol. Chem., 1927, **163**, 134—140).—Sub-normal calcium content of human blood is very rapidly restored to normal by food rich in calcium, and is further increased by doses of calcium chloride. Increase in calcium content is not accompanied by increased potassium content.

C. HOLLINS.

Effect of iodine on protein and sodium chloride equilibria in man. A. SLAUCK (Arch. exp. Path. Pharm., 1927, **121**, 250—258).—Subjects fed for 8 days on a daily diet of 2·5 litres of milk were treated with doses of sodium and potassium iodides varying from 10 to 18 g. Determinations were made of the nitrogen content of the blood during a period of 3—48 hrs. It was found that the nitrogen content rose to a maximum in 3 hrs. and became normal 24—48 hrs. afterwards; slightly higher maxima were observed for potassium iodide. Corresponding maxima were observed for the iodine and sodium chloride content of the blood 3 hrs. after the administration of sodium or potassium iodide and for the total chlorine and iodine content in the urine excreted during the 24 hrs. following the iodide treatment.

E. A. LUNT.

Iodine as a biological element. IX. Acceleration of the growth of young rats by administration of a diet rich in iodine to the lactating mother. E. MAURER and S. DIEZ (Biochem. Z., 1927, **182**, 291—300).—Administration of a diet of maize and milk which had been enriched in iodine to rats did not affect the body-weight of the mother, but the weight of the young was 20% greater than normal by the end of the lactating period. In both mother and young, the dry substance content was increased to a greater extent than the body-weight, but whereas in the mother loss of salts had taken place, the ash content of the young had increased with the body-weight. The changes of calcium, iodine, and phosphorus content of mother and young during the iodine-rich feeding are tabulated (cf. A., 1926, 1167).

P. W. CLUTTERBUCK.

Elimination of iodine after oral or intravenous administration of various iodine compounds. F. R. GREENBAUM and G. W. RAIZISS (J. Pharm. Exp. Ther., 1927, **30**, 407—427).—After administration of sodium iodide or potassium iodide, 90% of the iodine is excreted by the kidneys within 24 hrs. and the rest within the next few days. After administration of calcium iodide, most of the iodine is similarly eliminated during the first 24 hrs., but in this case a considerable proportion is in the fæces. After ingestion of "pepto-iodine," the iodine is rapidly eliminated by the kidneys in an ionised form, but damage of the kidneys by mercuric chloride does not lessen the elimination, as it does in cases of sodium and potassium iodides. The iodine of organic compounds such as tetraiodophenolphthalein or 4-iodoguaiacol is eliminated by the kidneys and by the fæces, but not in an ionised form. Elimination of iodine after administration of the additive compound of calcium iodide and thiocarbamide is very similar to that observed following administration of calcium iodide alone.

W. O. KERMACK.

Effect of Witte's peptone on blood-sugar. M. L. MENTEN and H. M. MANNING (J. Biol. Chem., 1927, **72**, 255—260).—No constant effect on the blood-sugar concentration of the rabbit was observed as the result of intravenous injection of Witte's peptone.

C. R. HARINGTON.

Proteinogenous toxicosis. L. A. TSCHERKES (Biochem. Z., 1927, **182**, 35—49).—White mice fed exclusively on a protein diet develop toxic symptoms which are fatal and to which the name proteinogenous toxicosis is given. The addition of fat or carbohydrate to the diet lessens the severity of the toxic effects in a measure more or less proportional to the amount of fat or carbohydrate fed. The toxic effects are not ascribed to the lack of vitamins or to starvation. In the case of white rats and pigeons, an exclusive diet of caseinogen is not followed by the toxic symptoms, but, on the other hand, a diet of egg-albumin does produce the effect in rats.

J. PRYDE.

Influence of urethane narcosis on specific dynamic action of glycine and dextrose in rabbits. M. S. GUTTMACHER and R. WEISS (J. Biol. Chem., 1927, **72**, 283—297).—The normal specific dynamic action of glycine and dextrose (caloric equivalents of which produce effects of equal magnitude) is observed in rabbits under urethane anæsthesia, provided that the anæsthesia be not so deep as to abolish nervous reflexes; this indicates that the nervous system is probably concerned in the phenomenon of specific dynamic action of foodstuffs.

C. R. HARINGTON.

Determination of small quantities of bismuth in tissue, excreta, blood, and bone. J. A. SULTZABERGER (J. Amer. Pharm. Assoc., 1927, **16**, 218—221).—Tissue, fæces, or urine (10—50 g.) is moistened with nitric acid, warmed overnight on a steam-heated sand-bath, and ignited until all carbon is removed. The residues are boiled with hydrochloric acid, evaporated to dryness, treated with 0·5 c.c. of hydrochloric acid and 5 c.c. of water, filtered, diluted to about 15 c.c., and compared

colorimetrically with a standard bismuth nitrate solution containing 0·05 mg. Bi per c.c. after the addition of 0·75 c.c. of 25% potassium iodide solution and 0·5 c.c. of 1% sodium hydrogen sulphite solution to the standard and unknown solutions. In the digestion of bone, the precipitation of the metal as sulphide is necessary, owing to the excessive concentration of salts. Bleaching of the bismuth potassium iodide colour occurred on the addition of sodium chloride, but the addition of hydrochloric acid restored the colour completely. If the ignition is carried out in the muffle furnace, loss of bismuth occurs. C. O. HARVEY.

Toxicological determination of tin. P. MANICKE and H. LAUTH (Pharm. Zentr., 1927, **68**, 161—163).—One treatment with potassium chlorate and hydrochloric acid does not completely destroy organic matter; subsequent treatment with hydrogen peroxide permits of precipitation of 90% of the tin present. When only small quantities of organic material are present, destruction with sulphuric acid and subsequent fusion with sodium hydroxide and nitrate allow of quantitative precipitation of the tin; if large quantities of organic material are present, it is necessary to treat with sulphuric acid, then with peroxide, and finally with nitric acid, heating each time until sulphur trioxide fumes are evolved.
S. I. LEVY.

Nitrates in biochemistry and toxicology. KOHN-ABREST and S. KAVAKIBI (Ann. Chim. anal., 1927, [ii], **9**, 65—75).—An alkaline extract of the organic material is treated with basic lead acetate, the excess of lead removed from the filtrate with sodium carbonate, and the resulting solution neutralised and evaporated to dryness. The residue is treated with sulphuric acid in the cold, and, after 30 min., shaken with mercury in an apparatus so arranged that the nitric oxide evolved can be collected in a gas pipette; the first measurement of the nitric oxide is confirmed by observation of the reduction of volume on treatment with saturated ferrous sulphate. In the case of milk, preliminary treatment with sodium metaphosphate and silver nitrate is substituted for that with lead acetate. The error of the method is 2%. No nitrates were found in the common vegetables or in fresh human viscera; cow's milk contained 0—0·08, and human milk 0·145—0·19 g. of N_2O_5 per litre; normal human urine contained 0·036 g. of N_2O_5 per litre. C. R. HARINGTON.

Effect of long-continued ingestion of zinc oxide by dogs and cats. Excretion and storage of zinc. K. R. DRINKER, P. K. THOMPSON, and M. MARSH (Amer. J. Physiol., 1927, **80**, 31—64).—The administration of 0·175—1 g. of zinc oxide daily for 3—53 weeks was without clinical or other evidence of physiological damage. Figures are given for the urinary and fæcal excretion of zinc and of the zinc content of the various tissues of the experimental animals. The main excretory route is the alimentary canal. Possible relations of the pancreas, adrenals, and sex glands to zinc are indicated.
R. K. CANNAN.

Effect of zinc on the reproduction and growth of the albino rat. Constant concentration of zinc in a given species regardless of age. P. K. THOMPSON, M. MARSH, and K. R. DRINKER (Amer. J. Physiol., 1927, **80**, 65—74).—The daily administration of 2—38 mg. of zinc, as oxide or as organic salt, to the albino rat before, during, and after pregnancy was without effect on the health or fertility of the mother or on the growth of the offspring. The normal zinc content of albino rats was about 0·039 mg. per g. of tissue, being independent of age. Feeding zinc leads to no significant storage of the metal by the tissues of the rat. R. K. CANNAN.

Changes in the cation content of organs on exposure to light and at high altitudes. L. PINCUSSEN (Biochem. Z., 1927, **182**, 359—365).—The potassium, calcium, and magnesium contents of the blood, lungs, brain, liver, and heart of dogs which have been irradiated or kept in the dark at different altitudes are tabulated and show that considerable displacement of the mineral content of the organism occurs both in bright light and at high altitudes.
P. W. CLUTTERBUCK.

Influencing biological reactions brought about by light. L. PINCUSSEN (Biochem. Z., 1927, **182**, 366—376).—Daphnids in water and potassium iodide solutions with and without addition of certain dyes, *e.g.*, eosin and sodium dichloroanthracenedisulphonate, are observed in the dark, in bright diffused light, in sunlight, and after irradiation with the quartz lamp. In the dark, there appears to be no difference between animals in water and in potassium iodide solution. In bright light, and still more so in sunlight and during irradiation with the lamp, the death rate is considerably increased by the presence of iodide, probably due to the setting free of iodine. This effect is enhanced by the presence also of the dyes, which have no action in themselves, waves of longer as well as shorter wavelength becoming able to set iodine free. Similar experiments with tadpoles in various salt solutions show that cations arranged in order of increasing ability to kill the animals are Ca, Na < Al < Sr < Mg < Li < K and that anions similarly arranged are Cl < Br < SO_4 < F, I. Irradiation of tadpoles in phosphate solutions show that although $M/3$ and $M/6$ solutions are injurious, more dilute solutions have a protective action against irradiation. When tadpoles in phosphate solutions of the same concentration but of different p_H are irradiated, animals in solutions of $p_H < 6·8$ show little injurious effect, of p_H 6·8 all remain alive, and of p_H 7·15—7·65 mostly die, the death-rate increasing with the p_H.
P. W. CLUTTERBUCK.

Temperature and enzymic activity. J. R. BAKER (J. Marine Biol. Assoc., 1927, **14**, 723—727).—The amylolytic activity of a fresh aqueous extract of the crystalline style of *Pecten* is at a maximum at 30° and at higher temperatures is destroyed with increasing rapidity. On keeping the extract for 1½—3 hrs. at 0—30°, the enzymic activity shows a marked increase. It is suggested that the latter may be a surface effect due to increased dispersion of the protein particles on which the enzyme is adsorbed. C. R. HARINGTON.

Liver amylase. G. S. EADIE (Biochem. J., 1927, **21**, 314—321).—The optimum p_H for liver amylase

is about 6. The previously accepted value, which is about p_H 7, is due to the presence in the liver of blood amylase. The effect of substrate concentration on the activity of liver amylase is in accordance with the theory of Michaelis and Menten (A., 1913, i, 540). The effect of sodium chloride on the activity of the liver enzyme is similar to that previously obtained with other amylases of animal origin. Langfeldt's claim that adrenaline enhances the activity of liver amylase is not confirmed (cf. A., 1921, i, 473).

S. S. Zilva.

Gluco- and fructo-invertases. II. R. Kuhn and H. Munch (Z. physiol. Chem., 1927, **163**, 1—72; cf. Kuhn, *ibid.*, 1925, **150**, 220).—From a review of earlier work and from new determinations of the velocity of sucrose hydrolysis in presence of added cleavage products, it is concluded that (1) a glucoside or disaccharide which is unattacked by a given enzyme also shows no affinity for the enzyme, (2) affinity of an enzyme for a hexose does not necessarily involve affinity for the related hexosides or disaccharides, and (3) hydrolysis of a disaccharide by an enzyme involves affinity of the enzyme for at least one of the component sugars. Gluco-derivatives of sucrose are attacked only by fructo-invertases, fructo-derivatives by gluco-invertases. The behaviour of 11 enzyme preparations is set out in 57 tables. It is shown that the optimum p_H for the inhibitory effect of αβ-dextrose depends on the β-dextrose only. For glycerol, the inhibition decreases uniformly with increasing p_H; for α-galactose increase in p_H has no effect on the inhibition.

C. Hollins.

Behaviour of whole blood towards maltose *in vitro*. A. Hynd and M. G. Macfarlane (Biochem. J., 1927, **21**, 322—326).—Using 1 c.c. of blood and determining the sugar by the Wood–Ost method, maltase could not be detected in the blood of the mouse, rat, guinea-pig, rabbit, kitten, ox, or sheep. In the case of the blood of the pig, almost a 100% hydrolysis of the maltose was recorded. If maltose counteracts the effects of insulin only after hydrolysis, the process cannot take place in the blood.

S. S. Zilva.

Relation of the catalase system to oxidation processes in animal organs. L. Stern (Biochem. Z., 1927, **182**, 139—154).—The author's catalase system is composed of catalase, anti-catalase, philo-catalase, and an activator of philo-catalase. The system is developed only in aerobic organisms, but has no direct relationship to the intensity of the oxidative processes of the organism. It exists in association with oxidases, but shows no parallelism to oxidones. By the action of oxidases, hydrogen peroxide is formed from the interaction of active hydrogen and molecular oxygen, whilst oxidones form water from the interaction of active hydrogen and active oxygen. The function of the catalase system is the decomposition of hydrogen peroxide and so it participates in the carriage of oxygen.

J. Pryde.

Effect of temperature on catalase reaction. V. Temperature correction in catalase determinations. S. Morgulis and M. Beber (J. Biol. Chem., 1927, **72**, 91—98).—The earlier observations (A., 1926, 976) that the total amount of hydrogen peroxide which can be decomposed by a given amount of catalase is at a maximum at 2° are confirmed. Assuming that the enzyme is completely active at this temperature, and designating the amount of catalase required to decompose 70% of the hydrogen peroxide as one enzyme unit, a curve has been constructed showing the relationship of relative enzymic activity to temperature. The curve is regular from 0° to 24°, but at higher temperatures exhibits a deviation, which is ascribed to the increase of the rate of enzyme action relative to that of enzyme destruction.

C. R. Harington.

Mechanism of autolysis. VII. Autolysis of organs. O. Steppuhn and Y. Duret-Delage (Biochem. Z., 1927, **182**, 134—138).—Autolysis of organs, especially of the liver and kidney, is much more marked in the range of activity of pepsinases (p_H 3·8) than in alkaline media (p_H 7·6), but the pancreas also shows considerable autolysis at the latter reaction.

J. Pryde.

Influence of the backward reaction in peptic hydrolysis of albumin. C. A. Morrell, H. Borsook, and H. Wasteneys (J. Gen. Physiol., 1927, 8, 601—617).—As the synthetic action of pepsin on the products of protein hydrolysis is greater within limits with increase of temperature, the optimum temperature for protein hydrolysis by pepsin would be expected to decrease as the concentration of the protein increases. The verification of this by experiment confirms the view that this synthetic action plays an important part in the dynamics of peptic hydrolysis. The retarding effects on the activity of pepsin of high concentrations of protein and of the addition of proteoses and peptones, either with the pepsin or separately, are also in accord with this view. No destruction of pepsin by heat is demonstrable at p_H 1·6 until a temperature of 40° is exceeded.

W. O. Kermack.

Influence of thorium-*X* on laccase. A. Maubert (Compt. rend., 1927, **184**, 781—783).—Measurements of the activity of laccase by Fleury's guaiacoquinone method (A., 1924, i, 921, 1144) show that addition of 1—5 γ of thorium-*X* to a mixture of 20 c.c. of 1% aqueous guaiacol, 50 c.c. of water, and 0·5 c.c. of laccase preparation causes activation of the laccase. With larger doses, the enzyme becomes inactive.

R. Brightman.

Influence of amino-acids on hydrolysis by pancreatic lipase. E. R. Dawson (Biochem. J., 1927, **21**, 398—403).—Amino-acids accelerate the hydrolysis, in alkaline or neutral but not in acid solutions, of ethyl butyrate and olive oil by pancreatic lipase.

S. S. Zilva.

Enzyme action. XL. Time changes in ester-hydrolysing enzymes of extracts of whole rats of different ages. H. M. Noyes and K. G. Falk. **XLI. Extracts of mice.** K. G. Falk and H. M. Noyes. **XLII. Extracts of human uterine muscle and uterine fibroids.** H. M. Noyes and K. G. Falk. **XLIII. Extracts of rabbit tissues.** K. G. Falk and H. M. Noyes (J. Biol. Chem., 1927, **72**, 449—465, 467—473, 475—488, 489—503).—XL. On preservation under sterile conditions, for

periods up to 23 months, extracts of whole rats show a gradual qualitative change in their capacity to hydrolyse esters, in all cases eventually approximating to the type of action exhibited by extracts of embryo rats and of a rat-carcinoma. The rate of change varied with the age of the animal from which the extract was prepared, being greatest in the case of the youngest and the oldest rats and least in that of the young adults.

XLI. Extracts of adult mice, on preservation, approximated in type of ester-hydrolysing activity to extracts of mouse-carcinoma, whilst extracts of young mice approximated to the different type of action of the mouse embryo.

XLII. Extracts of uterine fibroids fall into two types with respect to their ester-hydrolysing action; those of type I, similar in their action to embryonic extracts, showed a quantitative decrease of activity, but no change in type on preservation; those of type II, and also of uterine muscle itself, showed less decrease in total activity, but more change in type.

XLIII. Extracts of the liver, lung, kidney, and leg-muscle of rabbits show, on keeping, a change in type of ester-hydrolysing action, which becomes progressively more dissimilar to that which is characteristic of embryonic extracts. C. R. HARINGTON.

Specific effect of salts in extraction of urease from amœbocytes of *Limulus*. L. LOEB and O. BODANSKY (J. Biol. Chem., 1927, **72**, 415—431; cf. A., 1926, 434).—Urease is extracted from the amœbocytes of *Limulus* to a very small extent only by distilled water or by solutions of carbamide; sea-water, solutions of sodium and potassium chlorides isotonic with sea-water, and the protein-free serum of *Limulus* are slightly more efficient than water in extracting the enzyme; a somewhat greater power of extraction is observed with magnesium and manganese chlorides, and a very much greater power with the chlorides of calcium, strontium, and barium, which, in isotonic solution, are 20 to 100 times as effective as sodium chloride. The effect of these salts comes into play during the process of extraction, since their addition to a sodium chloride extract produces no increase in activity; the extracts prepared with their aid have a greater power of neutralising alkali, and thus keep the p_H nearer to the neutral point during the hydrolysis of the carbamide. The optimum concentration for extraction of the enzyme is greater in the case of salts with univalent than in that of those with bivalent cations. No specific effect of anions was observed. C. R. HARINGTON.

So-called selective fermentation. A. FERNBACH, M. SCHOEN, and M. MORI (Compt. rend., 1927, **184**, 551—553; cf. this vol., 279).—In continuation of the earlier work, the authors find that the difference in the rate of fermentation of optically inactive sugars, due to selectivity, varies, not only in the case of different yeasts, but also with the zymins prepared from these yeasts by the method of Albert, Buchner, and Rapp (A., 1902, ii, 521). The zymin from beer yeast reacts at first in the same way and at the same rate as the living yeast from which it was derived, but stops before all the fermentable sugar disappears, and before the appearance of an unfermentable reducing sugar. The same effect is found with the zymin from Sauterne yeast. When, however, *Saccharomyces exiguus* or *Schizosaccharomyces Pombe* is used, the living yeasts render an inactive solution lævorotatory, whereas the corresponding zymins produce a dextrorotation. Similar results are obtained with invert-sugar: zymin from beer-yeast increases the lævorotation by fermenting the dextrose, whilst the zymins from the other yeasts decrease it by fermenting preferentially the lævulose. It is suggested that selectivity depends on substances which accompany zymase, and may be modified in nature and proportion by temperature, concentration of the sugar, changes in the medium, or treatment of the yeast with acetone and ether. J. M. GULLAND.

Enzymic transformation of acetaldehyde. H. VON EULER and K. MYRBACK (Z. physiol. Chem., 1927, **165**, 28—44).—The ability to transform acetaldehyde (this vol., 175) is restored to washed yeast by addition of boiled yeast extract or of any preparation of co-zymase, whether derived from yeast or from animal tissues; moreover, the degree of activation bears a quantitative relationship to the amount of co-zymase which is added; the identity of co-zymase and co-mutase is therefore established. Co-zymase would thus appear to be involved in a reaction of the Cannizzaro type preceding the esterification of hexose with phosphoric acid. The bearing of this on the existing theories of alcoholic fermentation is discussed. A pure sample of hexosediphosphate was not fermented by yeast free from co-zymase; the recent views of Meyerhof (Naturwiss., 1926, 1175) are therefore questioned, and it is concluded that the observed facts are in better agreement with the original equation of Harden. C. R. HARINGTON.

Co-zymase. XI. K. MYRBACK and R. NILSSON (Z. physiol. Chem., 1927, **165**, 140—148).—Co-zymase was not affected by trypsin, erepsin, taka-diastase, urease, catalase, or phosphatase; it was destroyed to a very small extent by esterase. It is destroyed on keeping in contact with liver- or kidney-extracts, but is stable towards strong oxidising agents such as permanganate and hydrogen peroxide; it is destroyed by bacteria. C. R. HARINGTON.

Carbon monoxide poisoning in the absence of hæmoglobin. P. F. FRANKLAND (Nature, 1927, **119**, 491).—A reference to the behaviour of *Bacillus pyocyaneus*, Finkler's spirillum, and Koch's spirillum of Asiatic cholera in various gases (Proc. Roy. Soc., 1886, **45**, 292). A. A. ELDRIDGE.

Bacterial production of gas containing sulphur. H. YAOI (Japan Med. World, 1926, **6**, 139—144).—The principal gaseous product of the bacterial decomposition of *l*-cysteine is hydrogen sulphide; traces of a substance resembling ethyl sulphide are formed, but mercaptan is not produced except in presence of sugars. CHEMICAL ABSTRACTS.

Decomposition of hexosephosphates by *Bacillus coli communis*, Escherich. R. J. MANNING (Biochem. J., 1927, **21**, 349—353).—The products of decomposition of the sodium salts of hexose-monophosphoric and hexosediphosphoric acids by *B. coli communis*, Escherich, whether the decom-

position takes place in presence or absence of oxygen, are carbon dioxide, alcohol, formic, acetic, lactic, and succinic acids. The products of decomposition are therefore the same as in the case of dextrose (cf. Grey, A., 1918, i, 143, 144; 1920, i, 699). The more rapid the bubbling of oxygen through the bacterial digest, the greater was the amount of sugar decomposed completely to carbon dioxide.

S. S. ZILVA.

Ammonium sulphate precipitation of the active principle of the culture filtrates of *C. Diphtheriæ*. A. F. WATSON and E. LANGSTAFF (Biochem. J., 1927, 21, 426—433).—The substance which causes the specific *in vitro* flocculation with antitoxin can be salted completely out of culture filtrates of *C. diphtheriæ* adjusted to p_H 8·0 by saturation with ammonium sulphate. On the acid side of neutrality the precipitation is not complete. The presence of certain preservatives such as formaldehyde, phenol, or toluene prevents the complete removal of the active principle with ammonium sulphate. Although in general the chemical properties of the precipitates are the same, the active fraction salted out by complete saturation with ammonium sulphate is less pure than the acid precipitate obtained from the culture filtrates at the isoelectric point.

S. S. ZILVA.

Active principle of tuberculin. E. R. LONG and F. B. SEIBERT (Tubercle, 1926, 8, 111—122).—The protein-containing solution which accompanies tuberculin activity, on saturation with ammonium sulphate, yields a coagulable and a non-coagulable protein, and proteose. When the protein is destroyed by pepsin with little destruction of proteose, activity is destroyed; when the proteose alone is disintegrated by trypsin, the activity is unaffected. No non-protein has been found to be associated with tuberculin activity. Activity appears to be a function of a certain group of the protein molecule, but it is unlikely that an active group can be eliminated from the remainder of the protein molecule.

CHEMICAL ABSTRACTS.

Effect of various hydrogen-ion concentrations on the longevity of vaccine virus. R. D. DEFRIES and N. E. MCKINNON (Trans. Roy. Soc. Canada, 1926, [iii], 20, V, 359—370).—The virus, stored at 5—10° in a phosphate-buffered solution or a "universal" buffer, is resistant to minor changes in p_H, but outside the optimum range for storage (p_H 6—8) there is a distinct loss of potency. At p_H 5 and 10 the virus becomes inert in a few weeks, and at p_H values of 2, 3, 4, 11, and 12, destruction takes place within a few days.

A. WORMALL.

Relation between chemical constitution and germicidal activity of monohydric alcohols and phenols. F. W. TILLEY and J. M. SCHAFFER (J. Bact., 1926, 12, 303—309).—Phenol coefficients, calculated on a g.-mol. basis, of successive members increase uniformly with an average ratio between coefficients of 3·36, 3·0, 2·7, and 3·3 for the primary, secondary, and tertiary alcohols, and phenols, respectively.

CHEMICAL ABSTRACTS.

Significance of iron, zinc, and copper for micro-organisms (with special reference to *Aspergillus niger*). H. BORTELS (Biochem. Z., 1927, 182, 301—358).—Adsorption by blood-charcoal removes iron, zinc, and copper from culture media. Iron and zinc are essential to the growth of *A. niger*, zinc also inhibiting fructification, whilst copper is indispensable for the formation of the black pigment of the conidia. Copper also leads to an increase in the weight of dry substance. Iron and zinc are also necessary for the growth of *B. prodigiosus* and zinc for yeast, but copper does not appear to be essential for either. Prodigiosin is produced by the action of iron on a leuco-compound formed by the bacillus.

P. W. CLUTTERBUCK.

Influence of some hormones on the excretion of dyes from the blood. H. TANGL (Biochem. Z., 1927, 182, 411—417).—The injection of extracts of thyroid, thymus, pituitary, and testis retards the excretion of dyes from the blood.

P. W. CLUTTERBUCK.

Action of extracts of spleen on the excretion of dyes from the blood. G. FARKAS and H. TANGL (Biochem. Z., 1927, 182, 399—405).—The spleen brings about the excretion of dyes injected into the blood, not only by its reticulo-endothelial cells, but probably also by means of a hormone.

P. W. CLUTTERBUCK.

Influence of extracts of spleen, thymus, and thyroid on the growth of young rats. H. TANGL (Biochem. Z., 1927, 182, 418—423).—Injection of extracts of spleen and of thyroid exerts no influence on the growth of young rats, nor does it affect the growth-assisting action of thymus extracts.

P. W. CLUTTERBUCK.

Endocrine factors in oxalic acid metabolism. G. VIALE (Rev. sud-amer. endocrinol. immunol. quimioterap., 1926, 9, 967—977).—Insulin injections do not alter the oxalic acid content of the blood of rabbits and dogs, but cause a marked decrease of its excretion in urine. Adrenaline injections and pancreatectomy cause a considerable increase in oxalaturia. Phloridzin diabetes has scarcely any effect on the excretion of oxalic acid. It is concluded that oxalic acid is an intermediate product of sugar metabolism.

CHEMICAL ABSTRACTS.

Insulin. N. R. BLATHERWICK, F. BISCHOFF, L. C. MAXWELL, J. BERGER, and M. SAHYUN (J. Biol. Chem., 1927, 72, 57—89).—Details are given of a practical combination of various known methods for the extraction and purification of insulin. Under no conditions was insulin inactivated by hydrogen sulphide. The prolonged action of cyanide causes inactivation of insulin, as does also nitrite in concentrations above 0·05*N*; diazobenzenesulphonic acid in faintly alkaline solution, and in amount considerably less than is required to combine with the tyrosine and histidine of the insulin preparation, destroys the activity. Iodine destroys the activity, but the iodine absorbed bears no relation to the unit content of the insulin. Loss of activity accompanied benzoylation, nor could activity be recovered by hydrolysis of the product. The small proportion of these inactivating agents required to destroy the insulin indicates that the actual hormone is a small fraction only of the most active preparations. That

portion of the sulphur of insulin preparations which is labile to sodium hydroxide can be largely oxidised by dilute nitrite without loss of physiological activity, whilst the activity can be destroyed with iodine without affecting the sulphur labile to sodium carbonate; the supposed connexion between activity and content of alkali-labile sulphur (cf. Abel and Geiling, A., 1925, i, 1218) must therefore be regarded as fortuitous. C. R. HARINGTON.

Micro-methods for determination of labile and total sulphur in proteins. L. C. MAXWELL, F. BISCHOFF, and N. R. BLATHERWICK (J. Biol. Chem., 1927, **72**, 51—56).—The protein is heated with the selected concentration of alkali, the mixture acidified, and the hydrogen sulphide passed into a solution of hypobromite; the sulphate thus formed is precipitated with barium chloride in presence of ammonium nitrate and determined nephelometrically. Total sulphur is obtained by fusing the original material with sodium carbonate and sodium peroxide, followed by a similar nephelometric determination. C. R. HARINGTON.

Action of sugar in the organism. II. Decomposition of dextrose by very dilute alkali. F. FISCHLER.—See this vol., 449.

Action of sugar in the organism. III. Action of degradation products of dextrose on disturbances of carbohydrate metabolism. F. FISCHLER (Z. physiol. Chem., 1927, **165**, 68—102).—The clinical picture of hypoglycæmia in rabbits caused by overdosage with insulin exhibits two main features, a general stimulation of the central nervous system and a local abolition of tone in the muscles which may be due to deficiency of dextrose and glycogen. All symptoms of insulin hypoglycæmia are relieved by dihydroxyacetone as efficiently as by dextrose; methylglyoxal, on the other hand, exerted a toxic effect on normal animals, and in hypoglycæmic animals increased very much the severity of the symptoms. On administration of a mixture of methylglyoxal and dihydroxyacetone to a hypoglycæmic animal, the restorative effect of the latter compound predominated. Lactic and pyruvic acids, glycerol, acetone, acetaldehyde, glycol, and glycollaldehyde had no marked effect on the symptoms of hypoglycæmia. It is suggested that the toxic effects of overdosage with insulin may be due to increased formation of methylglyoxal (cf. Kermack, Lambie, and Slater, this vol., 282). C. R. HARINGTON.

Calcium metabolism. I. Action of the parathyroid hormone on the calcium content of the serum and on the absorption and excretion of calcium. C. P. STEWART and G. H. PERCIVAL (Biochem. J., 1927, **21**, 301—313).—Extensive hæmorrhage causes a lowering of the serum calcium in rabbits, but not in cats. Rabbits are less susceptible to the action of parathyroid extract than are cats. Parathyroid extract raises the serum calcium of cats when injected subcutaneously and more rapidly when injected intravenously. The action is prevented by the simultaneous injection of sodium hydrogen carbonate. Parathyroid exerts its full action on the serum calcium, even after complete removal of the alimentary canal. There is no diminution in the excretion of calcium when the hormone is administered while the serum calcium is high. The large intestine provides the main excretory route for calcium. The liver, spleen, pancreas, pituitary, thyroid, and central nervous system seem to have no special function in connexion with the effect of parathyroid on the blood calcium. The hormone probably controls the distribution of calcium between blood and tissues by regulating the proportion of the total diffusible serum calcium. S. S. ZILVA.

Iodine compounds of the thyroid. T. INGVALDSEN and A. T. CAMERON (Trans. Roy. Soc. Canada, 1926, [iii], **20**, V, 297—306).—Iodothyroglobulin, from beef thyroids, shows all the characteristics of a pseudo-globulin in regard to solubility and precipitation, and from this substance an impure thyroxin preparation containing 38·5% of iodine has been obtained. The specific test for thyroxin, the formation of an orange-red colour with nitrous acid, changing to red on addition of ammonia (Kendall and Osterberg, A., 1920, i, 180), is also given by di-iodotyrosine. The formation of the red colour, which appears to be specific for these two substances, is of equal intensity for molecular solutions, and appears to depend on the presence of two iodine atoms attached to the ring in a definite position. After treatment which should remove all the thyroxin from hydrolysed thyroid tissue, the above colour reaction is still markedly positive, and it is suggested that di-iodotyrosine may be present, although this substance could not be isolated. A. WORMALL.

Relative activity of thyroid fractions and derivatives. A. T. CAMERON and J. CARMICHAEL (Trans. Roy. Soc. Canada, 1926, [iii], **20**, V, 307—319).—The method used for comparing the activities of various preparations and extracts of the thyroid is that previously described (*ibid.*, 1), the method involving calculations based on the effects on growth and on the heart, liver, and kidneys of young white rats. The full activity of the thyroid appears to reside in the thyroglobulin, but thyroxin does not represent the full activity of the thyroid gland. Aqueous extracts of the thyroid show slight activity only. Thyroid activity is not destroyed by the action of pepsin or trypsin, whilst after enzymic hydrolysis of thyroglobulin, a solution is obtained which is distinctly active, but contains only a trace of thyroxin. Di-iodotyrosine has no activity alone, nor does it accentuate the effect of thyroxin when both substances are administered together. A. WORMALL.

Isolation of thyroxin. E. C. KENDALL (J. Biol. Chem., 1927, **72**, 213—221).—The author has been unable successfully to apply the method of Harington (A., 1926, 644) for the isolation of thyroxin from the thyroid gland; he also finds the distribution of thyroxin among the various fractions obtained in the process of isolation to be different from that described by the latter worker. It is therefore suggested that the process of isolation may have to be varied according to the place of origin of the thyroid glands employed. C. R. HARINGTON.

Some sterol colour reactions in their relation to vitamin-*A*. O. ROSENHEIM (Biochem. J., 1927, **21**, 386—388).—On evaporating to dryness a chloro-

form solution of cholesterol and benzoyl peroxide in equimolecular proportions, a chromogenic substance is obtained which gives with arsenious chloride a blue colour indistinguishable in appearance from that given by cod-liver oil with the same reagent. When, however, this purified chromogen is added to vegetable or animal oils which do not by themselves react with arsenious chloride, it fails to give the colour reaction. When a neutral solvent is used, the reaction is intense. The fading of the blue pigment produced by arsenious chloride with the artificial product is much slower than in the case of cod-liver oil. There is also a difference in the absorption spectrum of the two pigments. The two chromogens are therefore not identical. S. S. Zilva.

Effect of heat and oxidation on cod-liver oil as measured by colour tests. F. Wokes and S. G. Willimott (Biochem. J., 1927, **21**, 419—425).—The course of destruction of the chromogenic substance in cod-liver oil by aeration was studied at 88°, 98°, 108°, 118°, and 125°. The temperature coefficient for 10° was found to be about 1·4—1·5. The results were in agreement with those obtained by various workers on the destruction of vitamin-*A* in cod-liver oil as measured by the biological test. Qualitative agreement was obtained by the concentrated sulphuric acid, phosphorus pentoxide, arsenic trichloride, and antimony trichloride colour tests. The destruction of vitamin-*A* by aeration is probably due to volatile organic peroxides. S. S. Zilva.

Effect of 2 : 6-dihydroxyquinoline obtained from the β-acid of crude oryzanin on the polyneuritis of pigeons. Y. Sahashi (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1927, **5**, 191—198).—2 : 6-Dihydroxyquinoline hydrochloride prepared from the β-acid of crude oryzanin (cf. A., 1926, 846) has a temporary curative effect on the spastic symptoms of polyneuritis in pigeons, but lacks the curative powers of oryzanin. It is concluded that either 2 : 6-dihydroxyquinoline or its tautomeric form is a nucleus of the antineuritic substance from rice-polishings, or that oryzanin possesses a growth-promoting component besides its antineuritic factor. *N*-Chloro-α-quinolone appears to possess similar antineuritic powers to 2 : 6-dihydroxyquinoline, and in view of the similar properties reported for 2-hydroxypyridine (Williams, A., 1916, i, 697), phloroglucinol (Iwata, J. Agric. Chem. Soc. Japan, 1926, **2**, 466), and quinine, the author concludes that the active hydroxyl group of the β-acid possesses similar powers. R. Brightman.

Precipitation of the antiscorbutic factor from lemon juice. S. S. Zilva (Biochem. J., 1927, **21**, 354—355; cf. A., 1924, i, 588, 901; 1925, i, 1220).—Most of the antiscorbutic factor in decitrated lemon juice is precipitated by lead acetate within the p_H range of 5·4—7·2. An active fraction containing 0·1—0·2% of dry matter is thus quickly and conveniently obtained. S. S. Zilva.

Vitamin-*C* in cow's milk. Relation to concentration, homogenisation, and sterilisation. A. Lavialle (Bull. Soc. Chim. biol., 1927, **9**, 208—221).—An investigation to determine the influence of certain processes, particularly sterilisation, on the vitamin-*C* in milk. Dogs, initially in good health, show characteristic signs of scurvy after 7—10 months if fed on a diet deficient in vitamin-*C*, but if concentrated homogenised and sterilised milk has been added to the diet, no signs of scurvy are evident after 16 months. The concentrated milk loses its antiscorbutic properties when heated at 120—125° for 45 min. The use of preserved milks in cases of deficiency diseases, for which these milks are suitable on account of their richness and digestibility, and the necessity of supplementing them with fresh fruit juices, are discussed. A. Wormall.

Antirachitic substances. V. Action of ultra-violet light on ethers and esters of cholesterol. C. E. Bills and F. G. McDonald (J. Biol. Chem., 1927, **72**, 13—19).—No cholesteryl ether acquired antirachitic properties after irradiation; cholesteryl acetate, *iso*butyrate, and benzoate were all activated by ultra-violet light, but not the cinnamate, in view of which it is considered that the activation of the former esters is a property of the intact molecule, and is not due to liberation and subsequent activation of cholesterol itself. C. R. Harington.

Isolation of the antirachitic fraction of cholesterol irradiated by ultra-violet rays. I. I. Nitzescu, G. Popoviciu, and J. Denes-Goetz (Bull. Soc. Chim. biol., 1927, **9**, 126—136).—Methods involving successive recrystallisations and precipitation with digitonin have been applied to concentrate the active antirachitic fraction (vitasterol) of irradiated cholesterol. The antirachitic power of irradiated cholesterol diminishes by successive recrystallisations, but residues from the mother-liquors are about 10 times as potent as the crystalline products. The residues lose none of their activity when kept for at least three or four weeks in dark vessels. These results are opposed to the findings of Hess, Weinstock, and Sherman (A., 1926, 207). Fractions have been isolated which were active in quantities less than 0·5 mg. per 100 g. of the total diet. A. Wormall.

Catalytic action of irradiated cod-liver oil. B. Schimkus (Arch. exp. Path. Pharm., 1927, **121**, 230—237).—The lipoid peroxide content of cod-liver oil irradiated by sunlight was measured by the rapid titration of the iodine liberated from potassium iodide with sodium thiosulphate; concentrations from $N/250$ to $N/80$ were obtained. The peroxide catalyses the oxidation of iodide to free iodine. E. A. Lunt.

Parent substance of vitamin-*D*. O. Rosenheim and T. A. Webster (Biochem. J., 1927, **21**, 389—397).—Stigmasterol and sitosterol show absence of absorption bands in the spectroscopic test and cannot be antirachitically activated by irradiation. Purified cholesterol behaves similarly. Charcoal and potassium permanganate in acetone solution remove the provitamin from cholesterol. The provitamin forms a digitonide. Ergosterol shows the same characteristic absorption spectrum in the ultra-violet as unpurified cholesterol, the intensity of the absorption, however, being enormously increased. Assuming it to be ergosterol, the amount of the impurity present in ordinary cholesterol was judged

by comparative spectroscopical examination to be of the order of 1 : 2000. Irradiated ergosterol in daily doses of 0·0002 mg. cures and prevents rickets in rats on a rachitic diet. S. S. ZILVA.

Search for vitamin-*D* in the diatom *Nitzschia closterium* (W. Sm.). J. L. LEIGH-CLARE (Biochem. J., 1927, **21**, 368—372).—The diatom grown in glass and exposed to either diffused daylight or direct sunlight forms a very poor source of vitamin-*D*. It probably is not therefore the ultimate source of vitamin-*D* in cod-liver oil. S. S. ZILVA.

Free energy of nitrogen fixation by living forms. D. BURK (J. Gen. Physiol., 1927, **10**, 559—573).—From a study of free energy data, it is shown that the fixation of nitrogen from the atmosphere by living cells so as to form nitrate or ammonia is accompanied by a liberation of free energy as well as by a positive heat of reaction. The general bearing of such results on the process of nitrogen fixation by plants and bacteria is discussed in detail. W. O. KERMACK.

Nitrogenous material in a ligneous plant during a year's growth. R. COMBES (Compt. rend., 1927, **184**, 533—535).—The total and relative percentages of nitrogenous material in the foliage, stem, and roots of a 2-year-old beech for 16 months are recorded. J. M. GULLAND.

Light absorption by the leaves of plants and by chlorophyll solutions. P. LASAREFF (Biochem. Z., 1927, **182**, 131—133).—The primary and secondary absorption maxima of a solution of chlorophyll and of the green leaf show an approximate coincidence. Only 1—2% of the incident light energy passes through the green leaf. J. PRYDE.

Presence of sodium in plants. G. BERTRAND and J. PERIETZEANU (Compt. rend., 1927, **184**, 645—649).—Direct determinations of the percentage of sodium by means of the triple acetate of uranium, magnesium, and sodium (Streng, A., 1884, 366; Blanchetiere, A., 1923, ii, 579) afford values for the fresh plant ranging from 0·0006% in the case of milfoil to 0·5471% in the stem and leaves of seaweed. For the dried plants, the values found lie between 0·0017% for horse-chestnut (fruit) and 3·507% for seaweed, and for the ash the sodium content lies between the limits 0·016% (leaves of Japanese spindle-tree) and 16·78% (seaweed). Some of the plants examined had previously been reported free from sodium. Fresh leaves of the following plants gave the values indicated: lily 0·0008, pear 0·0014, mulberry 0·0007, horse-chestnut 0·0021, haricot 0·0012, iris 0·0017, maize 0·0093, plantain, 0·0464, tobacco 0·03882%. R. BRIGHTMAN.

Relation of stored food to cambial activity in the apple. E. L. PROEBSTING (Hilgardia, 1925, **1**, 81—106).—The cessation of radial increase of wood and modification of the thickness of the cell walls following defoliation of apple trees does not appear to be associated with a deficiency of stored food. Possible reasons for the cessation of growth are suggested. The concentration of reducing sugars is much greater in the bark than in the wood of young apple trees. CHEMICAL ABSTRACTS.

Use of the hydroquinhydrone electrode for p_H determination in the fluids of the organism. F. GROSSMAN (Biochem. J., 1927, **21**, 267—271).—Biilmann's hydroquinhydrone electrode (A., 1921, ii, 372) yields p_H values identical with those obtained with the hydrogen electrode in buffer solutions with p_H less than 7. In more alkaline buffer solutions higher values which increase with alkalinity are recorded with the first electrode. In physiological fluids such as blood-serum, cerebrospinal fluid, and blood, consistent values are obtained with the hydroquinhydrone electrode. These figures when corrected for the alkalinity of the medium by a formula introduced by the author agree well with those obtained with the hydrogen electrode. The quinhydrone, the quinoquinhydrone, and the hydroquinhydrone electrodes cannot be used for fluids with p_H greater than 9. The first two electrodes are unsuitable for serum and blood. S. S. ZILVA.

Determination of mineral matter in organic materials. A. VILA and R. ANCELLE (Bull. Soc. Chim. biol., 1927, **9**, 340—342).—An apparatus is described in which organic material may be destroyed by means of fuming nitric acid, whilst any volatile products are collected in a series of absorption vessels. W. O. KERMACK.

Determination of uric acid as ammonium urate. A. BOIVIN (Bull. Soc. Chim. biol., 1927, **9**, 149—161).—The various modifications of this method are investigated, in order to find the conditions which give most accurate results for uric acid solutions. The ammonium salt is best precipitated by the addition of ammonium chloride and ammonia; the precipitate is filtered off after 24 hrs., then dissolved in sodium hydroxide, and converted into the mercuric salt, in which the uric acid–nitrogen is determined by Kjeldahl's method after removal of the ammonia present. The precipitation of the ammonium salt, under the conditions stipulated, results in a loss of less than 0·01 g. of uric acid per litre, if the concentration of uric acid is greater than 0·1 g. per litre, and if the amount of other oxypurines is not greater than the amount of uric acid present. The concentration of uric acid, for accurate work, should be at least 0·2 g. per litre, and therefore the ammonium urate methods are not directly applicable to blood. A. WORMALL.

Micro-determination of uric acid. Determination of a few centigrams of uric acid per litre in presence of purine bases. A. BOIVIN (Bull. Soc. Chim. biol., 1927, **9**, 162—173).—Uric acid is precipitated as the mercuric salt, the precipitate is dissolved in a small volume of potassium cyanide solution, and then the ammonium salt is precipitated. The subsequent treatment is similar to that described before (preceding abstract). In the micro-determination, an addition to the result of 3 mg. per litre is made, and then the error is of the order of 1 mg. pe litre. A. WORMALL.

BRITISH CHEMICAL ABSTRACTS

A—PURE CHEMISTRY

JUNE, 1927.

General, Physical, and Inorganic Chemistry.

Present state of atomic physics. O. W. Richardson (Proc. Physical Soc., 1927, 39, 171—186).

Light source for exciting resonance spectra. G. Cario and W. Lochte-Holtgreven (Z. Physik, 1927, 42, 22—25).—A convenient lamp for producing intense sodium *D*-light is described. It consists essentially of a direct-current arc in sodium vapour through which argon is circulated at 10—20 cm., and consumes about 40 watts at 400 volts. The lamp is constructed so that a cylinder of sodium vapour is excited to intense luminosity, the light from which passes through a window at right angles to the axis of the cylinder. Great constancy of operation is claimed for this lamp. R. W. Lunt.

Use of the discharge in hydrogen as source of continuous spectrum in the ultra-violet. M. Lambrey and D. Chalonge (Compt. rend., 1927, **184**, 1057—1059).—If 2000—3000 volts are applied to a tube containing hydrogen under 2·5 mm. pressure, a continuous spectrum is obtained extending from the red into the Schumann region. The H_α ray is visible, but not the H_β or H_γ rays or the secondary spectrum. The spectrum is stable for at least 5 min., and the method is superior to the use of the positive crater of the carbon arc, the incandescence lamp with a metallic filament and quartz window, and condensed sparks, under water, from the points of view of stability, intensity, and purity of the spectrum. J. Grant.

Fine structure of the helium arc spectrum. W. V. Houston (Proc. Nat. Acad. Sci., 1927, **13**, 91—94).—Helium is shown, by interferometric methods, to give a spectrum of singlets and triplets. The unusual separation ratios of the triplets predicted by Heisenberg (this vol., 5) are confirmed. Helium thus behaves as a two-electron system, in accordance with spectroscopic theory, and the helium spectrum is removed from its anomalous position. W. E. Downey.

First spark spectrum of lithium. H. Schuler (Z. Physik, 1927, 42, 487—494).—A continuation of previous work (A., 1925, ii, 339). The fine structure of the line 5485 Å. has been studied in detail and the results are discussed in relation to theory. W. E. Downey.

Spectra of boron. R. A. Sawyer and F. R. Smith (J. Opt. Soc. Amer., 1927, **14**, 287—303).—Fewer than twelve spectral lines of wave-length longer than 1850 Å. have previously been attributed to boron, although more would be expected from a consideration of the series spectra. A new determination of the spark spectra between 2300 and 5800 Å. has been made and more than 100 new lines due to boron have been measured with an accuracy of ±0·1 Å.; 20 of these have been classified as series lines of B II and B III. C. J. Smithells.

Second green line of the auroral spectrum. (Lord) Rayleigh (Nature, 1927, **119**, 525).—Vegard's interpretation (this vol., 285) may be incorrect, since there is a band in about the same position in the negative band spectrum of gaseous nitrogen. A. A. Eldridge.

Structure of the second order spectrum of nitrogen [N II]. F. Croze and J. Gilles (Compt. rend., 1927, **184**, 1053—1055).—The N II spectrum of nitrogen conforms to the law of alternation of multiplicities, being formed by combinations between terms of odd multiplicity. Groups of terms $^3P^3D^3F$ exist, corresponding with the configuration $(ssp)nd$, of which ^3D and ^3F combine to give the multiplet DF, the corresponding ^3P terms being determined by the combinations forming the multiplets $^3S—^3P''$, $^3D—^3P$, and $^3P—^3P$. These values are given in full, and also those for the ^3P, ^3D, and ^3F levels, assuming Fowler's value of 70,000 for the $^3P_2$ level. Analogously with the spectrum O III, the order of the P_0, P_1, and P_2 terms is inverted (Mihul, this vol., 389). J. Grant.

Spectrum of ionised nitrogen (N II). A. Fowler and L. J. Freeman (Proc. Roy. Soc., 1927, A, **114**, 662—689; cf. A., 1925, ii, 250).—The spectrum of ionised nitrogen over the range 6836—830 Å. has now been examined by the use of condensed discharges in vacuum tubes containing gas at various pressures. Of 340 lines recorded in this region, about half have now been classified, and of the remaining lines, more than 100 are very faint. The spectrum is derived from singlet and triplet terms, the absolute values of which have been determined with the aid of a sequence of three $^3P'—^3P$ multiplets. For transitions of a single electron, the terms predicted by theory have been deduced by the application of Hund's rules (A., 1925, ii, 912), supplemented by data given by Laporte (this vol., 82). The predictions have greatly aided in the analysis of the spectrum by indicating, in the first instance, the character of the deepest terms, and next by giving approximate values of unidentified terms, and thence some idea of the location of multiplets arising from their combinations with terms already known. There is excellent agreement between observation and theory. Of the 19 deepest terms predicted, complex terms being counted

as one, all but one have been identified. The term 1^3P, recently identified by Bowen (this vol., 285) from a multiplet at 671, is probably the deepest, its value being 238,850, corresponding with an ionisation potential of 29·5 volts. A few multiplets which appear in the spectrum have been attributed to simultaneous transitions of two electrons.

L. L. BIRCUMSHAW.

Electronic configurations corresponding with the third order emission spectrum of oxygen. C. MIHUL (Compt. rend., 1927, **184**, 1055—1057; cf. this vol., 389).—The values of all the terms actually known, and the corresponding electronic configurations, are tabulated for the triplet and quintuplet systems of the O III spectrum, on the basis of the configurations $(ssp)np$ and $(spp)3p$, respectively. The wave-lengths of the corresponding rays are compared with those observed in practice. J. GRANT.

Regularities in the spectra of fluorine and chlorine. T. L. DE BRUIN (Proc. K. Akad. Wetensch. Amsterdam, 1927, **30**, 20—24).—The following constant wave-number differences have been found in the F I spectrum: 145·5, 160·1, and 274·6. Narrow triplets were found in the F II spectrum having the separations 12 and 20. Quadruplet and doublet terms have been detected in the F I spectrum, and the various detected term combinations are tabulated. The majority of the lines have Zeeman effects consistent with the suggested arrangement. The structure of the F I spectrum resembles those of N I and O II.

Existing data on the spectrum of chlorine, examined for constant wave-number differences, gave 40·5, 67·2, (107·7), and 530·5. The differences 40·5 and 67·2 have already been found and identified (Paschen, A., 1923, ii, 672). The difference 530·5 is probably a frequency difference in the Cl I spectrum.

J. S. CARTER.

Regularity in the spectrum of ionised neon. P. K. KICHLU (Nature, 1927, **119**, 671—672).—About 140 of the lines ascribed to ionised neon and not included in Paschen's scheme have been arranged in groups of multiplets. A. A. ELDRIDGE.

Duration of the metastable states of neon, argon, and helium. H. B. DORGELO and T. P. K. WASHINGTON (Proc. K. Akad. Wetensch. Amsterdam, 1927, **30**, 33—46; cf. A., 1926, 101).—Using an improved technique, the rate of disappearance of the metastable states of neon in its dependence on temperature and pressure has been investigated. At the ordinary temperature the duration of the metastable states first increases with increasing pressure, attains a maximum value, and then diminishes. Such behaviour indicates that the metastable states disappear by diffusion to the walls and by collisions of the first kind with normal neon atoms. With pure argon, similar phenomena are encountered, the durations of the metastable states being still greater. The duration is greatly influenced by the presence of impurities, hydrogen especially having a strongly destructive influence on the metastable states. The disappearance of the metastable states of helium is entirely determined by the diffusion to the wall.

J. S. CARTER.

Series spectra of ionised phosphorus, P II. I. S. BOWEN (Physical Rev., 1927, [ii], **29**, 510—512).—A table gives the intensity, wave-length, frequency, and designation of 110 strong lines of P II, which are classified as arising from various combinations between 32 terms of the triplet system. The observed terms are those demanded by Hund's theory.

A. A. ELDRIDGE.

Geissler discharge in argon. K. G. EMELÉUS and N. L. HARRIS (Nature, 1927, **119**, 602).—Earlier results for the glow discharge between cold electrodes (this vol. 293) are confirmed, the experiments being repeated in argon. A. A. ELDRIDGE.

Electrodeless discharge in quenched and sustained waves. Continuous spectra of cæsium and of potassium. G. BALASSE (Compt. rend., 1927, **184**, 1002—1005).—Electrodeless discharges in quenched waves on the vapour of cæsium at 150° gave spark spectra only, but as the temperature rose these were progressively replaced by arc spectra. From 200° a continuous spectrum, gaining in intensity, was obtained from the feebly excited portion of the tube. Measurements at increasing temperatures and tensions up to 40,000 volts showed that the continuous spectrum has its maximum intensity when the arc and spark spectra exist simultaneously and with comparable intensities. It does not appear in the presence of the spark and arc spectra only. Analogous results were obtained for potassium. Contrary to Bloch's interpretation of Bohr's theory, two spectra exist having different degrees of excitation but corresponding with the same degree of ionisation (A., 1923, ii, 350). Electrodeless sustained wave discharges for mercury, hydrogen chloride, iodine, cæsium, and potassium gave stable luminous discharges. Intense arc spectra were obtained for mercury, cæsium, and potassium, but no continuous spectra for the last two. For cæsium the frequency of the electro-magnetic field is without influence on the composition of the fluorescence. J. GRANT.

Intensity measurements on the spectra of cæsium and potassium. A. FILIPPOV (Z. Physik, 1927, **42**, 495—498).—The intensity of the second member of the principal series of cæsium does not agree with the intensity rule of Burger and Dorgelo. The intensities of the diffuse and fundamental series of cæsium and of the diffuse and sharp series of potassium, in general, are in agreement with the rule. W. E. DOWNEY.

New terms in the spectrum of calcium. R. J. LANG (Astrophys. J., 1926, **64**, 167—171).—A re-examination of the spectrum of calcium in the Schumann region. Two new terms appear to combine with many known terms. A. A. ELDRIDGE.

Multiplets in the spark spectrum of iron. H. N. RUSSELL (Astrophys. J., 1926, **64**, 194—203).—214 Lines have been grouped into 35 multiplets belonging to sextet and quadruplet systems, involving combinations between 16 terms. The lowest energy-level of the ionised atom of iron belongs to a ^6D-term, the next to a $^4F'$-term, and the next to a ^4D- and a $^4P'$-term. The observed energy levels are those to be anticipated by Hund's theory. A. A. ELDRIDGE.

Secondary arc spectrum of iron from 5167 to 6678 Å. W. KLEINEWEFERS (Z. Physik, 1927, **42**, 211—221).—Accurate determinations have been made by an interferometer method of 52 lines of the secondary arc spectrum of iron in the range named.

R. W. LUNT.

Diffusion of imprisoned resonance radiation in mercury vapour. M. W. ZEMANSKY (Physical Rev., 1927, [ii], **29**, 513—523).—The rate at which resonance radiation emerged from one face of a slab of mercury vapour after the exciting light, incident on the other face, was extinguished, decreased exponentially. For vapour densities less than 4×10^{15} atoms/c.c., the exponential constant varied approximately inversely as the square of the thickness of the slab. The inadequacy of Milne's theory is discussed. The probability of an impact of the second kind between a normal and an excited mercury atom is approximately 9×10^{-4}. In obtaining imprisonment of resonance radiation in a sealed-off cell, the presence of freshly evaporating mercury was not necessary.

A. A. ELDRIDGE.

Polarisation of resonance radiation of mercury vapour. Influence of magnetic fields and of foreign gases. V. VON KEUSSLER (Ann. Physik, 1927, [iv], **82**, 793—835).—A photo-electric apparatus for the measurement of polarisation in the ultra-violet is described. Investigations with the 2536·7 resonance line of mercury vapour have shown that the effect of weak magnetic fields on the polarisation is in conformity with the classical electron theory. The polarisation depends largely on the pressure of mercury vapour. The results require that the radius of the sphere of influence of mercury atoms should be fifty times that predicted by the kinetic theory of gases. By extrapolating to zero vapour pressure, the degree of polarisation is 80%, whilst at the lowest pressure of mercury vapour used, 2×10^{-5} mm., the value 79·5% was recorded. A suitably arranged high-magnetic field enabled the polarisation to be raised from 80% to 100%. The investigation of the depolarising action of foreign gases on the resonance radiation showed that for some gases the effective radius of the atom or molecule exceeded the gas-kinetic radius, although for other gases collisions provided a sufficient explanation for the depolarisation. The most marked effect was shown with water vapour, since the effective radius was calculated on the basis of the depolarisation to be four times the gas-kinetic radius. The least effective gases were the inert gases. For helium 17% of the collisions were effective in depolarising the resonance radiation. The magnetic effect on polarisation by addition of foreign gases accounts for the damping action of different gases.

R. A. MORTON.

Regularities in the spark spectrum of lead. H. GIESELER (Z. Physik, 1927, **42**, 265—275).—The lead spectrum from a Schuler lamp has been analysed in the region 9070—6880 Å. by a spectrograph, and in the region 6563—2167 Å. by a 1 metre grating. The lines observed, and those recorded by other workers in the region 9070—966 Å., have been correlated with the electron orbits of the lead atom.

R. W. LUNT.

Changes produced in the lines of sodium, magnesium, and aluminium by compound formation. T. WETTERBLAD (Z. Physik, 1927, **42**, 603—610).—Using the technique of Hjalmar (A., 1920, ii, 655; 1921, ii, 292), the wave-length of the $K\beta_1$ line has been determined for the following: sodium 11,550, sodium oxide 11,592 (sodium sulphate 11,591); magnesium 9499, magnesium oxide (and magnesium silicate) 9538; aluminium 7944, aluminium oxide 7965 X. The corresponding values for silicon, phosphorus, sulphur, and chlorine have been determined from the data of Backlin (A., 1926, 987) and of Lundquist (A., 1925, ii, 1014). From these values it is shown that the difference between the wave-length differences α_1—$K\beta_1$ for metal and oxide diminishes to zero as the atomic number increases from 11 to 18 (argon); and that sodium and magnesium show anomalies in agreement with the observations of Backlin, Siegbahn, and Thoræus (A., 1925, ii, 457, 614). The $K\beta_1$ line in sodium fluoride is 11,635, sodium chloride 11,631, sodium bromide 11,619, sodium iodide 11,612. It is seen that the difference between the wave-length in the compound and the metal decreases with increasing atomic number.

R. W. LUNT.

Spark lines of the K spectra of sodium, magnesium, and aluminium. T. WETTERBLAD (Z. Physik, 1927, **42**, 611—613).—Using the technique of Hjalmar (cf. preceding abstract), the following wave-lengths have been determined: sodium $\alpha_{1,2}$ 11,883·6, α' 11,836·3, α_3 11,803·9, α_4 11,785·9, α_5 11,717·7, α_6 11,687·1, β_3 11,702; magnesium 9867·75, α' 9825·3, α_3 9800·0, α_4 9784·2, α_5 9729·4, α_6 9704·4, β_3 9647; aluminium $\alpha_{1,2}$ 8319·40, α' 8285·2, α_3 8265·8, α_4 8250·1, α_5 8208·8, α_6 8188·6, β_3 8042 X. Wentzel's theory is found to account for these lines satisfactorily.

R. W. LUNT.

***L*-Emission spectra of lead and bismuth.** C. E. EDDY and A. H. TURNER (Proc. Roy. Soc., 1927, **A, 114**, 605—610; cf. A., 1926, 652).—Using the apparatus previously described (*loc. cit.*), it is found that the L-emission spectra of both lead and bismuth contain four lines, the ν/R values of which correspond with transitions between energy levels disallowed by Bohr's selection principle. In addition, several other "non-diagram" lines were found, and it is considered that all these lines could not be due to impurities in the metals. A crystal of calcite was employed, and the fibres were measured by the projection method described previously. The values assumed as standards for the tungsten lines were the means of those obtained by Siegbahn and Dolejsek (Z. Physik, 1922, **10**, 159) and by Duane and Patterson (A., 1921, ii, 363). Tables are given showing the ν/R units obtained from the observed wave-lengths of the lines, and these are compared with the difference between the ν/R values of the levels associated with each.

L. L. BIRCUMSHAW.

Zeeman effect in tungsten. H. BEINING (Z. Physik, 1927, **42**, 146—159).—Using a large concave grating, the Zeeman effect in a field of 30,000—34,000 gauss has been determined for a number of lines of the arc spectrum of tungsten in the range 2600—5800 Å. The Lande g-values are found to

correspond in a few cases only with those now determined. R. W. LUNT.

Second order Stark effect in hydrogen. P. S. EPSTEIN (Science, 1926, **64**, 621—622).—The shift of the central normal component of H_γ in very strong electric fields is determined by Kiuti as 0·28 Å. for a field of 100,000 volts/cm. This result is in better agreement with the author's new theory (A., 1926, 987, 1187) than with the old, the values of $\Delta_2\lambda$ being 0·251 and 0·217 Å., respectively. A. A. ELDRIDGE.

Electron velocities in the Compton effect. P. LUKIRSKY (Z. Physik, 1927, **42**, 516—531).—The velocity of Compton electrons was determined by irradiating graphite with approximately monochromatic *X*-rays. The velocity is dependent on the wave-length of the exciting rays and the direction of leaving the surface. W. E. DOWNEY.

Analysis of the time-effect in compound chemical reactions. M. BODENSTEIN (Ann. Physik, 1927, [iv], **82**, 836—840).—A critical reply to the views of Skrabal (this vol., 188) on Herzfeld's deductions (A., 1919, ii, 503). R. A. MORTON.

Periodicity of photo-electric thresholds. G. B. WELCH (Proc. Nat. Acad. Sci., 1927, **13**, 111—113).—The photo-electric threshold may be considered as a measure of the energy taken from the incident radiation in order to detach one of the outer electrons from its atom. If follows, therefore, that the curve showing the relation between photo-electric thresholds and atomic numbers exhibits a certain periodicity with maximum values for the alkali metals, and that the values show a decrease on proceeding towards the electronegative elements. W. E. DOWNEY.

Thermionic emission from solid and liquid metals. A. GOETZ (Z. Physik, 1927, **42**, 329—374).—A full description is given of the apparatus and technique that have been developed for the measurement of the thermionic emission of solid and liquid metals as a function of their temperature, including the construction of a furnace to work up to 2000°, the procedure adopted for temperature measurement, and recording devices for thermionic emission and temperature. Experimental results are to follow. R. W. LUNT.

Scattering of electrons by a single crystal of nickel. C. DAVISSON and L. H. GERMER (Nature, 1927, **119**, 558—560).—A narrow beam of electrons was directed normally against a target cut from a single crystal of nickel, and the intensity of scattering (the number of electrons per unit solid angle with speeds near that of the bombarding electrons) measured in various directions in front of the target. For bombarding potentials of 15—40 volts, if the bombarding potential and the co-latitude are fixed and exploration is made in azimuth, the variation in the intensity of scattering is slight; at 40 volts a hump appears in the co-latitude curve for the (111) azimuth, developing with increasing voltage into a spur. The spur is sharp in azimuth as well as in latitude, and forms one of a set of three such spurs, due to beams of scattered electrons which are nearly as well defined as the primary beam. Similar spurs occur in the (100) azimuth; thirteen sets of beams have been discovered in an exploration in the principal azimuths covering a voltage range of 15 to 200 volts. Tabulated data also show the ten sets of *X*-ray beams of longest wave-length which would occur within the angular range of the observations. Three-electron beams have no *X*-ray analogues. The correlation between the two sets of data is discussed. A. A. ELDRIDGE.

Energy losses of electrons. H. JONES and R. WHIDDINGTON (Proc. Leeds Phil. Lit. Soc., Sci. Sec., 1927, **1**, 160—161; cf. A., 1926, 1189).—A glowing filament in a high vacuum near a fine slit gives a magnetic spectrum consisting of a single line, corresponding closely with the maximum energy eV, when a moderate accelerating potential is applied. After introduction of gas at low pressure into the space surrounding the filament, a complex spectrum appears containing bands and lines corresponding with energies less than the full potential, provided that the introduction of the gas is accompanied by a large increase in the original current, due to the atoms and molecules taking part in the conduction. The energy differences represent quantum energy losses due to collisions. Hydrogen, air, and argon have so far been examined, and some, if not all, of the energy losses correspond with previously known critical potentials. M. S. BURR.

Cross-sectional area of hydrogen and nitrogen molecules against slow electrons. E. BRUCHE (Ann. Physik, 1927, [iv], **82**, 912—946).—Refinements in technique (cf. Mayer, A., 1921, ii, 234; Ramsauer, *ibid.*, 324) have brought electron velocities of 1—1·5 volt$^{\frac{1}{2}}$ within the range of accurate measurements by means of the magnetic method. The electron velocity expressed in terms of volt$^{\frac{1}{2}}$ is plotted against cross-sectional area in cm.^{2}/cm.^{3} at 0° and 1 mm. For hydrogen from 1 to 1·7 volt$^{\frac{1}{2}}$ the curve rises slowly to a maximum and then falls from about 50 to 5 at 7 volt$^{\frac{1}{2}}$. With nitrogen the curve rises from about 30 at 1 to 90 at 1·6 volt$^{\frac{1}{2}}$; it then falls very rapidly, but reaches a minimum near 2·8 volt$^{\frac{1}{2}}$, then follows a very flat maximum near 4·4 volt$^{\frac{1}{2}}$, falling off very slowly to 7 volt$^{\frac{1}{2}}$. The results agree with earlier data over the range 2—7 volt$^{\frac{1}{2}}$, but below 2 volt$^{\frac{1}{2}}$ differences are evident. The magnetic method shows a flatter maximum for hydrogen, and a sharper maximum for nitrogen, than is found with Lenard's method. R. A. MORTON.

Energy of photo-electrons produced by soft *X*-rays. E. RUDBERG (Nature, 1927, **119**, 704—705).—Measurements of the velocity of photo-electrons set free from copper under the influence of soft *X*-rays show that the preponderance of low-speed electrons is very great. A compound photo-electric mechanism may be involved. A. A. ELDRIDGE.

Transformation period of the initial positive air ion. L. M. VALASEK (Physical Rev., 1927, [ii], 29, 542—545).—The half-value period of the transformation of the initial positive air ion (mobility 1·87 cm./sec. per volt/cm.) to the final ion (mobility 1·36) is 0·0132 sec. and 0·0354 sec. for a relative humidity of 32 and 80%, respectively. A. A. ELDRIDGE.

Emission of positive rays. M. MORAND (Ann. Physique, 1927, [x], **7**, 103—183).—From considerations of the interatomic forces in a crystalline salt it is shown that the field necessary to detach positive

ions is of the order of 10^7—10^8 volts/cm., and an expression is derived for the current between plane parallel electrodes in terms of the applied field, the field necessary to detach a positive ion, and the charge and mass of the ion. An elaborate technique is described in which, with a heated platinum point thinly coated with a salt as anode, fields of the above order can be readily obtained, thereby producing an intense homogeneous and conveniently directed beam of positive rays. From measurements of the Stark effect at the anode, it is estimated that fields up to 1600 kilovolts/cm. were obtained. With a lithium salt on the anode, it is shown, from the magnetic deflexion of the beam, that it is composed of hydrogen ions, singly and doubly charged lithium atoms, and ions of greater mass, probably sodium and magnesium, which exist as impurities in the lithium. The magnetic deflexion of the beam has been employed to separate the isotopes of lithium, since the deflexion varies with the mass of the ion. In this way it has been estimated that the ratio of Li^7 to Li^6 is 15 approximately, and quantities of the order of 5×10^{-4} mg. of Li^6 have been obtained. The light emitted where the beam impinges on the cathode contains some lines of the arc and spark spectra of lithium. R. W. Lunt.

Scattering of canal rays in hydrogen. R. Conrad and J. Koenigberger (Z. Physik, 1927, **42**, 323—326).—A reply to Thomson (this vol., 182), whose criticisms are declared to be invalid. R. W. Lunt.

Secondary magnetic canal rays at electrodes. E. Goldstein (Z. Physik, 1927, **42**, 276—282).—The emission of secondary magnetic canal rays from electrodes of different shapes has been examined qualitatively. The structure of the beam is found to depend on the shape of the electrode, on the gas density, and on the direction and strength of the magnetic field. R. W. Lunt.

Magnetism and the periodic system. R. Ladenburg (Z. physikal. Chem., 1927, **126**, 133—152).—A review of the magnetic susceptibilities of ions, elements, and complex compounds considered qualitatively in relation to the electron groupings as deduced, with the aid of the quantum theory, from spectroscopic evidence (cf. A., 1920, ii, 301).

G. A. Elliott.

Theory of paramagnetism of oxygen and nitric oxide. J. H. Van Vleck (Nature, 1927, **119**, 670).—The susceptibilities of oxygen and nitric oxide may be accounted for numerically by the use of a new general derivation of the Langevin formula $N\mu^2/3kT$ for the susceptibility χ, based on the new quantum mechanics. Although calculations of the susceptibility for a mixture of nitric oxide molecules with 2 and 0 Bohr magnetons, with relative abundance determined by the Boltzmann temperature factor, do not agree with experiment, the value (9·12 Weiss magnetons) obtained when the component of spin magnetic moment perpendicular to the axis of figure is considered, but the perpendicular component of orbital moment is disregarded, is in agreement with Bauer and Piccard's experimental value (9·20).

A. A. Eldridge.

Isotopes. Atomic weight of chlorine in potassium salts of Alsace. (Milles.) E. Gleditsch and L. Gleditsch (J. Chim. phys., 1927, **24**, 238—244).—Four samples of Alsace potassium salts were transformed into sodium chloride by heating with sulphuric acid and treating the hydrogen chloride thus evolved with sodium carbonate. After several recrystallisations the densities of the saturated solutions were determined, and were within experimental error equal to one another and to that of purified commercial sodium chloride. Hence these chlorides, as also those examined previously (A., 1922, ii, 281), which vary in origin, age, and preparation, all contain chlorine of at. wt. 35·46 (O=16·00).

S. J. Gregg.

Isotopes and atomic structure. G. Piccardi (Atti R. Accad. Lincei, 1927, [vi], **5**, 439—443).—The author's theory of atomic structure (this vol., 394) has been extended with particular reference to isotopes.

R. W. Lunt.

Atomic weight of silver. B. Brauner (Nature, 1927, **119**, 526; cf. this vol., 289; Riley and Baker, A., 1926, 1190; this vol., 289).—The author insists that loss of silver may have taken place by volatilisation during the first fusion, followed by condensation to a fog which may have passed out of the apparatus.

A. A. Eldridge.

Atomic weight of silver. H. B. Baker and H. L. Riley (Nature, 1927, **119**, 703; cf. preceding abstract).—It has been confirmed experimentally that loss of silver by volatilisation could not have occurred.

A. A. Eldridge.

Factors involved in the calculation of the ages of radioactive minerals. A. Holmes and R. W. Lawson (Amer. J. Sci., 1927, [v], **13**, 327—344).—A first approximation to the age of a suitable radioactive mineral may be obtained from the expression, age$=$(Pb/U$+k$Th)c, in which U, Th, and Pb, respectively, denote the % of uranium, thorium, and lead of radioactive origin, the constants k and c denoting the amount of uranium equivalent in lead-producing capacity to 1 g. of thorium (k) and the reciprocal of the amount of lead produced by 1 g. of uranium in 10^6 years (c). The age is expressed in millions of years. On the basis of a critical review of the available data, it is suggested that the values $k=0{\cdot}38$ and $c=7{\cdot}400$ should be adopted generally pending better values. The ages of minerals calculated by different authors using agreed values would then be directly comparable. The correction for the disintegration of uranium and thorium during the life-time of a mineral is considered, and a simplified formula is derived which gives satisfactorily the corrected age in terms of the approximate age (see above): corrected age$=$approximate age$(1-x/2-x^2/3)$, where $x=1{\cdot}155$(Pb/U$+0{\cdot}38$Th). The ages of various minerals calculated in both ways are concordant among themselves and justify the construction of a tentative geological time-scale. R. A. Morton.

Radioactivity and the heat of the earth. R. W. Lawson (Nature, 1927, **119**, 703—704).—Polemical against Evans (this vol., 289; see also this vol., 225).

A. A. Eldridge.

Atomic disintegration by α-particles. G. Kirsch and H. Pettersson (Z. Physik, 1927, **42**, 641—678).—The discrepancies between the results

obtained by the Cambridge and Vienna schools on the disintegration of elements and on the ejection of *H*-particles when elements are bombarded by α-particles are discussed in great detail. The relative merits of various forms of scintillation microscope are analysed, and great attention is devoted to the methods of distinguishing *H*- from α-particles. Following a review of the technique of Rutherford and Chadwick, the Wilson cloud method, the photographic method, and that developed by the authors, it is concluded that the negative results of the Cambridge school, with carbon, for example, are to be attributed to the relatively insensitive optical method which they employed, and to the use of polonium instead of the weak preparations of radium-*C* preferred by the authors. R. W. LUNT.

Disintegration of carbon by α-particles. H. PETTERSSON (Z. Physik, 1927, 42, 679—703).—A technique is described whereby the *H*-particle emission from pure graphite and paraffin wax has been determined. The emission falls from about 60 to 10 per million α-particle impacts as the penetration of the α-particles is diminished by passing through the equivalent of 0·8—5·5 cm. of air. Similar results were obtained using polonium as the source of α-particles. The results obtained have been confirmed by using the Wilson cloud method, the ionisation method, and the photographic method.
R. W. LUNT.

Tracks of *H*-particles. R. HOLOUBEK (Z. Physik, 1927, 42, 704—720).—The Wilson track method has been modified and elaborated in order to observe the tracks of *H*-particles ejected from atoms bombarded with α-particles. The emission from aluminium, iron, beryllium, oxygen, diamond chips, and graphite has been determined in this way; the value for diamond chips is slightly less than that for graphite, and the emission per million α-particle impacts is independent of the intensity of the polonium source. R. W. LUNT.

Disintegration of aluminium by α-particles. E. A. W. SCHMIDT (Z. Physik, 1927, 42, 721—740).—Using a scintillation method with elaborate precautions, the *H*-particle emission from aluminium bombarded with α-particles from radium-*C* and from polonium has been re-examined. The author claims to have established definitely that the minimum penetration of α-particles necessary to eject *H*-particles from aluminium is less than 1 cm. of air (Rutherford and Chadwick say 3—4·9 cm.). The emission of *H*-particles produced by α-particles from radium-*C* which have passed through aluminium foil equivalent to 1 cm. of air corresponds with 30 per million α-particle impacts, a value approximately fifteen times as great as that of Rutherford and Chadwick. The results now obtained on the frequency of distribution of *H*-particles between different ranges are in very good agreement with those of Holoubek (cf. preceding abstract), obtained by an independent method; the minimum penetration of *H*-particles from aluminium is found to be less than 1 cm. of air; the value given by Chadwick is 9—12 cm. The data now recorded are held to invalidate the theory of atomic disintegration by α-particles which has been advanced by the Cambridge School. R. W. LUNT.

Determination of the mass of the particles ejected from aluminium, carbon, boron, and iron when bombarded with α-particles. G. STETTER (Z. Physik, 1927, 42, 741—758).—The principle of the mass spectroscope has been employed to design an apparatus in which the charged particles proceeding from a surface bombarded with α-particles are brought to foci on a fluorescent screen, where their numbers are determined visually by scintillations. Data have been obtained using reflecting surfaces of aluminium, carbon, boron, and iron; in all cases maxima have been observed corresponding with He^{++} and H^{+} within 2% of the predicted position, the maximum experimental error being ±5%. The metals were freed from occluded gases before examination; the results are therefore held to establish the emission of *H*-particles from these substances.
R. W. LUNT.

Loss of charge of *H*-particles. G. STETTER (Z. Physik, 1927, 42, 759—762).—The technique described (preceding abstracts) has been employed to determine the fraction of *H*-particles that becomes neutralised in moving from the surface where they are emitted to the point of detection. The results show that not more than 5% become neutralised under the conditions in which the *H*-particle emission has been determined (cf. preceding abstract).
R. W. LUNT.

Continuous spectrum of β-rays. C. D. ELLIS and W. A. WOOSTER (Nature, 1927, 119, 563—564).—Measurement of the heating effect of a known quantity of radium-*E* in a thick-walled calorimeter showed that the average energy emitted at each disintegration of radium-*E* is 340,000+30,000 volts. The result confirms the hypothesis that the continuous spectrum is emitted as such from the nucleus.
A. A. ELDRIDGE.

Number of dispersion electrons for the continuous spectra and series spectra of hydrogen. Y. SUGIURA (J. Phys. Radium, 1927, [vi], 8, 113—124).—Theoretical. On the basis of the theory of mechanics recently developed by Heisenberg and Schrödinger, the absolute number of dispersion electrons associated with the series rays of hydrogen, and also with the continuous spectra, has been determined. The time of emission of the rays H_α and H_β has also been calculated for each state n_k, where n—1, 2, 3, and 4, but the values are not in very good agreement with those determined experimentally.
M. S. BURR.

Electron configuration in atoms. II. H. LESSHEIM and R. SAMUEL (Z. Physik, 1927, 42, 614—626).—The authors' theory (this vol., 88) has been extended to include the elements between yttrium and palladium, and between lanthanum and hafnium. R. W. LUNT.

Light quanta and interference. W. BOTHE (Z. Physik, 1927, 41, 332—351).—Experiments have been carried out with *X*-rays from a tungsten anticathode excited by electrons of 100—120 kilovolts and with practically monochromatic radiation of wave-length 0·257 Å., from which it is concluded that no con-

tinuity can be associated with light quanta in an interference field of dark bands. R. W. LUNT.

Action of radiation and perturbations on atoms. J. C. SLATER (Proc. Nat. Acad. Sci., 1927, **13**, 104—111).

Relation between the reciprocal impenetrability of matter and Pauli's exclusion principle. Correction. P. EHRENFEST (Nature, 1927, **119**, 602; cf. this vol., 183).

Theory of matter and electricity. G. D. BIRKHOFF (Proc. Nat. Acad. Sci., 1927, **13**, 160—165).—A mathematical theory of matter and electricity is put forward which satisfies the fundamental requirements of determinateness and stability. W. E. DOWNEY.

Hydrogen atom and the Balmer formula. G. D. BIRKHOFF (Proc. Nat. Acad. Sci., 1927, **13**, 165—169).—Mathematical. On the theory of the preceding paper, it is shown that a formula of the Balmer type is obtained for the frequencies of the small oscillations of a hydrogen atom. W. E. DOWNEY.

Absorptivity [of radiation] of stellar material. S. C. ROY (Z. Physik, 1927, **42**, 499—515).—An expression is deduced for the absorption coefficient of radiation absorbed by matter in various states of ionisation. W. E. DOWNEY.

Infra-red spectrometer of large aperture. A. H. PFUND (J. Opt. Soc. Amer., 1927, **14**, 337—338).—An arrangement of mirrors is described which makes it possible to increase the aperture of an infra-red spectrometer from $f/8$ to $f/2$ without loss of definition. This is achieved by ensuring that all light is reflected from the concave mirrors of the system along their optic axes. C. J. SMITHELLS.

Comparison of three spectrophotometric methods. L. TAYLOR (J. Opt. Soc. Amer., 1927, **14**, 332—336).—The accuracy and sensitivity of spectrophotometric measurements made visually, photographically, and by means of a photo-electric cell are compared. With an arbitrary intensity of 10, visual observations gave an error of 4%, which increased to about 16% for an intensity of 1. Intensities of 0·005 could be measured with an error of 5—25% by the photographic method with an exposure of 2—20 hrs., whilst the error with the photo-electric cell was only 2—6%, the time of observation being 3—5 min. C. J. SMITHELLS.

Band spectra and the periodic system. R. MECKE (Z. Physik, 1927, **42**, 390—425).—A theoretical paper in which the band spectra of a large number of molecules, hydrides, oxides, nitrides, and halides are discussed with reference to their atomic constants and the position of the constituent atoms in the periodic table. R. W. LUNT.

Connexion between visible and ultra-violet bands of hydrogen. O. W. RICHARDSON (Proc. Roy. Soc., 1927, **A**, **114**, 643—650).—Theoretical. From a study of the absorption and emission spectra of hydrogen, Dieke and Hopfield (this vol., 89) have extended the band system of which the Lyman bands (cf. Witmer, A., 1926, 552) and Werner bands (this vol., 1) form a part, and they have shown that each set of vibration bands have different initial electronic states, but the same final electronic state. Values were given for the constant w_0, which measures the vibration frequency at infinitesimal amplitude, and the constant xw_0, which determines the deviation from simple harmonic motion for these states. These constants have now been examined with a view to distinguish between the claims of $2\sigma=29330{\cdot}30$ and $2\pi=29502{\cdot}82$, both of which have been found to be final states for bands in the visible region. L. L. BIRCUMSHAW.

Doppler effects and intensities of lines in the molecular spectrum of hydrogen positive rays. M. C. JOHNSON (Proc. Roy. Soc., 1927, **A**, **114**, 697—710).—The grouping of lines in the secondary spectrum was studied by longitudinal observation of positive rays in hydrogen. The grouping of lines excited by positive ions falling through a very high voltage was compared with the grouping arising from collision with electrons at low voltages (ionisation potentials), and with the grouping in the Geissler tube spectrum. From the large Doppler effect which appears in the Balmer lines when the positive rays are photographed, the proportion of the atomic spectrum carried by neutralised positive rays and the proportion excited in the stationary gas by the impact of positive ions were determined, and from the manner in which these proportions vary along the Balmer series they are related to the intensity grouping of the adjacent regions of the molecular spectrum. The apparatus has been previously described (this vol., 182) and measurements of the wave-length of the positive-ray line in air, the estimated positive-ray intensity, the intensity in Merton and Barratt's Geissler tube, and the Richardson classification, where a line belongs to the Q branch of his associated bands, are given. Of the four lines recorded by Rau (A., 1924, ii, 134) as showing faint Doppler effects, it is suggested that one, 4568, is really a red component of 4561. Four other probable Doppler components were observed in the secondary spectrum: (1) the line 4420 is displaced to the violet of its comparison spectrum; (2) the line 4517 has a faint haze to the violet; (3) and (4) two lines in the red region, 6589·05 and 6532·62. From these data it is considered probable that the Balmer moving series is carried by neutralised atoms which were already free atoms, and had not been incorporated into molecules, when accelerated in the dark space. The relation of the character of the molecular spectrum to the Doppler effect in the atomic spectrum and the carriers of the spectra are also considered. L. L. BIRCUMSHAW.

Interpretation of molecular spectra. II. F. HUND (Z. Physik, 1927, **42**, 93—120; cf. this vol., 183).—By an extension of principles previously advanced, the author proceeds to a theoretical consideration of a number of characteristics of molecular spectra. A theoretical basis has been provided for the empirical classification developed by Millikan and Birge. The laws governing the term relationships in molecules containing two unequal nuclei have been examined, and are illustrated by reference to the spectra of BO, CO^+, CN, CO, and CaH. From a consideration of the stationary states characteristic of a molecule containing two equal nuclei, an explanation

is offered for the empirical combination rule, and for the intensity variations in the band spectrum, which is illustrated by reference to the hydrogen molecule. From this point of view an expression is developed for the temperature variation of the specific heat of hydrogen. R. W. LUNT.

Absorption bands in nitrogen. H. SPONER (Proc. Nat. Acad. Sci., 1927, **13**, 100—104).—The ultra-violet band system found by Birge and Hopfield (A., 1925, ii, 737) in nitrogen in emission is found to be a true absorption system of nitrogen. The system does not belong to NO. The absorption system known to be missing in the known term scheme of N_2 has not been found. W. E. DOWNEY.

Structure of the third positive nitrogen group. (FRL.) M. GUILLERY (Z. Physik, 1927, **42**, 121—145).—The fine structure of the four nitric oxide bands 2721, 2594, 2477, and 2558 Å. has been determined using a low-tension arc between copper electrodes in air as light source, and a 6·4-metre grating. The lines have been tabulated, and analysed according to the procedure of Mecke (Physikal. Z., 1925, **26**, 217). R. W. LUNT.

Absorption of quartz and fused silica below 4·1 μ. T. DREISCH (Z. Physik, 1927, **42**, 426—427).—The absorption of quartz and fused silica has been determined in the range 2·5—4·1 μ. Perpendicular to the optical axis, quartz is characterised by four absorption maxima, 2·91, 2·97, 3·02, and 3·75 μ (very weak); fused silica exhibits maxima at 2·75 and 3·75 μ (very weak). R. W. LUNT.

Absorption of optical glasses and borax below 4·1 μ. T. DREISCH (Z. Physik, 1927, **42**, 428—434).—The absorption of a number of optical glasses and of borax has been examined in the range 2·0—4·1 μ. At 2 μ they are characterised by very low absorption, which rapidly increases as the frequency diminishes. Borax glasses show maxima at 2·8, 3·68, and 4·05 μ, the intensity of which increases with the B_2O_3 content of the glass; they correspond with the absorption maxima of borax, 2·95, 3·65, and 4·1 μ. R. W. LUNT.

Classification of absorption spectra. R. RITSCHL (Z. Physik, 1927, **42**, 172—210).—The absorption spectra of chromyl chloride and of the four cuprous halides in the vapour state have been determined in the visible region, using a concave grating with a dispersion of 5·55 Å./mm. The spectra consist of diffuse lines which were not resolved by a 6-metre grating. These have been arranged in groups corresponding with a Deslandres equation of the general type $\nu=\nu_0-an+bn^2$, where n is an integer, and a and b are constants. The existence in some cases of two sets of constants is attributed to the isotopes of fluorine, bromine, and chlorine. The absorption maxima of cuprous iodide were found to correspond with the emission maxima of Mulliken (A., 1925, ii, 346). R. W. LUNT.

Absorption spectrum of chromium oxychloride. A. C. S. VAN HEEL (Proc. K. Akad. Wetensch. Amsterdam, 1927, **30**, 95—103).—The wave-lengths, wave-numbers, and intensities of 181 lines between 5899·25 and 5018·3 Å. in the absorption spectrum of chromium oxychloride vapour are listed. J. S. CARTER.

Mercury band-spectrum of long duration. (LORD) RAYLEIGH (Proc. Roy. Soc., 1927, **A**, **114**, 620—642; cf. A., 1925, ii, 738).—An improved method is worked out for obtaining the mercury band spectrum of long duration. The stream of vapour is excited by a discharge from a Wehnelt cathode, and is observed spectroscopically after leaving the region of discharge. Under suitable conditions (rapid distillation of the vapour and a current of less than one milliamp.) a predominant band spectrum is obtained. As shown previously (*loc. cit.*), a portion of the intensity of the line 2537 is associated with the band spectrum, but the other resonance line 1850 is absent. The important divisions of the band spectrum are: (*a*) the band at 2345, with attendant bands of shorter wave-length; (*b*) the resonance line 2537, with bands a few Å. from it; (*c*) the fainter maximum at 2650, which seems to be associated with a series of flutings (approximate wave-lengths of these bands are given); (*d*) the broad maximum at about 3300; (*e*) the green visual band. When the vapour is examined after excitation, all these features are found to decay at about the same rate. The time taken to decay to half intensity is measured as $1·82\times10^{-3}$ sec. If the excited stream of vapour is passed through a tube heated locally to bright red heat, the band (*e*) is extinguished, (*a*) and (*c*) are slightly weakened, whilst (*b*) and (*d*) are unaffected. The visual green band (*e*) recovers intensity to some extent, as it passes up the cooler part of the tube, and (*a*) and (*c*) tend to regain their intensity relative to (*b*) and (*d*). The forbidden line 2270 (cf. Takamine, A., 1926, 767) is present in the spectrum, and may be brought out by long exposure. It appears to be connected intimately with the band spectrum, since a region of apparently continuous spectrum begins at this point, extending in the direction of long waves as far as the band 2345. The other forbidden line, 2656, is also present, and in intensity greater than that of 2270. L. L. BIRCUMSHAW.

Absorption spectra of five-membered heterocyclic compounds. S. MENCZEL (Z. physikal. Chem., 1927, **125**, 161—210).—The ultra-violet absorption spectra of the following substances have been investigated: solutions in various solvents of thiophen, furan, pyrrole, furan-2-carboxylic acid, furfuryl alcohol, furfuraldehyde, indole, fluorene, carbazole, isatin, rhodanine, phthalic, succinic, and maleic anhydrides, liquid thiophen and furan, vaporised thiophen and furfuraldehyde. L. F. GILBERT.

Influence of different centres of absorption on the spectra of substances. J. E. PURVIS (J.C.S., 1927, 780—783; cf. A., 1926, 557).—The ultra-violet absorption spectra of several aromatic esters and other compounds are compared. The spectra of benzoic anhydride, benzoyl peroxide, and phenyl benzoate are very similar to that of benzoic acid. Benzyl phenylacetate and phenylacetaldehyde give spectra which show remnants of the characteristic benzene bands, whilst the spectra of benzyl salicylate and cinnamate exhibit the characteristic bands of

the acidic part of the molecule only. It is concluded that the various centres of absorption do not act independently, and that in some cases one centre may overpower the influence of the others.

G. A. ELLIOTT.

Dependence of the intensity of the fluorescence of dyes on the wave-length of the exciting light. II. S. J. VAVILOV (Z. Physik, 1927, **42**, 311—318; cf. A., 1922, ii, 181).—A quantity proportional to the ratio of the energy emitted as fluorescence to that absorbed, k_λ, has been determined for the following solutions and in the following ranges of wave-length: fluorescein (+ammonia) in water ($c=2\times10^{-3}$ g./c.c.), 5020—2530 Å., fluorescein in ethyl alcohol ($c=10^{-2}$ g./c.c.), 5350—2530 Å.; æsculin in water ($c=10^{-3}$ g./c.c.), 4050—2530 Å. For fluorescein $k_\lambda\lambda^{-1}$ is approximately constant from 2500 to 4300 Å., in agreement with Einstein's law; it remains approximately constant over the region corresponding with the fluorescence maximum, 4400—4900 Å., and then diminishes rapidly. The value of $k_\lambda\lambda^{-1}$ for æsculin is approximately constant in the range 2500—4050 Å.

R. W. LUNT.

Luminescence of quinine sulphate. A. PETRIKALN (Z. Physik, 1927, **42**, 435—442).—The luminescence spectrum of quinine sulphate consists of two continuous bands in the range 3500—4500 Å. with an emission minimum at 4130 Å. Superimposed on these bands are a number of small bands (20—30 Å. in width) of the following wave-lengths: 3580, 3750, 3800, 3880, 3990, 4050, 4200, 4270, 4330±10—15 Å. They are characterised by two frequency differences, 350 cm.$^{-1}$ and 1620 cm.$^{-1}$, the former to be associated with the neutral molecule, and the latter with the excited state; a scheme of energy levels has been constructed on this basis. The continuous bands are therefore concluded to be due to the loss of water from quinine sulphate.

R. W. LUNT.

Specific inductive capacity of phosphorescent substances. F. DACOS (Bull. Acad. roy. Belg., 1927, [v], **13**, 33—41).—The intensity of the phosphorescent light emitted by calcium sulphide containing various percentages of impurities, and the specific inductive capacities of such mixtures, have been determined as functions of the percentage of impurity. The mixture exhibiting the greatest phosphorescence has a minimum specific inductive capacity; excitation of phosphorescence has no effect on the specific inductive capacity.

H. F. GILLBE.

Origin of the ultra-violet spectrum of the glow of phosphorus. H. J. EMELÉUS and R. H. PURCELL (J.C.S., 1927, 788—793).—An investigation of the phosphorescence spectrum of phosphorus pentoxide at low temperatures showed the presence of a band in the visible region with a maximum intensity near 4600 Å. (cf. Ebert and Hofmann, A., 1900, ii, 517). There was no evidence of an ultra-violet spectrum. The spectrum of the discharge through phosphorus pentoxide vapour contained in a silica tube with external electrodes of copper foil was also studied. A complex band-spectrum was recorded which included all the known bands in the ultra-violet spectrum of the glow of phosphorus. The spectrum of the latter was re-examined and three new broad bands (2300—2325, 2600—2700, and 2740—2795) in the ultra-violet, as well as two in the red (5200—5900, and 6000—6800) were discovered. These bands were also present in the spectrum of the discharge through phosphorus pentoxide vapour. It is concluded that the ultra-violet spectrum of the glow of phosphorus has its origin in the molecule of an oxide.

G. A. ELLIOTT.

Glow of arsenic. H. J. EMELÉUS (J.C.S., 1927, 783—788).—The glow of arsenic in air or oxygen appears suddenly, at temperatures between 250° and 310°, when the pressure is reduced below a certain critical value—the "glow pressure." The glow of arsenic differs from that of phosphorus, since it is not affected by the presence of small quantities of carbon tetrachloride, nitrobenzene, ors ulphur dioxide, and since the glow temperature in air is only 10° lower than the corresponding value in oxygen. Also, the non-luminous reaction preceding the glow is much more vigorous with arsenic. The appearance of the glow is favoured by a rapid removal of the arsenic trioxide formed in the reaction, and it is suggested that the velocity of removal of this product by evaporation and condensation is the determining factor in the formation of the glow.

G. A. ELLIOTT.

Ionisation potential of hydrogen fluoride. S. C. BISWAS (Nature, 1927, **119**, 707).—The ionisation potential of fluorine is computed to be 16·7 volts, whence that of hydrogen fluoride is 18·04 volts. That of hydrogen chloride is 13·8 volts. The ionisation products of hydrogen fluoride may be $(HF)^+$ and e.

A. A. ELDRIDGE.

Radiating potentials of the band systems of carbon monoxide. O. S. DUFFENDACK and G. W. FOX (Science, 1926, **64**, 277—278).—The radiating potential of a band system is defined as the excitation potential of the zero vibrational and zero rotational levels of the initial state. The energy levels for neutral and ionised carbon monoxide are shown diagrammatically. Several bands usually included in the Ångstrom system are excluded, but two bands with edges at 3680·5 and 3894·3 Å. belong to the system. Certain bands between 3000 and 5000 Å. are ascribed to carbon dioxide formed after dissociation of carbon monoxide.

A. A. ELDRIDGE.

Influence of water of crystallisation on the photo-electric effect in crystal hydrates. A. PREDVODITELEV and W. BLINOV (Z. Physik, 1927, **42**, 60—76).—Measurements have been made of the photo-electric current, using a constant source of ultra-violet light, given by copper sulphate, potassium alum, and lead acetate during dehydration in a vacuum. It is found that the photo-electric current increases to a maximum corresponding with complete dehydration, and that at any given time during dehydration the ratio of the current from the partly dehydrated salt to the maximum current (completely dehydrated salt) is independent of the state of division of the salt. An equation of Thomson and Whiddington relates the velocity of photo-electrons emitted by metal atoms surrounded by an absorbing shell with the velocity from the unshielded metal atoms and with the density of the absorbing shell.

This equation has been employed to calculate the amount of dehydration from the data now obtained by considering the water of crystallisation as an absorbing shell. The curves for the variation of dehydration with time (calculated from the photo-current time data) are similar in form to those obtained from direct measurements of the change of weight in a vacuum at the ordinary temperature. The greater velocities of change observed in the photo-electric experiments are attributed to the increased rate of dehydration due to the increase in temperature of the salt during exposure to ultra-violet light. It is thought that the observed change in photo-electric effect during dehydration could take place only if the water molecules were arranged in a shell surrounding the metal atoms, as in Werner's co-ordination hypothesis. The results are therefore held to afford proof of this theory. R. W. LUNT.

Photo-electric investigations with ammonia-charged platinum. H. LEUPOLD (Ann. Physik, 1927, [iv], **82**, 841—872).—At atmospheric pressures ammonia shows an absorption band in the ultra-violet in the region 217—230 with a maximum at 221 When ammonia is allowed to enter an evacuated absorption chamber, the quartz end-plates adsorb the gas. The adhering layer has a coefficient of absorption (β) differing from that (α) of the gas in bulk. The product βd (in which d is the thickness of the film and cannot be evaluated) is determined and plotted against wave-length. The maximum of the curve has not been measured, but appears to lie on the short-wave side of 217 $\mu\mu$.

In order to obtain an adsorbed film of ammonia on platinum, it is only necessary to outgas the surface and leave it for a few days in contact with gaseous ammonia. By replacing an adsorbed film of air with ammonia, the photo-electric sensitivity of platinum is markedly increased, especially in the long-wave ultra-violet region. The increase is so great as to give the idea that the red limit had been shifted in the direction of longer waves as a result of the adsorption of ammonia. In the neighbourhood of the absorption band the photo-electric liberation of electrons is decreased, because when the adsorption of ammonia is at a maximum, *i.e.*, at atmospheric pressure, the thin layer of gas absorbs the short-wave light and the intensity incident on the platinum foil is much reduced. R. A. MORTON.

Dielectric constants and refractive indices. W. HERZ (Z. anorg. Chem., 1927, **161**, 217—220).—The values of (*a*), $M(D-1)/d(D+2)$ and of (*b*), $M(n^2-1)/d(n^2+2)$, where M is the mol. wt., d the density, n the refractive index, and D the dielectric constant at various temperatures in the range 10—22°, have been determined for a large number of organic liquids. The ratio a/b is nearly unity for the hydrocarbons, carbon tetrachloride, and thiophen, showing that these are not dipolar compounds. With halogenated hydrocarbons, esters, alcohols, aldehydes, ketones, and organic acids the ratio increases with the magnitude of the dipolar moment; in homologous series the ratio decreases with increasing carbon content.

A. R. POWELL.

Dielectric investigation of the anisotropic melting of *p*-azoxyanisole. W. KAST (Z. Physik, 1927, **42**, 81—92).—Earlier work (Ann. Physik, 1924, [iv], **73**, 145) has been extended by measuring the change in dielectric constant which takes place in the anisotropic melting of *p*-azoxyanisole in a magnetic field perpendicular to the plane of the parallel plate condenser used for the determinations for different values of the angle between the field and the normal to the plane of the condenser. A modified form of Ornstein's equation (*ibid.*, **74**, 445) has been employed to calculate the magnetic moment in which a correction for cohesive forces is applied. The value assigned to the magnetic moment, μ, is $4{\cdot}6\times10^{-15}$ ($=1{\cdot}5\times10^{5}$ Bohr magnetons). R. W. LUNT.

Molecular and atomic volumes. XIII. Examples from organic chemistry of the volume law for solids. W. BILTZ. **XIV. Molecular volumes of the methyluric acids.** W. KLEMM and L. KLEMM (Annalen, 1927, **453**, 259—278, 279—288; cf. this vol., 188).—XIII. The validity of the law that the volume of a compound at 0° Abs. is equal to the sum of the volumes of its constituents at 0°, each multiplied by a constitutive factor expressed by the ratio of two integers, has been examined for a variety of organic compounds. Zero volumes may be calculated from density data (cf. Herz, A., 1926, 117), or, with carbon and many inorganic substances, but not with organic substances, may be taken as equal to the volumes at the ordinary temperature, since the coefficients of expansion are small. For carbon as diamond and as graphite the values are C_{diamond} 3·4 c.c., and C_{graphite} 5·4 c.c. In all the compounds examined, the normal zero volume of hydrogen, 11·6 c.c., must be multiplied by the factor 0·5. Nitrogen does not appear to contribute anything to the zero volumes of compounds into the composition of which it enters. The aliphatic normal saturated hydrocarbons obey the additive law if the value C_{diamond} is used, whilst the same is true for the aromatic hydrocarbons if the value is used. A double linking raises the zero volume by 4 c.c., and a treble linking by 12 c.c. The halogenated hydrocarbons also obey the additive rule, the zero volumes of chlorine, bromine, and iodine being 16·5, 19·5, and 24·3 c.c., respectively, and the constitutive factor unity. In the carbonyl group, the value for oxygen is the actual zero volume, 10·7, whilst for hydroxyl oxygen and ether oxygen the value is about one third of this. With allotropic modifications, the more unstable form has, in general, the larger volume, and similarly for geometrical isomerides; *e.g.*, maleic acid has a larger heat of combustion and a larger zero volume than fumaric acid. Closing the chain to form hexamethylene reduces the volume by about 10 c.c., but it seems likely that the formation of a ring of four carbon atoms, as in α-pinene, may cause an increase in volume. In the dibasic aliphatic acids of the series ${}_nCH_{2n-2}O_4$, the volume is rather larger than the theoretical value when n is odd, and somewhat smaller when n is even. At present, the law of additive zero volumes is of little use in deciding questions of constitution, owing to the inaccuracy and scantiness of the necessary experimental data.

XIV. The values of d_4^{25} for the methylated uric

acids have been determined, and used to calculate the molecular volumes. The volume of a methyl group is 4 c.c. greater in the pyrimidine ring than it is in the glyoxaline ring. For a number of isomerides, the greater the volume, the greater is the dissociation constant. The volumes of 1 : 7- and 1 : 9-dimethyluric acids are abnormal. R. CUTHILL.

Absorption of radiation in the extreme ultraviolet by the inert gases. C. CUTHBERTSON (Proc. Roy. Soc., 1927, **A**, **114**, 650—658).—The apparent number of electrons per molecule which affect dispersion and their free frequency can be deduced from dispersion measurements (A., 1910, ii, 85, 561) by the use of the expression $\mu-1=N'qe^2/[2\pi m(n_0^2-n^2)]$ (a one-term formula of Drude's type), N' being the number of molecules in unit volume and q the number of dispersion electrons per molecule. An investigation of the actual position of the absorption bands has shown that, certainly in the case of xenon and krypton, and probably in the case of the three other inert gases, strong absorption bands exist in the neighbourhood of the positions predicted by the simple formula. A concave grating in a vacuum spectrograph was used, the position of the absorption band being deduced from the wave-lengths of the bright lines blocked out by the gas, which was admitted between the source of radiation, the carbon arc, and the photographic film. In xenon, the calculated free frequency is at 1001, the absorption band begins near 1036 at a pressure of 0·545 mm., and culminates between 903·7 and 687. In krypton, the calculated free frequency is at 840, and the absorption begins near 904 at a pressure of 0·218 mm. and culminates on the long-wave side of 687. In argon and helium the calculated free frequencies are at 726 and 507, respectively, and the beginning of the absorption band, about 800, is easily recognised. With neon, the calculated free frequency is at 481, and the absorption begins beyond 595. In all five cases the maximum of absorption is on the short-wave side of the calculated free frequency.

L. L. BIRCUMSHAW.

Relation between refractive and dispersive constants of inert gases. C. CUTHBERTSON (Proc. Roy. Soc., 1927, **A**, **114**, 659—661).—By plotting the cube roots of the refractive constants of the inert gases for long waves against the square of the effective number of dispersion electrons derived from dispersion measurements by means of a one-term formula of Drude's type (preceding abstract) a straight line is obtained. The equation for the line is $A+q^{\cdot}=$ 1)$^{\frac{1}{3}}$, A and B being constant for all five gases and equal to 16·7 and 5·483, respectively. The interpretation of the figures is considered.

L. L. BIRCUMSHAW.

Dispersion of light in gases within the ultraviolet spectrum. [Refractivity of methane and ammonia.] S. FRIBERG (Z. Physik, 1927, **41**, 378—384).—The refractivity of methane and ammonia has been determined for 21 wave-lengths from 5462·23 to 2302·86 Å. Formulæ involving four constants, which have been evaluated, are proposed to represent the change of refractivity with wave-length. The pressure coefficient, β, in Mascart's equation, $(n-1)p^{-1}(1+\beta p)^{-1}=$const., has been found to be $2{\cdot}10\times10^{-5}$ and $13{\cdot}9\times10^{-5}$ cm.$^{-1}$, respectively.

R. W. LUNT.

Variation of the refractive indices of gases with pressure from 1 to 10 atm. M. OPLADEN (Z. Physik, 1927, **42**, 160—171).—The refractivity of air and carbon dioxide has been determined by an interferometer method for the wave-lengths 5462 and 4359 Å. in the pressure range 1—10 atm. The following values were obtained for the constants in Mascart's equation, $n-1=kp(1+\beta p)$: air, $k_{\lambda_1}=0{\cdot}3617\times10^{-6}\pm0{\cdot}0002\times10^{-6}$, $\beta_{\lambda_1}=0{\cdot}51\times10^{-6}\pm0{\cdot}05\times10^{-6}$, $k_{\lambda}=0{\cdot}3659\times10^{-6}\pm0{\cdot}0002\times10^{-6}$, $\beta_{\lambda_2}=0{\cdot}53\times10^{-6}\pm0{\cdot}05\times10^{-6}$; carbon dioxide, $k_{\lambda_1}=0{\cdot}5468\times10^{-6}\pm0{\cdot}0005\times10^{-6}$, $\beta_{\lambda_1}=8{\cdot}72\times10^{-6}\pm0{\cdot}32\times10^{-6}$, $k_{\lambda_2}=0{\cdot}5533\times10^{-6}\pm0{\cdot}0005$, $\beta_{\lambda_2}=8{\cdot}71\times10^{-6}\pm0{\cdot}30\times10^{-6}$. The refractivity of air at 0° at 760 mm. is accordingly $n_0-1=293{\cdot}03\times10^{-6}\pm0{\cdot}17\times10^{-6}$, in good agreement with the results of other workers. R. W. LUNT.

Refractive indices of a crystalline liquid over its entire range of existence. C. MAUGUIN (Bull. Soc. chim. Belg., 1927, **36**, 172—178).—Ethyl *p*-(*p*-ethoxybenzylideneamino)-α-methylcinnamate melts at 95° to an anisotropic liquid which changes into the isotropic state at 123°. Under certain conditions the anisotropic liquid may be supercooled to 74°, at which temperature it changes to a viscid, stratified liquid. The ordinary (n_0) and extraordinary (n_e) refractive indices of each of the two birefringent liquids have been measured over their possible ranges of existence. A lower limiting temperature for the existence of the very unstable, stratified phase has not been determined. Measurements have, however, been made at a temperature as low as 40°. The change from the stratified to the anisotropic liquid at 74° is accompanied by a change in the values of n_e and n_0 (for the *D*-line) from 1·852 to 1·842 and from 1·513 to 1·523, respectively. The values at 120° of n_e and n_0 for the anisotropic liquid are 1·708 and 1·562, respectively. The value of n_D^{123} for the isotropic liquid is 1·603. J. S. CARTER.

Refractive indices of nicotine. J. W. GIFFORD and T. M. LOWRY (Proc. Roy. Soc., 1927, **A**, **114**, 592—593).—Using the apparatus employed recently for measuring the refractive indices of benzene and *cyclo*hexane (A., 1923, ii, 705), the refractive indices of nicotine have been measured for thirteen wave-lengths. L. L. BIRCUMSHAW.

***X*-Ray diffraction in liquids.** C. V. RAMAN and C. M. SOGANI (Nature, 1927, **119**, 601).—The *X*-ray liquid-haloes of hexane and *cyclo*hexane differ in such a manner as to indicate the effect of the geometrical form of the molecules on the *X*-ray scattering by a liquid, the structure of the latter being much more homogeneous than that of the former. The diffraction haloes of *cyclo*hexane and benzene are closely similar. On the other hand, for ordinary light, hexane and *cyclo*hexane exhibit similarity, and differ from benzene. A. A. ELDRIDGE.

Magnetic double refraction. C. V. RAMAN and J. R. K. RAO (Nature, 1927, **119**, 528).—Experiments on aliphatic hydrocarbons, alcohols, ethers, and esters have definitely established the existence

of magnetic birefringence in all of the liquids examined. A. A. ELDRIDGE.

Rotatory power of tartaric acid. E. VELLINGER (Compt. rend., 1927, **184**, 1010—1012).—Polemical against the criticism by Longchambon of the author's results (A., 1926, 1201; this vol., 17). The author repeats the interpretation of his observations more precisely. J. GRANT.

Rotation of camphor in alcoholic solutions. N. SCHOORL (Pharm. Weekblad, 1927, 64, 338—344).—The rotations and specific gravities, and the temperature coefficients for the rotation and specific gravity, of pure camphor in concentrations of 10 and 20 g. per 100 c.c. in 70% and 90% (by volume) alcohol are recorded. The specific rotations $[\alpha]_D$ are for 70% alcohol $+33{\cdot}80°+0{\cdot}2c+0{\cdot}090t$, and for 90% alcohol $+37{\cdot}05°+0{\cdot}145c+0{\cdot}090t$, for values of c from 5 to 25 (g. per 100 c.c. of solution) and for t 10—30°. The m. p. of the camphor used was 177·5°±0·2°, corr. S. I. LEVY.

Rotatory dispersion of certain aspartic esters. F. P. MAZZA and G. DELLO JOJO (Atti R. Accad. Lincei, 1927, [vi], **5**, 294—301).—Measurement of the optical rotations of β-ethyl hydrogen *l*-aspartate, β-*iso*amyl hydrogen *l*-aspartate, diethyl *l*-aspartate, and *diisoamyl* l-*aspartate* (b. p. 198—199°/20 mm., d^{16} 0·989, $[\alpha]_D$ −8·50°) shows that the dialkyl aspartates exhibit normal rotatory dispersion, whereas the monoalkyl esters (in aqueous solution) show a distinct maximum of the dispersion for 5209 Å. Clough (J.C.S., 1915, **107**, 1509) found that, in hydrochloric acid solution, diethyl *l*-aspartate is dextrorotatory; this change in the direction of rotation can be due only to conversion of the nitrogen from the ter- to the quinque-valent form. It appears probable that, in aqueous solution, the α-carboxyl group of the monoalkyl aspartates is salified by the amino-group and that there exists the equilibrium,

$$CO_2R\cdot CH_2\cdot CH_2\cdot\underset{NH}{\overset{CO}{<}}>O+H_2O \rightleftharpoons CO_2R\cdot CH_2\cdot CH(CO_2H)\cdot NH_3\cdot OH \rightleftharpoons CO_2R\cdot CH_2\cdot CH(NH_2)\cdot CO_2H+H_2O.$$

Such an equilibrium, depending on the temperature and concentration, would explain the change in sign of the alkyl hydrogen aspartates with change of temperature (cf. Piutti and Magli, A., 1907, i, 296).

It cannot be assumed that aspartic acid has the normal molecular structure in aqueous solution, but the sodium salt and the dialkyl esters must have it, and as these are lævorotatory, it seems the more rational to term *l*-aspartic acid the acid which is dextrorotatory in aqueous solution (cf. Karrer and Kaase, A., 1919, i, 570). T. H. POPE.

Statistical mechanics and its application to physico-chemical problems. R. C. TOLMAN (J. Franklin Inst., 1927, **203**, 661—678).—A discussion of the applications of statistical mechanics to systems in equilibrium.

Valency and structure of hydrogen and helium. R. DE (J. Sci. Assoc. Maharajah's Coll. Vizianagaram, 1927, **3**, 10—19).—The structure of the helium atom and of the hydrogen molecule is analysed on the basis of certain very arbitrary assumptions concerning interatomic forces; explanations are advanced for the group displacement law of radioactivity, and a structure is suggested for H_3. R. W. LUNT.

Structure and kinetic phenomena of hydrogen. R. DE (J. Sci. Assoc. Maharajah's Coll. Vizianagaram, 1927, **3**, 26—29).—The author's theory of the structure of the hydrogen molecule (preceding abstract) is used to contend that a simple harmonic motion of the molecule is a necessary condition of its stability, and that this motion is to be identified with the velocity of thermal agitation. R. W. LUNT.

Ionisation potentials of hydrogen. R. DE (J. Sci. Assoc. Maharajah's Coll. Vizianagaram, 1927, **3**, 20—25).—The author's theory (cf. preceding abstracts) is extended to calculate and discuss the ionisation potentials of hydrogen. R. W. LUNT.

Molecular structure of elements and compounds. I and II. A. E. MAKOVETZKY (J. Russ. Phys. Chem. Soc., 1926, **57**, 549—604).—Theoretical. Atoms and molecules are assumed to be perfect spheres, and the conception of "true" density, *i.e.*, the ratio of the mass of the substance to the volume actually occupied by the atoms, is developed from geometrical and kinetic considerations. An equation of state is deduced for all states of aggregation.

From these considerations, expressions are developed for the physical behaviour of gaseous, liquid, and solid substances; the results are shown to be *in* good agreement with the published experimental values. For the thermal expansion of gases, it is assumed that only the space between the molecules increases, and an expression is deduced connecting apparent densities of the gas at different temperatures.

On the assumption that all substances expand by 1/273 of the volume actually unoccupied by the molecules for an increase of temperature of 1°, these expressions are extended to liquids and solids also. For gases they reduce to the simple gas laws.

The formulæ obtained were tested by Young's values for the thermal expansion of organic liquids. The agreement for them, as also for the elements bromine, mercury, and water (ice), was found to be satisfactory. For "liquid" gases the formulæ were modified, as the coefficient of expansion depends on the range of existence of the gas as a liquid. The experimental and theoretical values for hydrogen, nitrogen, chlorine, and ammonia agree closely.

The expressions were further tested by a consideration of the degree of filling of space by spherical molecules of known radius in contact and the change due to a gradual separation on expansion. Formulæ so deduced were found to be identical in form with those above, and to give values closely similar to Young's data.

The thermal expansion of gases, liquids, and solids at constant pressure is considered, and it is concluded that for equal relative expansions between two corresponding temperatures, the heat of expansion is entirely determined by the fraction of the volume of the substance occupied by molecules, and is independent of the size of the molecules or the mass and positions of the atoms. The connexion between the

molecular heat capacities at different temperatures and the work of expansion against the internal pressures is discussed, and its dependence on the "true" density of a substance, and, consequently, on the number and arrangement of the atoms in a molecule, demonstrated. For similarly constituted molecules, where these considerations can be neglected, the expressions reduce to Dulong and Petit's and Neumann's rules.

An expression is given for the "true molecular density" of a substance. It is Avogadro's law extended to all states of aggregation, and is an equation of state connecting the apparent density with the mol. wt. and structure. The value of the "true" density of hydrogen is calculated from the known data of atomic sizes on the assumption that the hydrogen molecule consists of two spherical atoms in contact. It is further checked by a comparison of the properties of hydrogen with helium, and its behaviour at the f. p.; it is approximately 0·4. The kinetic and geometrical aspects of mono-, di-, tri-, and some varieties of poly-atomic molecules are discussed and diagrams given, from which the values of the fractions of the volumes of molecules occupied by atoms are obtained. Most of the theoretically possible structures were found to correspond with known elements or compounds. Taking the value of the true" density of hydrogen as 0·4, the deduced physical properties of silica, diamond, sulphur dioxide, hydrogen, carbon tetrachloride, chlorine, benzene, water, and *n*-pentane and its homologues were found to be in close agreement with experiment. The silica molecule is probably $(SiO_2)_3$; liquid chlorine is $(Cl)_5$, with a structure identical with that of carbon tetrachloride, stannic chloride, silicon tetrachloride, and phosphorus oxychloride, benzene and water appear to possess condensed molecules almost identical with the crystallised state, the structures being probably hexagonal rings: C_6H_6 and $(H_2O)_4$. M. ZVEGINTZOV.

Sulpho-salts. L. FERNANDES (Atti R. Accad. Lincei, 1927, [vi], 5, 302—303).—A statement of work to be carried out on variations in the co-ordination forces of a salt which occur when oxygen is replaced partly or wholly by sulphur. T. H. POPE.

Electronic formulation of organic compounds. R. MULLER (Z. Elektrochem., 1927, 33, 152—155).—Probable modes of sharing electrons between carbon atoms in unsaturated chains and rings of various types are discussed. In cases where conjugated double linkings are usually written, it is supposed that the electrons will tend to be shared equally among the carbon atoms concerned. Although this is possible in ring systems of certain types, it is not possible in open chains. A displacement of electron orbits is postulated in such cases, and certain physical and chemical properties are accounted for on this basis. H. J. T. ELLINGHAM.

Polarisation of a medium and molecular structure. Electric moments of dihalogen derivatives of benzene. J. ERRERA (Bull. Soc. chim. Belg., 1927, 36, 310—311).—See A., 1926, 779.

Florentium or illinium? L. ROLLA and L. FERNANDES (Nature, 1927, 119, 637—638).—A claim for priority in the discovery of element 61, and for the name "florentium." A. A. ELDRIDGE.

Elements of atomic numbers 43, 61, 75, 85, and 87. HERSZFINKIEL (Compt. rend., 1927, 184, 968—970).—A brief account with discussion is given of attempts by the author and others to isolate these elements. J. GRANT.

Variation of the atom form factor with the wave-length of the scattered radiation. G. GREENWOOD (Phil. Mag., 1927, [vii], 3, 963—972).—Using photometric methods, it has been shown that the scattering power F of an atom is a function of $\sin\theta/\lambda$, as demanded by theory. The relative advantages of the photographic and ionisation methods in measuring intensity are discussed. W. E. DOWNEY.

Investigation of metallic layers by *X*-rays. K. BECKER (Z. Physik, 1927, 42, 222—225).—An *X*-ray reflexion method is described which is particularly adapted for the investigation of change in crystal structure produced in wires by mechanical deformation (cf. this vol., 503). R. W. LUNT.

Symmetry of atoms in crystals. K. HERRMANN (Z. Physik, 1927, 42, 631—636).—The problem of the symmetry of atoms in a crystal structure is discussed with particular reference to the views expressed in the books by Schoenflies and Wyckoff, and it is concluded that it is not necessary to ascribe a hexagonal characteristic symmetry to atoms or ions in a crystal. R. W. LUNT.

Carbon atom model and the structure of diamond. R. B. LINDSAY (Physical Rev., 1927, [ii], 29, 497—509).—The dimensions of the four 2_1 orbits of the carbon atom are computed with the following alternative assumptions: (*a*) spherical distribution of charge about the nucleus, (*b*) orientation in orbital planes with random phase relations, (*c*) orientation in orbital planes with definitely assigned phase relations. The aphelial distance is approximately $2{\cdot}00a_0$, where a_0=0·532 Å., the radius of the smallest orbit in hydrogen. The "radius" of the carbon (diamond) atom calculated from the atomic volume is $2{\cdot}06a_0$. With simplifying assumptions, the models thus worked out are applied to the diamond lattice. The lattice constant, a, has an upper limit of $3{\cdot}00a_0$ (the experimental value being $2{\cdot}90a_0$); the lattice energy for $a=2{\cdot}74a_0$ is $0{\cdot}55Rh$, where R is the Rydberg number, the corresponding value of the heat of sublimation being 171 kg.-cal./mol., and the experimental value 168—177 kg.-cal./mol. A. A. ELDRIDGE.

Structure of certain silicates. W. L. BRAGG and J. WEST (Proc. Roy. Soc., 1927, **A**, 114, 450—473).—The silicates present an interesting but difficult problem for *X*-ray analysis owing to their complexity and low symmetry, and an attempt is made to determine their atomic arrangement by utilising some characteristic features of oxygen compounds, the chief being that the form of the structure is almost entirely determined by the packing of the oxygen atoms, the other atoms being inserted into the interstices. The properties of both cubic and hexagonal close-packed assemblages of oxygen atoms are considered, and it is shown that the refractive index

of any compound in which oxygen atoms are in close packing at a distance of 2·7 Å. apart must be at least 1·71. Since the atoms of beryllium, aluminium, and silicon cause no expansion of the oxygen groups and have a very small ionic refractivity, crystals based on this arrangement will have a refractive index in the neighbourhood of 1·71. Beryllium oxide, corundum, chrysoberyl, and cyanite fulfil these conditions. Rotation photographs made on the last give the following dimensions of the unit cell: $a=7·18$, $b=8·00$, $c=5·55$ Å. (cf. Rosbaud and Mark, A., 1926, 889); there are four molecules in the unit cell and it is based on a simple cubic assemblage of close-packed oxygen atoms. The aluminium atom probably lies at the centre of six oxygen atoms and the silicon atom at the centre of four oxygen atoms. The spinel group is shown to be a structure based on hexagonal close packing of oxygen atoms, the oxygen atoms being close to the positions of a cubic face-centred lattice, with magnesium atoms surrounded by four oxygen atoms and aluminium atoms surrounded by six oxygen atoms. The *X*-ray spectra of olivine, chondrodite, humite, and clinohumite have been studied. The unit cell in olivine is a rectangular block containing sixteen oxygen atoms, and the cells of the others grow by the addition of layers of oxygen atoms parallel to the (001) plane. There are four such layers in olivine and five in chondrodite. The magnesium and silicon atoms are presumably surrounded by six and four oxygen atoms, respectively, in the chondrodite group, as they are in olivine. The structure of silicates with a more open arrangement of oxygen atoms is also discussed, and such compounds as have been analysed indicate that the packing of oxygen atoms remains the predominant feature of the structure. L. L. Bircumshaw.

Crystal structure of electrodeposited chromium. F. Sillers, jun. (Trans. Amer. Electrochem. Soc., 1927, **51**, 309—315).—*X*-Ray examination of electrodeposited chromium in both the "bright" and the "grey" or "burnt" conditions reveals only the body-centred cubic structure, as exhibited by chromium obtained by ordinary fusion methods. No indications were obtained of an allotropic form such as has been reported (A., 1926, 112), and, if present, might limit the applicability of chromium plating. The lattice parameter of the electrolytic chromium is in agreement with precise measurements previously reported for ordinary chromium.

H. J. T. Ellingham.

Magnetism and crystal structure of manganese–aluminium–copper. F. Heusler (Z. anorg. Chem., 1927, **161**, 159—160).—It is suggested that in manganese–aluminium–copper at red heat the aluminium atoms are completely dissociated from the manganese and copper atoms, and remain so when the mass is quenched. If now the alloy is aged at 80°, combination occurs between aluminium and copper atoms and between aluminium and manganese atoms, but without any change in the crystalline form, and the metal becomes ferromagnetic. R. Cuthill.

Iron crystals. L. W. McKeehan (Nature, 1927, **119**, 705—706).—By electrical heating, single body-centred cubic (α) crystals of iron can be obtained of length 20 cm. in wire of diameter 1 mm. The optimal rate of travel of the heated portion is 4 cm. per hr.; the best results have been obtained in hydrogen at atmospheric pressure, and the chemical purity and previous mechanical history of the iron are relatively unimportant. The magnetic and magnetostrictive properties of the crystals have been investigated.

A. A. Eldridge.

Structure of a protective coating of iron oxides. R. M. Bozorth (J. Amer. Chem. Soc., 1927, **49**, 969—976).—A study of *X*-ray powder photographs, taken with different characteristic radiations, of the protective coating produced by the action of steam on iron at 700° with subsequent cooling in air indicates that the coating is built up of layers of ferrous oxide, magnetite, and ferric oxide in the order of oxidation, the respective thicknesses being estimated as 1×10^{-2}, 2×10^{-4}, and 2×10^{-5} cm. A high-tension automatic voltage regulator suitable for use with *X*-ray tubes of the gas type is described.

S. K. Tweedy.

Compounds Fe_3S_4, Co_3S_4, and Ni_3S_4, and their structure. W. F. de Jong and H. W. V. Willems (Z. anorg. Chem., 1927, **161**, 311—315).—Rontgenographic examination of linnæite and polydymite show them to have similar structures to magnetite and to synthetic Co_3S_4 and Ni_3S_4. The compound Fe_3S_4 does not appear to occur in nature, and cannot be obtained, like Co_3S_4, by heating the monosulphide *in* hydrogen sulphide. A. R. Powell.

Crystal structure of hexamminecobaltic perchlorate. R. W. G. Wyckoff, S. B. Hendricks, and T. P. McCutcheon (Amer. J. Sci., 1927, [v], **13**, 388—398).—Pure hexamminecobaltic perchlorate has been prepared by neutralising the hexammine base with perchloric acid at such a concentration that the perchlorate crystallises on keeping. The *X*-ray spectrum shows the crystal unit to be a cube of side 11·39 Å. The density of the salt is 2·05, corresponding with four molecules in the unit cube. The crystal structure is developed from a face-centred space-group, and it is demonstrated that the crystal cannot be holohedral. The atomic arrangement is discussed, and it is shown that the positions of the ionic groups must resemble the positions of higher symmetry occupied by the corresponding atoms in hexamminecobaltic iodide, which yields data agreeing very closely with those for the perchlorate. H. F. Gillbe.

***X*-Ray studies of catalytically active metals.** G. Bredig and R. Allolio (Z. physikal. Chem., 1927, **126**, 41—71).—Sputtered films of platinum, palladium, and nickel were prepared in the glow discharge in different gases, and their catalytic activities in effecting the combination of hydrogen with oxygen and with ethylene were compared with the results of *X*-ray examinations by the powder method. Films prepared in hydrogen are inactive or very slightly active. For platinum and palladium the lattice constant is increased by sputtering (0·9% and 2·9%, respectively), but the nature of the lattice is unaltered. This increase is attributed to saturation of the film with hydrogen. For nickel the lattice changes from a cubic to a hexagonal form. Sputtering of the

metals in oxygen at low pressures (0·1 mm.) produces oxide films which are inactive, but become active on subsequent reduction. *X*-Ray examination of the active and inactive forms revealed no differences, apart from variation in the sizes of the particles, and it is concluded that catalytic activity is a property of the uncombined metals. G. A. ELLIOTT.

Crystal structure of a few compounds of the general formula MG_6LR_6. O. HASSEL (Z. physikal. Chem., 1927, **126**, 118—126).—Data are given for the crystal structures of compounds of this series for which M=Zn, Mg, Ni, etc., L=Si, Zr; G=H_2O, and R=F, Cl, etc. These compounds all crystallise in the trigonal system. The fundamental rhombohedron of the crystal corresponds with one molecule of the compound, and it consists of eight LR_6 groups at the corners and one MG_6 group in the centre. The distributions of the G and R elements in relation to M and L, respectively, await further investigation. G. A. ELLIOTT.

Crystal structure of cæsium fluogermanate. R. W. G. WYCKOFF and J. H. MÜLLER (Amer. J. Sci., 1927, [v], **13**, 347—352).—The structure of cæsium fluogermanate has been determined by the powder method to be cubic, resembling potassium and ammonium chloroplatinates. The parameter for fluorine has a value near to 0·20. The length of the edge of the unit cube containing four molecules of cæsium fluogermanate is 8·99 Å., whence $d_{calc.}$ = 4·10, whilst $d_{obs.}$—3·899, the discrepancy being due probably to the adherence of air to the small crystals. R. A. MORTON.

***X*-Ray investigation of the grain size and of tempering in tungsten wire.** K. BECKER (Z. Physik, 1927, **42**, 226—245).—A modification of the Debye–Scherrer technique is described suitable for the investigation of the grain size and of the effect of tempering in metallic wires in which the disappearance of the $K\alpha$ doublets is used to detect the distortion of the grating. The variation in the grain size and the effect of tempering at various temperatures have been examined by this method for ordinary and for single-crystal tungsten wires after mechanical deformation by stretching. R. W. LUNT.

Crystal structure of thallium. K. BECKER (Z. Physik, 1927, **42**, 479—480).—The relative intensities of the *X*-ray spectrum of a completely filled hexagonal grating have been computed qualitatively for various orientations of the grating; they differ considerably from the intensities, for the same orientations, observed by Levi for crystalline thallium (Nuovo Cimento, 1924, **1**, 1; 1926, **3**, 297). Levi's conclusion that crystalline thallium has a completely filled hexagonal grating is therefore unsound. R. W. LUNT.

***X*-Ray investigation of certain long-chain compounds.** A. MÜLLER (Proc. Roy. Soc., 1927, **A**, **114**, 542—561).—An *X*-ray analysis has been made of well-developed crystals of stearic, bromostearic, stearolic, and behenolic acids. All the four crystals are monoclinic–prismatic, with the symmetry plane perpendicular to the large face. There are four molecules in the unit cell, and the lattice belongs to simple Γ type. For the four acids, respectively, a=5·546, 11·039, 9·551, 9·551; b=7·381, 4·904, 4·686, 4·686; c=48·84, 52·84, 49·15, 59·10 Å. From the experimental data it is concluded that chains of carbon atoms exist in all of the four crystals, the carbon atoms being arranged in sets which are equally spaced along straight, or nearly straight, lines (chain axes). These chains are packed in the crystal with their axes parallel, or nearly parallel, to each other. The distance between two successive carbon atoms in the chain is considerably smaller than the distance between one chain and its neighbours, so that the mass density along a chain axis is higher than that along any other straight line in the crystal. The monoclinic angle β is a measure of the tilt of these chains relative to the basal plane of the crystal; for stearic acid it is 63° 38′, for bromostearic acid 43° 17′, for stearolic acid 53° 4′, and for behenolic acid 53° 30′. The crystal molecule has a chain of carbon atoms, their number being equal to that in the chemical molecule. The above statements are expressed in a mathematical form, and it is shown that it is possible to predict certain general features of the intensity distribution from the structure factor alone. With regard to the general structure of the substances, the following conclusions are reached: the chain can be represented as a rod of elliptical cross-section; the axial ratio of the ellipse is approximately 0·64; in the crystal these rods are packed in parallel bundles and in such a way that they occupy an average cross-section of $18{\cdot}3\times10^{-16}$ cm.^{2} Consideration of data previously given for octadecane (A., 1925, ii, 367) suggests that the carboxyl group occupies a smaller space along the c axis than the methyl group, and it is concluded that the length of the methyl group in the c direction is 1·4 Å. L. L. BIRCUMSHAW.

***X*-Ray investigation of the polymorphism of fatty acids.** G. M. DE BOER (Nature, 1927, **119**, 634—635).—The influence of temperature on the modifications of the odd and even saturated fatty acids has been determined. Values for the m. p., transition point, β_I-, β_{II}-, and α-spacing are: for the acid $C_{11}H_{22}O_2$, 28·2°, 17°, 30·1 Å., —, 25·4 Å.; for $C_{13}H_{26}O_2$, 41·2°, 32°, 35·1 Å., 31·5 Å., 29·8 Å.; for $C_{15}H_{30}O_2$, 52·1°, 44°, 39·7 Å., 35·9 Å., 34·4 Å.; for $C_{17}H_{34}O_2$, 60·6°, 54°, —, 40·2 Å., 38·7 Å. The stable modification of the C_{13} acid is β_I, and of C_{15}, β_{II}. The even fatty acids appear to have only monotropic modifications, of which the *C*-modification is stable. A. A. ELDRIDGE.

Isodimorphism of the alkaline-earth sulphates and alkali perchlorates. D. VORLÄNDER and H. HEMPEL (Ber., 1927, 60, [*B*], 845—848; cf. Grahmann, A., 1913, ii, 586; Vorlander and Kaascht, A., 1923, ii, 487).—Barium and strontium sulphates pass into regular modifications when strongly heated, and lead sulphate becomes completely isotropic. Contrary to Grahmann, anhydrous crystalline calcium sulphate similarly passes into the regular form, double refraction persisting only in larger, isolated fragments. If the heating has not been sufficiently intense to cause decomposition, the crystals revert to the rhombic form when cooled. Transformation could not be observed with the alkaline-earth chromates or

selenates or with calcium tungstate, lead tungstate, or lead molybdate. H. WREN.

Theory of crystal growth. H. BRANDES (Z. physikal. Chem., 1927, **126**, 196—210).—A mathematical theory of crystal growth is developed for the cubic, rhombododecahedral, and octahedral systems by considering the energy conditions when a new centre of growth is formed on a completed crystal surface. H. F. GILLBE.

Formation of mixed crystals by the contact of solid phases, and by precipitation from solution. L. VEGARD and T. HAUGE (Z. Physik, 1927, **42**, 1—14).—Using the Debye–Scherrer method, the formation of mixed crystals by contact of the solid phases, dried by phosphorus pentoxide, has been established for the system KBr–KCl. Evidence is thereby afforded for the exchange of atoms between crystal gratings in contact. No definite evidence of mixed crystal formation was obtained by grinding or hammering a mixture of powdered gold and copper; a small increase was observed in the copper grating constant due to the presence of a few gold atoms. Mixed crystals are also formed by contact of the dry solid phases in the system HgCl–HgBr. Mercurous nitrate solution yields with a solution of potassium chloride and bromide in any proportion homogeneous mixed crystals corresponding in composition with that of the alkali halide solution. R. W. LUNT.

Formation of twin metallic crystals. G. D. PRESTON (Nature, 1927, **119**, 600—601).

Recrystallisation of metals. R. KARNOP and G. SACHS (Z. Physik, 1927, **42**, 283—301).—The temperature at which recrystallisation commences has been determined, using the procedure of Carpenter and Elam (B., 1925, 211), for the following varieties of aluminium rods 5 mm. in diameter after mechanical deformation by stretching: crystallised, recrystallised, die-drawn crystal after recrystallising, and ordinary rod. For the first two varieties the temperature at which recrystallisation commences is approximately the same for the same reduction in cross-section. A similar relationship holds for the other two varieties; the temperature is, however, considerably lower for the same reduction in cross-section. For single crystals the temperature at which recrystallisation commences increases with the temperature at which the crystals are stretched, and decreases as the cross-section is reduced. The tensile strength as a function of the temperature (0—900°) has been determined for stretched copper strips before and after recrystallisation, and the extensibility of copper strip before and after recrystallisation has been measured in the same temperature range. R. W. LUNT.

Hardness of compressed powdered metals after heating. B. GARRE (Z. anorg. Chem., 1927, **161**, 152—154).—The hardness of compressed pastilles of powdered silver, copper, lead, aluminium, and magnesium after having been heated at various temperatures has been measured. Up to 150° there is little increase in hardness, but, in agreement with the results of Tammann and Mansuri (A., 1923, ii, 300), the increase beyond 200° is considerable. Since with a mixture of two metals the occurrence of a reaction below the m. p. depends on internal diffusion, the hardness of the compressed mass increases considerably at the reaction temperature. In particular, the formation of compounds which dissociate at the m. p. can be detected in this way. The mixture corresponding in composition with the compound gives the hardest mass. A pastille of the eutectic composition gives a harder product than other mixtures when heated at a temperature somewhat below that of the eutectic. Hence internal diffusion occurs in the solid state even when no mixed crystals or compounds are formed. R. CUTHILL.

Texture of rolled and recrystallised regular surface-centred metals. I and II. (FREIHERR) VON GOLER and G. SACHS (Z. Physik, 1927, **41**, 873—906).—The crystalline structure of rolled and of recrystallised aluminium and copper sheet has been examined by an *X*-ray method and the results obtained are given and discussed. R. W. LUNT.

Motion of electrons in metallic conduction. A. E. MALINOVSKI (Z. Physik, 1927, **42**, 319—322).—The problem of whether the sudden starting of a current in a conductor produces a mechanical reaction due to the co-ordination of the random motion of the conductivity electrons in the direction of the electric field has been investigated in the following way. A ring, half of copper and half of bismuth, was suspended by a fine tungsten wire in a high vacuum. By illuminating one of the copper–bismuth junctions with light from an arc lamp, a current of 0·54 *amp.* could be set up in the ring. The ring suspension was provided with a mirror, and the sensitivity of the system was 9·2 g. cm./sec. Negative results were obtained, from which it is concluded that the motion of the conductivity electrons is independent of the self-induction of the conductor. R. W. LUNT.

Influence of pressure on the electrical conductivity of gold. A. MICHELS, P. GEELS, and (MISS) C. VERAART (Proc. K. Akad. Wetensch., Amsterdam, 1927, **30**, 47—51; cf. this vol., 99).—The change in the resistance (r) of a gold wire with increase of pressure has been examined. The values at 16° of $-\Delta r \times 10^6/r$ at pressures of 101·5 and 251·5 kg./cm.^{2} are 5·03 and 11·8, respectively. The decrease in resistance apparently does not vary in a linear manner with the pressure. J. S. CARTER.

Galena and iron pyrites as detectors [of wireless waves]. A. SCHLEEDE and H. BUGGISCH (Z. anorg. Chem., 1927, **161**, 85—107).—Lead sulphide crystals containing the theoretical amount of sulphur and prepared by fusion of precipitated sulphide are of little use in the rectification of wireless waves, even if crystallisation has been slow or foreign substances have been added. Sublimation of the precipitated sulphide in a current of hydrogen sulphide yields, however, crystals which contain a slight excess of sulphur and are practically as effective for detection as the best natural crystals of galena, which also contain an excess of sulphur. The surface of crystals obtained by fusion may be rendered active by treatment with melted sulphur. A fairly good preparation is obtained by heating precipitated lead sulphide at 1000° under high pressure; the product also contains

an excess of sulphur. If the mass is actually fused under pressure, the amount of sulphur in the product is further increased, and the activity improved correspondingly. The presence of silver sulphide in the sintered mass has no effect, or is actually detrimental. The sensitivity of active crystals prepared artificially is, unlike that of active natural crystals, uniform throughout the mass. It thus seems likely that the insensitive parts of natural crystals contain only the theoretical amount of sulphur, or even less. The sensitivity of a single crystal, whether natural or artificial, is the same throughout the crystal. Contrary to the statements of other authors (cf. Gaubert, A., 1926, 229), the sensitivity of natural crystals is not related to their crystalline form. This is very probably the case also for natural crystals of iron pyrites. A theoretical content of sulphur seems, however, to be essential for the sensitivity of these crystals. Attempts to prepare artificial specimens have been unsuccessful. R. CUTHILL.

Thermo-electric effect in single-crystal zinc. E. G. LINDER (Physical Rev., 1927, [ii], **29**, 554—565).—The thermo-*E.M.F* thermo-electric power, and Peltier heat of single-crystal zinc against copper have been determined as functions of crystal orientation between —182° and 400°. The thermo-electric power of liquid against solid zinc at the m. p., $e_l - e_s$, is —7·89 microvolt per degree for polycrystalline zinc. Polycrystalline zinc may be considered as an alloy of Zn⊥ and Zn∥ (2 : 1). A. A. ELDRIDGE.

Accidental thermo-electric effect in bismuth. T. TODESCO (Atti R. Accad. Lincei, 1927, [vi], **5**, 377—379).—From experiments on the thermo-electric effect in samples of bismuth in which the orientation of the crystals has been controlled it is concluded that the effect has its origin in the contact of two crystals asymmetrically oriented. R. W. LUNT.

Surface heat of charging. L. TONKS and I. LANGMUIR (Physical Rev., 1927, [ii], **29**, 524—531).—Methods are given for the calculation of the surface heat of charging of a conductor for pure metals, for oxide-coated metals, and for monatomic films. The relation between this quantity and certain assumptions fundamental to the theory of electron emission is briefly considered. A. A. ELDRIDGE.

Transverse magneto-resistance effect in single crystals of iron. W. L. WEBSTER (Proc. Roy. Soc., 1927, **A**, **114**, 611—619).—The change of resistance in a transverse magnetic field has been measured in single crystals of iron with the current along a (100), (110), or (111) crystal axis, and with the magnetic in a series positions in the planes normal to these directions. Below 5000 and above 12,000 gauss there is always a gradual decrease in resistance which is approximately proportional to the field strength. In the region between, there occurs a rapid change of resistance, which is positive when the current is along a cubic axis and negative from the other two directions; the magnitude of this depends on the direction of the magnetic field; it vanishes when the field is along a cubic axis. It is suggested that the phenomenon is of a double nature, that the gradual change of resistance is to be ascribed to some direct action of the field on the conducting electrons, and that the intermediate rapid change is due to the change of orientation of the atoms accompanying magnetisation. L. L. BIRCUMSHAW.

Magnetic permeability of iron and magnetite in high-frequency alternating fields. G. R. WAIT (Physical Rev., 1927, [ii], **29**, 566—578).—No anomalous change in the permeability of iron was observed at any frequency (cf. Wwedensky and Theodortschik, Ann. Physik, 1922, [iv], **68**, 463). The absolute value of the permeability of powdered magnetite decreases from 1·532 at λ 132·2 metres to 1·401 at λ 85·8 metres. A. A. ELDRIDGE.

Experiment on and theory of the nature of anisotropic liquids. V. FREEDERICKSZ and A. REPIEWA (Z. Physik, 1927, **42**, 532—546).—The behaviour of anisotropic liquids in a magnetic field is used to ascertain the forces at work in the body of such liquids. The diamagnetic action of the magnetic field permits the calculation of the forces on the surface. All types of anisotropic liquids are affected (cf. Friedel, A., 1923, ii, 223). W. E. DOWNEY.

Optical constants of single-crystal bismuth. (MISS) F. E. DIX and L. H. ROWSE (J. Opt. Soc. Amer., 1927, **14**, 304—308).—Since the bismuth crystal is rhombohedral-hexagonal, it is optically uniaxial and has two sets of optical constants. Previous measurements of polycrystalline material have given some average of the crystal constants. If a single crystal is split along the natural cleavage plane perpendicular to the principal axis, which is also the optic axis, a very fine reflecting surface is obtained. Monochromatic plane-polarised light reflected from this surface is transformed into elliptically-polarised light, from an analysis of which the optical constants for light travelling parallel to the optic axis have been obtained for wave-lengths between 670 and 350 mμ. C. J. SMITHELLS.

Chlorides of sulphur. I. Freezing points. T. M. LOWRY, L. P. MCHATTON, and G. G. JONES (J.C.S., 1927, 746—756).—Mixtures containing sulphur and chlorine attain a state of equilibrium when heated at 100° in sealed tubes, or on addition of a trace of iodine as catalyst. They then give a f.-p. curve which shows, in addition to the familiar maxima due to the crystallisation of S_2Cl_2 and SCl_4, two well-defined breaks which are attributed to the crystallisation of SCl_2 and S_3Cl_4. An equilibrium mixture of composition SCl_2 deposits SCl_4 on freezing. Freshly prepared mixtures of sulphur monochloride with an equilibrium mixture containing about 70% of chlorine behave differently and exhibit a maximum f. p. at the composition SCl_2. A solid of this composition is obtained on freezing. The temporary formation of the dichloride in this way is attributed to the interaction of the monochloride and the tetrachloride which were present in the original components of the mixture. G. A. ELLIOTT.

Isotropic point of crystalline liquids. W. HERZ (Z. anorg. Chem., 1927, **161**, 228—230).—From published data for 84 compounds the relation between the m. p. (Abs.) and the temperature (Abs.) at which an anisotropic crystalline liquid becomes

isotropic has been found to be approximately a constant, the weighted mean value of which is 0·94.
A. R. Powell.

Heat of evaporation and [degree of] association of hydrogen fluoride. N. de Kolosovski (Bull. Soc. chim., 1927, [iv], 41, 422—428).—The molecular heat of evaporation of hydrogen fluoride, λ, calculated from the differential Clapeyron–Clausius equation, is 1927±90 g.-cal., indicating a probable mol. wt. of 60·02 at the b. p. Correction of an error in calculation brings Simons' value of λ to 6279 g.-cal. (A., 1924, ii, 848). S. K. Tweedy.

Internal pressures and latent heats of evaporation of liquids. K. M. Stachorsky (J. Russ. Phys. Chem. Soc., 1926, 58, 966—982).—Theoretical. The relation of the molecular internal pressures to the other physical properties of liquids is discussed. By combining van der Waals' expression $d\log p/dT - f T_c/T^2$, where $f = a/V/RT_c$, when $T = 0{\cdot}5T_c$, with the Clapeyron–Clausius equation, the relation $a/V^2 = l/v$ is obtained, where l is the latent heat of evaporation and v the specific volume, *i.e.*, the internal molecular pressure is equal to the latent heat. The values of the internal pressures calculated by van Laar's and van der Waals' empirical expression agree satisfactorily with the experimental values for l for non-associated liquids. Similar agreement is found for $T = 0{\cdot}64T_c$. By applying the theory of capillarity, the relation $a/V^2 = k\gamma$, where γ is the surface tension, is obtained. Using the known values of V^2 and γ for different corresponding temperatures, the expression $a/V^2 = 235{\cdot}9\,\gamma T/T_c$ is deduced.

The connexion between the internal pressure (*i.e.* the latent heat) and the coefficients of expansion (α) and compressibility (β), $l = T\alpha v/41{\cdot}35\beta$, is shown to apply over a wide range of temperatures and pressures. By the introduction of Poisson's coefficient of capillarity, the rules of Kistiakovski and Walden and of Trouton are shown to be particular cases of more general laws which apply to other corresponding temperatures. M. Zvegintzov.

Surface tension and latent heat of evaporation. W. Herz (Z. anorg. Chem., 1927, 161, 304).—A reply to Verschaffelt and de Block's criticism (this vol., 108) of an earlier paper by the author (A., 1926, 1008).
A. R. Powell.

Wiedemann–Franz law. II. A. Eucken and K. Dittrich (Z. physikal. Chem., 1927, 125, 211—227; cf. A., 1924, ii, 648).—The thermal conductivities of pure iron, nickel, and thallium, and of copper–manganese, lead–thallium, and copper–nickel alloys have been determined at 80° and 273° Abs. Variation of the grain size of alloys between wide limits had no effect on the conductivity. This is in accordance with the theory that the mean free path of electrons must be smaller in these alloys than in the pure metals, and is of the order of the diameter of single crystals of alloy. The non-metallic conductivity of compressed constantan was 20% less than that of the untreated alloy at 80°, a difference which disappeared on allowing recrystallisation to take place. Bridgman's explanation (Proc. Amer. Acad. Arts Sci., 1922, 57, 113) for the influence of pressure on the Wiedemann–Franz number is not considered adequate, and another explanation is put forward.
L. F. Gilbert.

Emissivity methods of investigating thermal conduction in metals. H. Gregory and C. T. Archer (Phil. Mag., 1927, [vii], 3, 931—944).—The determination of thermal conductivity by measuring the emission of heat from an electrically heated wire is discussed. Using conditions so controlled that Newton's law of heat emission is found to be valid, the thermal conductivity of platinum is determined for a limited temperature range. Further modifications of the method are suggested which will enable thermal conductivity to be measured at higher temperatures. W. E. Downey.

Determination of gas density with the gas density balance. II. Ethylene as a comparison gas. A. Stock and G. Ritter (Z. physikal. Chem., 1927, 126, 172).—The density of ethylene has been recalculated; the new value is 1·26026 g./litre at 0° and 760 mm. pressure, replacing the earlier value of 1·26057 (this vol., 102). H. F. Gillbe.

Vapour pressure. III. Toluidines. J. F. T. Berliner and O. E. May. **IV. Naphthols.** J. F. T. Berliner, O. E. May, and D. F. J. Lynch (J. Amer. Chem. Soc., 1927, 49, 1007—1011, 1012—1016; cf. A., 1926, 1198).—The vapour pressures of *o*-, *m*-, and *p*-toluidines have been measured from about 40° to a few degrees above the b. p., which, at 760 mm., are 199·84°, 202·86°, and 200·35°, respectively. The observed vapour pressures agree with those calculated, and the heats of vaporisation vary linearly with the temperature. The entropies of vaporisation at a concentration of $0{\cdot}00507M$ indicate that the toluidines are highly associated substances.

The b. p. of α- and β-naphthol at 760° are 288·01° and 294·85°, respectively. Observed vapour pressures are in agreement with those calculated from derived latent heat equations, and the entropies of vaporisation indicate that the naphthols do not form normal liquids. F. G. Willson.

Vapour pressure of intensively dried nitrogen tetroxide. J. W. Smith (J.C.S., 1927, 867—874).—Nitrogen tetroxide was dried by repeated distillation through phosphorus pentoxide during periods of from 4 to 6 months. An increase in vapour pressure resulted (cf. Smits, A., 1926, 1206), which amounted in the most favourable case to approximately 2·5 cm. After a sudden change in the temperature of the dried material, the corresponding change in vapour pressure was established slowly, several hours being required to attain the steady value. G. A. Elliott.

Malonic anhydride (carbon suboxide), C_3O_2. M. J. Edwards and J. M. Williams (J.C.S., 1927, 855—857).—Pure gaseous malonic anhydride is very stable in the absence of mercury, when dry and contained in a glass vessel which has not been contaminated with the polymerised form. Its vapour pressures have been measured between −62° and 4°, and it is concluded that the b. p. at atmospheric pressure is 6·8°, whilst the heat of vaporisation is calculated to be approximately 6 kg.-cal. The velocity of polymerisation of the anhydride in a

contaminated glass vessel is not in accordance with any simple formula, and the reaction is probably a catalytic surface reaction. G. A. ELLIOTT.

Adequacy of the assumption of molecular aggregation in accounting for certain of the physical properties of gaseous nitrogen. F. G. KEYES and R. S. TAYLOR (J. Amer. Chem. Soc., 1927, **49**, 896—911).—The equation (I) $p=RT/(v-\beta e^{\alpha/v})-A/(v+l)^2$ holds for gas mixtures, and may, therefore, probably be applied to associated gases. For slightly associated gases it is developed into the form $pv=RT(1+B/v+C/v^2+\ldots)$, B being the slope of the pv isotherm at $p=0$. This equation assumes that the aggregation depends on v and T, in accordance with the mass law and perfect gas equation. It is shown that the graph of B against $1/T$ should be linear at sufficiently high temperatures and concave towards the $1/T$ axis at lower temperatures. An equation is deduced for B for nitrogen; the observed results fit the linear portion of this curve between 0° and 150°, but above this they trend away from the theoretical curve. Hydrogen, helium, and neon, for which A/R is small (as with nitrogen), exhibit similar behaviour; argon, for which A/R is larger, shows no departure from the theoretical curve below 400°. Equation (I), modified so as to account for association, agrees with the experimental p-T relationships for nitrogen up to 150° or 200°; above this, the theoretical equation gives a linear graph from which the experimental points deviate. Holborn and Otto's results for nitrogen (A., 1925, ii, 851) may be represented between 0° and 200° by equation (I) with $R=2{\cdot}9286$, $\beta=1{\cdot}766$; $\alpha=-1{\cdot}065$, $A=1687{\cdot}1$, $l=0{\cdot}136$ (p in atm., and v in c.c./g.). An equation is deduced for the specific heat at constant volume of a slightly associated gas; it represents the observed C_v—p relationships for air very well. S. K. TWEEDY.

Limits of validity of gas equations. III. W. HERZ (Z. Elektrochem., 1927, **33**, 155—156; cf. A., 1926, 342).—The ratio of the density of the saturated vapour of various substances to their vapour density, calculated from the gas equation for the same temperature, but for normal pressure, has been computed at the temperatures $\frac{2}{3}T_c$, $\frac{1}{10}T_c$, and T_c, where T_c is the critical temperature. At $\frac{2}{3}T_c$ the values range from 0·57 to 4·86. The sequence of substances arranged according to the magnitude of this ratio is different at the three temperatures. At a given temperature, substances of analogous structure and the same mol. wt. give similar values. In an homologous series the ratio falls with increasing mol. wt. H. J. T. ELLINGHAM.

Refinement of the Eotvos reflexion method for the measurement of surface tensions. H. MOSER (Ann. Physik, 1927, [iv], **82**, 963—992).—Three methods have been used: (1) reflexion of horizontal rays a distance h apart, (2) an entirely different arrangement for measuring the same constants as in (1), and (3), measurement of the horizontal separation of two vertically reflected rays from the meniscus. The values obtained for the surface tension of water in mg./mm. at 18° by the three methods were 7·421 (±0·14%), 7·424 (±0·14%), and 7·431 (±0·09%), respectively. R. A. MORTON.

Absolute value of surface tension of pure water according to the wire-hoop method and its dependence on temperature. H. MOSER (Ann. Physik, 1927, [iv], **82**, 993—1013).—In addition to the values obtained by the reflexion method (cf. preceding abstract), the value 7·431 (±0·1%) is obtained by Lenard's method (*ibid.*, 1924, [iv], **74**, 381), which is described in an improved form. The value 7·427 mg./mm. or 72·87 dynes/cm. at 18° may be taken as the weighted mean of the author's determinations and those available by the method of capillary rise. The temperature coefficient is −0·0158 mg./mm. per 1°. R. A. MORTON.

Rigidity of solid unimolecular films. H. MOUQUIN and E. K. RIDEAL (Proc. Roy. Soc., 1927, **A**, **114**, 690—697).—The rigidity of unimolecular films of palmitic and stearic acids on water has been determined by a method involving the rotation of a brass disc immediately below the surface of the film, thereby exerting a drag on it through the intermediary of the viscosity of the water. The unimolecular film was formed by heating the water above the m. p. of the fatty acid, which was present as a small crystal on the water surface; on cooling, a rigid, unimolecular film of the acid was obtained on the free surface of the water. Displacements were measured by microscopical observations of dust particles on the surface of the film. The coefficient of rigidity, μ, is given by the equation $\delta=-(\Omega\eta/8\mu h)(r^3-a^2r)$, where δ is the displacement of the particle at a distance r from the axis of the disc, Ω is the angular velocity of the disc, η the viscosity of the water, h the depth of immersion of the rotating disc, and a the radius of the disc. The true rigidity constant, μ/x, where x is the film thickness, is found to be almost identical for the two acids and equal to $4{\cdot}9\times10^7$ dynes per cm.^{2} at 20°. The temperature coefficients of the rigidities are of the character anticipated for waxy solids, in that the rigidity decreases rapidly with increase of temperature when approaching the m. p.

L. L. BIRCUMSHAW.

Viscosity of liquid chlorine. E. VAN AUBEL (Bull. Acad. roy. Belg., 1926, [v], **12**, 369—373).—The formula proposed by Batschinski (A., 1913, ii, 26) connecting fluidity ϕ and specific volume v of a liquid, viz. $v=\omega+c\phi$, where ω and c are constants, yields satisfactory results for liquid chlorine, according to data of Steacie and Johnson (A., 1925, ii, 376), except in the neighbourhood of the b. p. The author's formula $\log(T_c-T)$, connecting fluidity and temperature, where m and n are constants, is also applicable with the same limitation.

C. H. D. CLARK.

Speed of diffusion and the solvent. G. MUCHIN, G. FAJERMANE, I. DOGOPOLSKY, and L. LEVIN (Ukraine Chem. J., 1926, **2**, 153—157).—See A., 1926, 786.

Molecular combination and molecular volumes of mixtures of ether and hydrogen bromide. J. RUSSELL and W. E. SULLIVAN (Trans. Roy. Soc. Canada, 1926, [iii], **20**, III, 301—306).—The density at 0° of various binary mixtures of ethyl ether with hydrogen bromide, methyl bromide, and ethyl bromide has been measured. If the molecular

fractions of the bromides in the various mixtures are plotted against their molecular volumes, the resulting graph is, for the alkyl bromides, an approximately straight line. Hydrogen bromide does not give a straight line, the maximum deviation being manifested by the mixture corresponding in composition with the compound $Et_2O,2HBr$ (cf. McIntosh, A., 1911, i, 256). The deviations almost disappear, however, if the mixtures are regarded as solutions of this compound in ether or hydrogen bromide, as the case may be, so that it would seem that the compound must be only very slightly dissociated in solution. Vapour-pressure determinations point in the same direction. R. CUTHILL.

Viscosity of cellulose nitrate in various mixtures of butyl acetate, ethyl acetate, ethyl alcohol, and benzene as solvents. J. R. COCHRANE and G. W. LEEPER (J.S.C.I., 1927, **46**, 117—119T).—The viscosities of 5% solutions of cellulose nitrate in binary and ternary mixtures of the various solvents have been determined. Solutions of minimum viscosity are obtained with mixtures containing from 40% to 60% of alcohol. The viscosity–concentration curve for mixtures of ethyl acetate and butyl acetate is practically a straight line. Benzene acts simply as a diluent, causing an increase in viscosity when mixed with the pure esters, but in presence of alcohol it often shows definite solvent properties and causes a diminution in viscosity. M. S. BURR.

Rotatory power of solutions of tartaric acid. G. BRUHAT and M. PAUTHENIER (J. Phys. Radium, 1927, [vi], **8**, 153—160).—See A., 1926, 661.

Surface tension of liquid mixtures in the neighbourhood of the critical state. P. BRUN (Compt. rend., 1927, **184**, 966—967).—Measurements by the drop-counting method show that the surface tensions of conjugate liquid pairs become equal at the critical solution temperature. J. GRANT.

System sodium sulphate–water. I. Densities and specific volumes of aqueous solutions of sodium sulphate between 25° and 40°, and the fictive volumes of sodium sulphate in solution. R. E. GIBSON (J. Physical Chem., 1927, **31**, 496—510).—The densities of solutions (1—28%) have been determined at 25°. The expansion between 25° and 40° was also measured. The fictive volumes of sodium sulphate and water in solutions of sodium sulphate have been calculated. There are no sudden changes at the transition temperature. Considerable hydration of the salt in dilute solutions at the lower temperatures is indicated; the hydration diminishes with increase of concentration and of temperature. L. S. THEOBALD.

Dependence of physical properties of mixtures of water and sulphuric anhydride on concentration. G. TAMMANN (Z. anorg. Chem., 1927, **161**, 363—373).—A review of the experimental data. Certain properties such as the vapour pressure, surface tension, and, over a certain range of concentrations, the specific resistance and the density, show very little relationship with the molecular composition of the solution. Others, such as the compressibility and the heat and volume changes on mixing, are dependent directly on the internal pressure. Properties closely related to the number and composition of the molecules in the solution are the m. p. and, in some cases, the viscosity. G. A. ELLIOTT.

Absorption of solutions of erythrosin and Kundt's rule. P. VAILLANT (Compt. rend., 1927, **184**, 939—941).—The absorption curves for solutions of erythrosin when diluted with water, sucrose solution, glycerol solution (70%), ethyl alcohol, alcohol containing 70% of mineral oil, and alcohol containing 70% of benzene, show a continuous displacement of the absorption bands towards the red. The maxima on the curves are given by $\lambda_m=4006+1096n-228d$, where n is the mean refractive index and d the density at 20° of the solutions. The results support the view that the wave-lengths corresponding with the maxima for the excitation of phosphorescence vary as the square root of the dielectric constants of the diluents. J. GRANT.

Internal friction of molten metals and alloys. III. Internal friction of copper, antimony, lead, and copper–antimony, copper–tin, and lead–bismuth alloys. A. BIENIAS and F. SAUERWALD (Z. anorg. Chem., 1927, **161**, 51—75; cf. this vol., 14).—The value of the factor in the Hagenbach correction for Poiseuille's law is found by experiment to be 1. The viscosities of copper, antimony, and lead were measured over the temperature ranges 1145—1189°, 700—1000°, and 441—844°, respectively. Copper gives relatively high values, probably due to association. In support of this view, the temperature coefficient of the surface tension is found to be positive. The viscosities of lead–bismuth alloys are either additively constituted of the viscosities of the components, or else show slight negative deviations from the mixture rule. Alloys of copper with tin and antimony exhibit both positive and negative deviations, and the viscosity isotherms have points of inflexion corresponding with the compounds Cu_6Sn and Cu_3Sb, respectively. For all the metals and alloys examined, the fluidity is approximately a linear function of the temperature. R. CUTHILL.

Hardness of alloys. A. MALLOCK (Nature, 1927, **119**, 669; cf. this vol., 300).—Curves show the relation between the hardness and composition of alloys of copper with tin, zinc, cadmium, aluminium, antimony, and bismuth. Except for bismuth, the hardness is more or less maximal around 30% of the alloying metal. Coefficients of friction of the alloys under such high pressures as exist at the cutting edges of saw teeth and the point of the conical test-piece were determined. At these high pressures, lubrication has no practical effect. A. A. ELDRIDGE.

Solubility of the rare gases in water. S. VALENTINER (Z. Physik, 1927, **42**, 253—264).—The heats of dissolution per mol. of argon, krypton, and xenon have been determined from the data of von Antropoff (A., 1919, ii, 511); they are of the form $-r_t=2\cdot3R(a_0+a_1t)$, where t is the temperature and a_0 and a_1 are constants. These constants have been evaluated, and have been used to integrate the equation $-r=RT^2d\log_e l/dT$, where l is the solubility of the gas; this equation then becomes $\log_{10} l=(273a_1-a_0)/T+2\cdot3a_1\log_{10}T$ The three corre-

sponding equations have been employed to calculate l in the temperature range 0—80°: the values so obtained are in good agreement with those obtained experimentally by von Antropoff. Values of a_0 and a_1 for helium, neon, and radon have been obtained by extrapolation of the curve obtained by plotting the values for argon, krypton, and xenon against the at. wt. From these values the solubilities of helium, neon, radon, and of a helium–neon mixture have been calculated. Again good agreement is obtained with available data. The solubility in each case reaches a minimum at 80°. The results support the view that hydrates are formed in solution.

R. W. Lunt.

Solubility of naphthalene in benzene, toluene, and xylene. P. Schlapfer and R. Flachs (Helv. Chim. Acta, 1927, **10**, 381—385).—The solubility of naphthalene decreases with increasing mol. wt. of the solvent. The results for toluene and xylene, recorded from −26° to 41°, practically agree with those of Rhodes and Eisenhauer; the values for benzene are recorded over the interval −5° to 41°.

S. K. Tweedy.

Solubilities of some rare-earth oxalates. L. A. Sarver and P. H. M.-P. Brinton (J. Amer. Chem. Soc., 1927, **49**, 943—958).—The solubilities in water of the oxalates of lanthanum, cerium, praseodymium, neodymium, and samarium were determined at 25° by gravimetric and conductivity methods; together with that of gadolinium oxalate, the solubilities were also determined in hydrochloric, nitric, and sulphuric acids, mixtures of hydrochloric and oxalic acids, and mixtures of nitric and oxalic acids. Compared with the first-named oxalates, the solubility of gadolinium oxalate is not in accord with the position of this metal in the periodic table. In the quantitative precipitation of these oxalates it is recommended that hot, concentrated oxalic acid solution be added with stirring to the boiling solution of rare-earth salts which is 0·5*N* with respect to hydrochloric acid and the precipitate kept for several hours before filtering. A thermostat specially designed for solubility work and the technique attending the rapid and accurate determination of solubility are described.

S. K. Tweedy.

Reciprocal solubility of the normal propyl ethers of αβ-propylene glycol and water. Closed solubility curves. II. H. L. Cox, W. L. Nelson, and L. H. Cretcher (J. Amer. Chem. Soc., 1927, **49**, 1080—1083; cf. A., 1926, 344).—When heated with *n*-propyl alcohol in an autoclave at 180—205°, propylene oxide is converted into a mixture of the isomeric propylene glycol mono-*n*-propyl ethers, b. p. 147—153°. These were separated by treatment with phthalic anhydride in boiling benzene (cf. Stephan, A., 1899, i, 920), under which conditions the primary alcohol is much more rapidly esterified than the secondary isomeride. *α-Hydroxy*-β-n-*propoxypropane* has b. p. 150·5—151°/730 mm., d_4^{20} 0·8925; *β-hydroxy*-α-n-*propoxypropane* has b. p. 148·5—149°/730 mm., d_4^{20} 0·8886. Miscibility data for mixtures of water and each of the above ethers, which give closed solubility curves, are detailed.

F. G. Willson.

Adsorptive force of silica for water. P. G. Nutting (J. Physical Chem., 1927, **31**, 531—534).—A theoretical treatment of the data of Bellatti and Fmazzi (Atti R. Ist. Veneto Sci., 1900, **59**) and Parks (Phil. Mag., 1903, [vi], **5**, 517) on the heat of wetting of dry silica by water.

L. S. Theobald.

Adsorption from the vapour phase at a liquid–vapour interface. L. I. A. Micheli (Phil. Mag., 1927, [vii], **3**, 895—911).—A continuation of Iredale's work (A., 1923, ii, 379) on the adsorption of organic vapours at liquid interfaces using the drop-weight method of determination of surface tension. Benzene and paraffin hydrocarbon vapours form unsaturated unimolecular layers when adsorbed from the vapour phase at a water–air interface. The paraffin hydrocarbon molecules are probably oriented on end. Similar results are obtained at a mercury–air interface, but in this case the adsorbed layer is closely packed. A partial explanation of the differences is to be found in the difference of volatility of mercury and water. The water surface is broken at a rate comparable with the rate of formation of the adsorbed layer. The average value of the heat of adsorption at a water–air interface is 12 kg.-cal.

W. E. Downey.

Adsorption of metallic hydroxides. II. Adsorption of acids, alkali, and salts by precipitated ferric hydroxide. K. C. Sen (J. Physical Chem., 1927, **31**, 525—530; cf. this vol., 408).—The adsorption of 26 of the commoner organic acids by precipitated ferric hydroxide has been quantitatively studied with salts such as sodium citrate and sodium phosphate; some adsorption of the negative ion takes place. A comparison of the amounts of sodium hydroxide and of sulphuric acid adsorbed shows the hydrogen ion to be adsorbed more strongly than the hydroxyl ion, an effect attributed to the basic nature of the ferric hydroxide.

L. S. Theobald.

Adsorption and osmosis of alkalis in a gelatin gel with and without addition of lecithin. I. Suganuma (Biochem. Z., 1927, **183**, 477—484).—Adsorption by gelatin gels of strongly surface active amines (diethylamine, trimethylamine) is not greater but rather less than that of ammonia, and adsorption and osmosis of potassium hydroxide and ammonia and diethylamine are decreased by addition of lecithin. When an aqueous solution of alkali or amine is placed over a layer of gelatin gel or gel to which lecithin has been added, those surface active amines which are considerably soluble in water (diethylamine, trimethylamine) favour the aqueous layer, whilst those which are sparingly soluble (dipropylamine, aniline) favour the lecithin layer. A simple relationship between surface activity and the velocity of adsorption and osmosis in lecithin-free gels could not be obtained. The diffusion velocity of those amines (ammonia, trimethylamine) which are more readily adsorbed by lecithin-free gels is greater in these gels, and the greater diffusion velocity of dipropylamine in gels containing lecithin corresponds with its greater adsorption and osmosis in these gels.

P. W. Clutterbuck.

Adsorption and diffusion in the electric field. R. Fürth (Z. physikal. Chem., 1927, **126**, 238—246).—Theoretical. See A., 1926, 1092.

H. F. Gillbe.

Effect of higher aliphatic acids on the surface tension of a heavy hydrocarbon oil. E. C. GILBERT (J. Physical Chem., 1927, **31**, 543—546).—The surface tensions of solutions of *n*-nonoic and *n*-tetradecoic acids in a heavy hydrocarbon oil have been measured by the modified ring method. The surface tension drops rapidly at low concentrations until the surface layer is saturated, when an increase in concentration has little further effect. The adsorption of the acids on the surface of the oil, together with the apparent thickness of the surface layer and the area per mol., have been calculated.

L. S. THEOBALD.

Polishing of surfaces. J. W. FRENCH (Nature, 1927, **119**, 527).—Experiments are described which show (*a*) that once a group of molecules has been torn from the embrace of its associates, it is practically impossible under polishing conditions to force it back within the region of molecular cohesion, and (*b*) that no considerable rise of temperature occurs such as would be anticipated if the "hill-tops" become fused. A. A. ELDRIDGE.

Application of kinetic theory to surface films. K. C. SEN (Phil. Mag., 1927, [vii], **3**, 925—930).—Surface films formed from weak solutions behave in a similar manner to highly compressed gases. When, however, the surface film is more than one molecule thick, the analogy does not apply. For weak solutions and unimolecular layers, the effect of the layer on the surface tension is due to thermal agitation alone. Schofield and Rideal's conclusions (A., 1925, ii, 960) are confirmed for the latter conditions. W. E. DOWNEY.

Anomaly in the rate of evaporation of solutions of sodium oleate and of digitonin at high dilutions. P. L. DU NOUY (Compt. rend., 1927, **184**, 1062—1064).—Measurements of the rates of evaporation of dilute solutions of sodium oleate show maximum values for the three concentrations for which the surface tension had previously been found to be a minimum (A., 1925, ii, 109). This confirms the existence of a unimolecular layer at these concentrations. For digitonin a maximum was obtained at a concentration of 1 : 240,000, corresponding with a unimolecular layer 22 Å. thick. J. GRANT.

Light scattering of aqueous salt solutions. C. W. SWEITZER (Trans. Roy. Soc. Canada, 1926, [iii], **20**, III, 347).—The light scattering and polarisation of aqueous solutions of a variety of salts and acids have been measured, and the values obtained for the relative light scattering are found to agree with those calculated from the Einstein–Smoluchowski–Cabannes formula. The orientation scattering, calculated from the total scattering and the depolarisation factor, is approximately a linear function of the volume concentration of the salt, and is greater for the nitrates of the alkali metals than it is for the chlorides, and for the cations of these salts increases in the order potassium, sodium, ammonium. No experimental figures are given. R. CUTHILL.

Preparation of red colloidal gold. H. NICOL (J.S.C.I., 1927, 46, 179—180T).—Hydrogen peroxide is added in less than theoretical amount to the mixture of an alkaline gold salt solution and ethyl alcohol at 80°; after boiling to complete the reaction and expel volatile substances, a bright red, stable sol is invariably formed. This sol is suitable for use in the Lange pathological reaction. It is unnecessary to use twice-distilled water: water freshly distilled into clean resistance glassware is preferable. Water which has been kept is not suitable for the production of bright red sols, probably on account of the presence of colloidal silica, since dissolved oxygen is without effect.

Preparation of cellulose nitrate solutions of low viscosity. J. REITSTOTTER (Kolloid-Z., 1927, **41**, 362—365).—Experiments with a number of samples of technical cellulose and cotton wool show that from the viscosity of a solution of cellulose in Schweizer's reagent, important conclusions can be reached with reference to the viscosity of the solution of the nitration product in alcohol, and in mixtures of alcohol and ether. The viscosities of the former solutions diminish rapidly with age. By heating cellulose in a vacuum to temperatures of 90—140°, products are obtained which, on nitration, give cellulose nitrate which forms solutions of low viscosity in organic solvents. The nitrogen content of the nitration product, and its solubility in mixtures of alcohol and ether and in pure alcohol, are independent of the preliminary treatment.

L. L. BIRCUMSHAW.

Hydrogels. III. Hydrates of antimony pentoxide. A. SIMON and E. THALER (Z. anorg. Chem., 1927, **161**, 113—142; cf. A., 1926, 124).—The isobaric decomposition of hydrated antimony pentoxide prepared by hydrolysis of the pentachloride has been followed with the aid of Hüttig's tensi-eudiometer (A., 1921, ii, 195). The desiccation curves are of the continuous form characteristic of colloidal metallic oxide hydrogels. At the lower temperatures, the gels hold water more tenaciously the greater their dispersity, *i.e.* the lower the temperature at which they were prepared. With rise in temperature, however, these differences become less, and near 200° the composition of all the gels approaches $3Sb_2O_5,5H_2O$, the curves having a point of inflexion at this temperature. This seems to indicate that with rise of temperature, or even on keeping, the antimonic oxide commences to crystallise, some water being fixed in the lattice, so that the amounts of water and oxide tend towards a definite stoicheiometric ratio. This view is supported by *X*-ray interference measurements. If Zsigmondy's formula for the diminution of the vapour pressure in colloidal systems is applied to systems in which the diameter of the capillaries is of the order of the lattice constants, which appears to be the case for antimonic oxide gels above about 150°, and is combined with the corresponding expression for a true solution, the equation $\log_e p_0/p=k/n$ results. Here p_0 is the vapour pressure of the free component (water), p is the vapour pressure of the system, n is the number of g.-mol. of the free component per g.-mol. of the fixed component (antimonic oxide), and k is a constant characteristic of the system. For the antimonic oxide gels, the experimental curve deviates from the

theoretical curve throughout, probably owing to the influence of capillarity at the lower temperatures and partly to loss of oxygen, with consequent destruction of the lattice at higher temperatures. This deviation also points to the occurrence of crystallisation, and to the formation and decomposition of compounds. If the crystallisation of the gel is promoted by heating it with water under pressure, the decomposition curve of the product clearly shows the existence of a *hydrate*, $3Sb_2O_5,5H_2O$, and also gives indications of the existence of a dihydrate and a hemihydrate. In the absence of such treatment, which aids in the breaking down of the gel structure, the existence of hydrates is partly masked by capillarity effects. R. CUTHILL.

Hydrogels. IV. Hydrates of arsenic pentoxide. A. SIMON and E. THALER (Z. anorg. Chem., 1927, **161**, 143—151; cf. preceding abstract).—By cooling at −20° to −30° a solution of arsenic acid which has been evaporated at 130°, a *hydrate*, $As_2O_5,7H_2O$, is obtained. The isobaric decomposition curve of the hydrate $As_2O_5,4H_2O$ does not give any indication of the existence of hydrates other than $3As_2O_5,5H_2O$. Contrary to the conclusions of Menzies and Potter (A., 1912, ii, 1165), neither solid solutions nor mixed crystals appear to be formed.

R. CUTHILL.

Mean size of particles of colloidal solutions from Smoluchowski's formula. H. J. C. TENDELOO (Kolloid-Z., 1927, **41**, 290—293; cf. Kruyt and Tendeloo, A., 1925, ii, 113).—The viscosity of an arsenious sulphide sol is increased by the addition of potassium chloride solution, passing through a maximum. This effect is attributed to a rise in the ζ potential. By determining the viscosity, the conductivity, the electrokinetic potential, and the relative volume of the particles for arsenious sulphide sols in presence of varying quantities of potassium chloride, the mean size of the particles can be calculated from Smoluchowski's equation. The mean values of the particle radius, for 2·73%, 3·22%, and 2·94% sols, respectively, are $5·8\times10^{-7}$, $6·4\times10^{-7}$, and $5·8\times10^{-7}$ cm. L. L. BIRCUMSHAW.

Complexity and micelles. G. MALFITANO and M. SIGAUD (J. Chim. phys., 1927, **24**, 259—288).—The theory of complexity (this vol., 412) is applied to colloidal structure. The state of the complexes depends on ionisation, and hence on the valency of the ions. Complex formation explains the impossibility of freeing from the reactants the precipitates obtained in inorganic chemistry, and also the fact that multivalent acids combined with multivalent bases give insoluble salts, whereas with univalent bases they give soluble salts. In organic chemistry nearly all reactions proceed with the formation of intermediate compounds which contain inorganic constituents and are best explained as complexes. In biological chemistry these complex substances play the major role, molecular compounds being of only secondary importance; the mineral part of the complex determines the type of reaction—oxidation, reduction, hydrolysis, etc.—and the organic part the specificity of the reaction—*i.e.*, that the compound shall react with one compound and not with another. Complexity as an explanation of colloidal substances is superior to the view which interprets them by the phase rule, since only the former can explain the limit of size of the particles. Von Weimarn identifies flocculation with the process of crystallisation, but *X*-ray work on gold sols shows the existence of two types of colloidal particle, primary and secondary, the latter being formed by co-ordination of the former. The forces inducing particles of matter to unite are vectorial, but co-ordination need not take place such that the units remain polarised (crystallisation), but may be accompanied by their almost complete neutralisation, so that the number of units in the group is limited. A further theory regards a colloidal particle as a very large molecule, ferric hydroxide sol, for instance, being condensed from ferric oxide molecules by a process resembling etherification; the isoelectric point of the amino-acids is explained by the simultaneous presence of acid and basic functions in the molecule. This view, however, does not explain the extreme sensitivity of the isoelectric point to the hydrogen-ion concentration; and, furthermore, the theory cannot explain deflocculation, nor the important part played by the medium, where the gel sometimes assimilates a hundred times its own volume of solvent. Complexity is also discussed in connexion with Sorensen's work on proteins, and with the structure of cellulose, and the wider philosophical implications of the idea of complexity are also considered. S. J. GREGG.

Determination of the velocity of transference of colloidal ions in the electric field. L. ENGEL and W. PAULI (Z. physikal. Chem., 1927, **126**, 247—266).—Direct measurement of the rate of movement of the boundary layer does not permit of the accurate determination of the transference velocity of an ion. Ferric hydroxide sols, for instance, in presence of different electrolytes of the same conductivity, give widely different values for the velocity. Ultramicroscopical observation of individual particles is applicable only at low concentrations.

A form of transference apparatus is described which is especially suitable for the determination of transference velocity. The chief characteristics of the apparatus are: (1) the conductivity of the solution to be analysed is followed; (2) products of electrolysis at the electrodes are prevented from entering the liquid to be analysed; (3) the colloid is not allowed to flocculate in the apparatus. The apparatus has been tested by measurements of the transference velocity of the iodine ion in 0·01*N*-potassium iodide solution, and of the colloid ions in aluminium hydroxide and ferric hydroxide sols.

H. F. GILLBE.

Mastic-sol and proteins. K. HOTTA (Biochem. Z., 1927, **183**, 72—80).—The conductivity and hydrogen-ion concentration of solutions of mastic indicate that the substance is purely acidic in character; both conductivity and hydrogen-ion concentration increase on keeping, possibly owing to the liberation of free resin acids. Gelatin solutions (0·003—0·045%) of any degree of dispersion give an irreversible precipitation with aqueous-alcoholic mastic solutions; neutralisation of the mastic with

potassium hydroxide has no effect, but the presence of neutral salts shifts the precipitation zone towards lower concentrations of protein; the presence of both salts and alcohol favours the precipitation of highly dispersed protein. Similar results were obtained with egg- and serum-albumins, the precipitation zone lying between 0·2 and 0·01% of protein. Addition of alkali to albumin prevents the precipitation, whilst that of acid does not; in the latter case, however, the precipitation is reversible on addition of excess of protein. C. R. HARINGTON.

Coagulation of hæmoglobin in presence of alcohols. I. B. JIRGENSONS (Kolloid-Z., 1927, 41, 331—334).—The influence of methyl, ethyl, and *n*-propyl alcohols on the coagulation of hæmoglobin by potassium chloride has been investigated. Methyl and ethyl alcohols act as sensitising agents, but propyl alcohol shows this effect only when it is present in low concentration. At higher concentrations, a stabilising effect is observed. For a given concentration, the coagulation is further retarded by increasing the amount of potassium chloride present. L. L. BIRCUMSHAW.

Colouring matters. III. Determination of the electric charge of dyes. IV. Determination of the degree of dispersion of solutions of dyes. R. FURTH (Kolloid-Z., 1927, 41, 297—299, 300—304; cf. A., 1925, ii, 1057).—III. Previous views are not completely confirmed by subsequent work. The assumption that the potential gradient along the "half-conductor" and in the solution may be neglected in comparison with the very high fall of potential at the liquid/electrode boundary is not justifiable.

IV. A simple apparatus is described, by means of which the diffusion coefficient of a coloured solute can be measured rapidly and with an accuracy of 3—6%. The diffusion of the substance in a solution contained in a small cell is followed colorimetrically by comparison with a solution of known concentration in a similar adjoining cell, observations being made through a low-power microscope. The displacement, x, of a band of known concentration is thus obtained as a function of the time t. The degree of dispersion is obtained from the equation $D=x^2/t\times f(v)$, where v is the dilution, and from the values of D the degree of dispersion is found by calculating the particle radius by means of Einstein's formula. L. L. BIRCUMSHAW.

Colouring matters. V. Degree of dispersion of solutions of dyes. R. FURTH and E. ULLMANN (Kolloid-Z., 1927, 41, 304—310; cf. preceding abstract).—Measurements of the diffusion coefficient, D, of neutral-red and trypan-red in colloidal solution at various concentrations show that D decreases with increasing concentration, and on extrapolation to infinite dilution the respective values $4{\cdot}3\times10^{-6}$ and $3{\cdot}5\times10^{-6}$ are obtained. The particle radius, calculated from Einstein's formula, decreases with the concentration. At infinite dilution the values $4{\cdot}6\times10^{-8}$ and $5{\cdot}8\times10^{-8}$ are obtained for neutral-red and trypan-red, respectively. It is suggested that these numbers correspond with molecules of the substance, which becomes more and more polymerised as the concentration increases. There is thus a gradual change from crystalloidal to colloidal solution. Experiments with solutions of potassium permanganate show that in the concentration range 0—0·5%, D sinks to about a third of its value at infinite dilution, and then approaches a constant limiting value, $15{\cdot}2\times10^{-6}$, which agrees well with that calculated from Nernst's ionic mobility formula. The addition of acid to basic or acid dyes causes polymerisation, and finally coagulation, whilst the addition of base to basic or acid dyes causes depolymerisation or peptisation. Neutral salts coagulate basic dyes, but peptise acid dyes. L. L. BIRCUMSHAW.

Alcohol sols of the pea globulin. A. FODOR and K. MAYER (Kolloid-Z., 1927, 41, 326—330; cf. Fodor and Reifenberg, A., 1925, i, 756).—An alcoholic globulin sol may be prepared by macerating pea seeds and leaving the maceration liquor until the p_H has fallen from 5·55 to 4·45, when a fine precipitate separates. This is separated by centrifuging, washed, and suspended first in dilute, then in concentrated alcohol. The absolute alcohol sol is fairly stable, and contains 0·063—0·078% of globulin. No change is observed on the addition of alcoholic solutions of lithium, calcium, and aluminium chlorides, but alcoholic sodium hydroxide causes a slight increase in the viscosity, accompanied by swelling, and finally, when the viscosity and swelling have reached a maximum, protein coagulation occurs. It is proved that the swelling is associated with the formation of an alkali–protein compound, and is not due to a solvation process. The combination of the alkali with the protein causes a partly irreversible change in the protein, as shown by the fact that the solubility of the latter in sodium chloride solution diminishes with increasing addition of sodium hydroxide. L. L. BIRCUMSHAW.

Influence of salts on the ionisation of egg-albumin. S. P. L. SØRENSEN, K. LINDERSTRØM-LANG and E. LUND (J. Gen. Physiol., 1927, 8, 543—599).—The conditions which exist at equilibrium in an aqueous solution containing an ampholyte, such as egg-albumin, acid, or base and a neutral salt are discussed in the light of the Debye–Hückel theory of strong electrolytes. A distinction is made between the isoelectric and the isoionic points, the former being defined as the hydrogen-ion activity at which the mean valency of the ampholyte is zero, the latter as the hydrogen-ion activity at which the quantity of acid or base combined with the ampholyte is zero. Equations are deduced for the effect of neutral salts on the isoelectric and isoionic points and on the ionisation curves in the case of ampholytes capable of combining only with hydrogen ions, in which case the isoelectric and isoionic points coincide. These theoretical results are applied to the treatment of experimental data relating to the behaviour of egg-albumin in the presence of ammonium chloride and potassium chloride, and it is shown that, qualitatively at least, the expected results are obtained. Calculations on the basis of the theory indicate the radius of a molecule of egg-albumin to be approximately $2{\cdot}21\times10^{-}$ cm., corresponding with a mol. wt. of 35,000 and containing thirty acidic and basic groups. W. O. KERMACK.

Action exerted on colloidal solutions by electrolytes added in quantities below the minima necessary to produce coagulation. G. Rossi and A. Marescotti (Annali Chim. Appl., 1927, **17**, 167—175).—The results of experiments on the action of electrolytes on colloidal sulphur solutions support those obtained by Boutaric and Peneau (A., 1924, ii, 595), and show that the addition of an electrolyte in proportion insufficient to cause coagulation may result in the stabilisation of a colloid. In some cases the effect may be of opposite character, and in others it is not measurable. No general rule can be laid down to show what will be the behaviour in any particular instance, since the effect of any coagulating electrolyte varies with the nature of the other electrolytes present and with the concentration of the colloidal sulphur solution. T. H. Pope.

Anomalous flocculation of clay. A. F. Joseph and H. B. Oakley (Nature, 1927, **119**, 673).—A reply to Comber (A., 1926, 1004), and a summary of the facts established by the authors.

A. A. Eldridge.

Depolymerisation and hydrolysis of cellulose. F. G. C. Klein (Kolloid-Z., 1927, **41**, 372—375).—Experiments on cellulose and starch, viscose, oxycellulose, cellulose benzoate and acetate and allied substances between the years 1909 and 1912 are briefly reviewed and discussed from the colloid chemical point of view. The breakdown of cellulose to cellobiose or dextrose takes place in two essentially different stages in depolymerisation and hydrolysis. The mechanism of these stages is discussed.

L. L. Bircumshaw.

Activity in protein solutions. I. Inert gases. The question of hydration. J. L. Stoddard (J. Biol. Chem., 1927, **71**, 629—692).—The various factors which affect the solubility of a substance in a mixture of two other substances are discussed. It is inferred that association takes place when alcohol and water or sulphuric acid and water are mixed together. An apparatus is described for the determination of the solubility of nitrogen in solutions of protein and in water. The solubilities of nitrogen in solutions of plasma-protein and of hæmoglobin and in pure water have been determined. It appears that the high solubility of nitrogen in solutions of plasma-protein is just counterbalanced by the association between the protein and the water molecules, and so there is little difference between its solubilities in such solutions and in pure water.

W. O. Kermack.

Dispersion of cellulose according to von Weimarn's theories. A. Steingroever (Cellulosechem., 1927, **8**, 37—40).—According to the theory of "dispersoid parasitism," adsorption of the molecules of the dispersing agent neutralises the cohesive forces in the elements of the aggregate, inducing disintegration, and then, if these molecules have a strong affinity for the solvent medium, they carry the elementary particles of the dispersoid homogeneously through the liquid. High concentrations, high temperatures and pressures are favourable factors. Calcium thiocyanate and lithium chloride are powerful dispersing agents. If cellulose be heated in a saturated solution of lithium chloride, whilst the water is evaporated off by ebullition, the swollen fibres suddenly dissolve when the temperature of 160° is reached. When heated with a saturated solution of calcium thiocyanate in closed tubes, the amount of cellulose dissolved is a function of the temperature and time. The dispersions so prepared gelatinise on cooling, and solid films may be prepared by washing the gel and dehydrating with alcohol. On dilution of the hot concentrated dispersion the cellulose is deposited as a flocculent precipitate. A very large number of neutral salts and salts of heavy metals possess this property in a less degree. So far as the salts of the alkaline earths are concerned, the classification in order of decreasing power is: thiocyanates, iodides, bromides, chlorides; and for bases: calcium, strontium, barium. Calcium chloride and sodium chloride in highly concentrated solutions disperse cellulose only under extreme conditions, for instance at 170° under 8 atm. pressure. These dispersions do not solidify on cooling, but the cellulose is deposited in flakes. Prolonged heating induces decomposition, which also acts adversely on gelatinisation. Another type of dispersoid parasitism is illustrated at the other end of the scale, when the concentration of the dispersing salt is so small that the factors determining coagulation are inoperative. For instance, a permanently stable dispersion of cellulose at the ordinary temperature is obtained by adding a small quantity of the flocculated dispersion of cellulose in concentrated lithium chloride to a large volume of water and dialysing until the correct concentration of salt is reached. Such permanent solutions may contain per litre 0·08 g. of cellulose and 0·07 millimol. of lithium chloride. Other dispersoid substances besides cellulose are susceptible to the action of concentrated salt solutions; for instance, a solution of calcium chloride boiling at 115° will dissolve silk in a few minutes with practically no action on cellulose. J. F. Briggs.

Optical double refraction of artificial silk and films. O. Faust (Cellulosechemie, 1927, **8**, 40—41).—According to Zocher (A., 1922, ii, 102; 1926, 122), colloidal solutions in which the particles are not spherical show double refraction under motion and appear brilliant in polarised light, owing to a streamline "set" of the particles. Viscose, however, does not show this phenomenon, and a thread of viscose coagulated by squirting without tension into ammonium chloride solution, as well as the cellulose thread regenerated from it by the action of acids, are devoid of optical double refraction. These threads, however, become doubly refractive when strained, and if the viscose is coagulated under a spinning tension, the threads, both before and after regeneration, of the cellulose show double refraction. Similarly, sheets prepared by rolling undissolved plastic viscose masses show strong double refraction and a great variety of brilliant colours in polarised light due to varying degrees of strain. It has recently been observed by Gerngross and Katz (A., 1926, 793) that the Röntgen diagram of normal caoutchouc or gelatin is that of an amorphous solid, whereas strongly stretched caoutchouc shows a crystalline

Röntgen diagram. It is possibly the same with artificial silks, especially in view of the conflicting observations with regard to their Röntgen diagrams. Hence it is inferred that the optical double refraction induced by strains or mechanical deformation of the coagulated particles is of a different order from the double refraction of the natural cellulose fibre, which is inherently connected with the structure.

J. F. Briggs.

Cataphoresis in colourless sols. I. Charge on caoutchouc in benzene. R. H. Humphry and R. S. Jane (Kolloid-Z., 1927, **41**, 293—297; cf. Humphry, A., 1926, 577).—Cataphoresis in colourless sols in a non-aqueous medium may be observed by a method in which use is made of the difference between the refractive indices of the sol and dispersion medium. It is found that charges of both signs are present in a moist sol of caoutchouc in benzene, but that in sols prepared from carefully dried materials no appreciable charges are observable. The addition of small quantities of benzoic or dichloroacetic acid has no effect on the charge, and it is argued that the decrease in viscosity thus caused cannot be attributed to the so-called "quasi-viscous" effect. The bearing of the results on metal sols stabilised by rubber in non-aqueous media is discussed. L. L. Bircumshaw.

Electropy. L. Karczag (Kolloid-Z., 1927, **41**, 310—315; cf. A., 1924, i, 688).—A review of previous work on the process of "electropy." It is shown that electropical methods may be employed in the investigation of a large number of biological and pathological problems, and the new facts thus established justify the claims made for electropy.

L. L. Bircumshaw.

Influence of plasticising on the mechanical-elastic properties of artificial and natural plastic substances. O. Manfred and J. Obrist (Kolloid-Z., 1927, **41**, 348—361).—Optical investigations indicate that various plastic materials exhibit rod-like double refraction, whilst flowing sols show streaming anisotropy. These facts lead to the view that plastic substances consist of rod-like particles dispersed in a solid medium. During the mechanical plasticising process, the particles become partly oriented, and become fixed in this position during the subsequent process of hardening or of removing the dispersion medium. The fibrillar structure of many colloids is conceived as a linking up of rod-like elements by a streaming process during preparation. The process of plasticising consists in a disintegration of the raw material to dispersoid dimensions, followed by a more or less completely oriented re-aggregation. The degree of disintegration and re-aggregation determines the degree of plasticity. Methods of plasticising, with particular reference to the technology of artificial horn, are fully discussed from the point of view of the disaggregation and re-aggregation. A consideration of the elastic data for a series of artificial horn products, for an artificial resin, and for celluloid, shows the great influence of the plasticising process on the mechanical behaviour of the end product. The analogous change in the properties of metals and non-metals, produced by mechanical treatment, appears to justify the conclusion that the causes in both cases are fundamentally the same, and it is considered that an investigation of this type of change would lead to a solution of the plasticity problem. L. L. Bircumshaw.

Formation of Liesegang rings. P. B. Ganguly (J. Physical Chem., 1927, **31**, 481—495).—The stabilisation of silver and lead chromates by gelatin and agar-agar, respectively, and the influence of an excess of one of the reacting substances on the compounds formed have been studied. The chromates were prepared from the respective nitrates and potassium chromate, and stabilisation was followed nephelometrically. A device to ensure uniform and simultaneous mixing was essential to reproduce results. The turbidities resulting from the addition of solutions of silver nitrate of increasing concentration to equivalent solutions of potassium chromate varied in a periodic manner, the amount of stabiliser being constant. Maximum turbidities were shown in two distinct zones. These coagulation zones become less marked with increasing concentration of gelatin, and an excess of silver or chromate ions has a stabilising effect on the silver chromate formed. Below a critical concentration, free silver ions have a slight coagulating effect. Free chromate ions, which are adsorbed, favour peptisation of lead chromate by agar-agar, but lead ions have no such effect. Silver nitrate solutions reacting with those of potassium chromate will give turbid mixtures only when one of two conditions is fulfilled. (1) With equivalent solutions which are not too concentrated, precipitation occurs when the amount of silver chromate formed lies within certain limits which depend on the concentration of gelatin. With amounts of silver chromate other than this, peptisation occurs. (2) When one of the reacting solutions is in excess, for a given gelatin concentration and a given quantity of silver chromate, precipitation occurs only when a certain weight of the reacting substance remains in excess. Above or below this amount, peptisation results. The Liesegang phenomenon is explained in the light of the above. The distribution of concentrations of silver nitrate and potassium chromate solutions in a gelatin gel has been calculated, using Fick's diffusion equation. L. S. Theobald.

Advantages of the ring method for the study of the surface equilibria of colloidal solutions. P. L. de Noüy (Nature, 1927, **119**, 598).—Instances are cited of the author's successful use of the improved ring method (cf. Harkins, this vol., 17).

A. A. Eldridge.

Permeability of membranes. I. Diffusion of ions across the dried collodion membrane. L. Michaelis and W. A. Perlzweig (J. Gen. Physiol., 1927, **10**, 575—598).—A method is described for the preparation and testing of dried collodion membranes containing a very large number of very fine pores. When such a membrane separates a solution of 0·1*M*-potassium chloride from distilled water, the rates of diffusion both of potassium ion and of chlorine ion are very small, but equivalent quantities diffuse in a given time. If, however, the distilled water is replaced by a solution of another electrolyte

such as 0·1*M*-sodium nitrate, the potassium diffuses much more readily and the ratio of diffused potassium to diffused chlorine is on the average about ten to one. From these and other diffusion experiments the conclusion is reached that such membranes are relatively permeable to cations and relatively impermeable to anions. W. O. KERMACK.

Decomposition of hydrogen bromide by the silent electric discharge. J. J. CANFIELD and A. HAYES (Proc. Iowa Acad. Sci., 1925, **32**, 326—327).—Equilibrium in the reaction $2HBr \rightleftharpoons H_2+Br_2$ at 33° and atmospheric pressure with 10,000—15,000 volts is reached at 33·5% HBr, 33·25% H_2, and 33·25% Br_2. Assuming no appreciable dissociation of the bromine, this value corresponds with thermal equilibrium near 2800° Abs. Moser and Isgarischev's results (A., 1910, ii, 926) for the equilibria $CO_2 \rightleftharpoons CO+0·5O_2$ and $2HCl \quad H_2+Cl_2$ correspond with thermal equilibria at 2500° and 2000° Abs., respectively, whilst Davies' results for ammonia (A., 1909, ii, 30) correspond with thermal equilibrium at 900° Abs. The equilibrium of a gaseous system under the influence of the silent electric discharge corresponds with that at a high temperature if the reaction velocities are slow when the reactions occur without the influence of the discharge.

CHEMICAL ABSTRACTS.

Ebullioscopic determination of the molecular equilibria of resorcinol in aqueous solutions of potassium chloride. F. BOURION and E. ROUYER (Compt. rend., 1927, **184**, 941—942).—The b.-p. elevations of solutions of potassium chloride containing various amounts of resorcinol have been determined. The b.-p. constant for the potassium chloride solution is said to differ from the constant for water. J. GRANT.

Ebullioscopic constant of aqueous solutions of potassium chloride and the molecular equilibria of resorcinol in this medium. F. BOURION and E. ROUYER (Compt. rend., 1927, **184**, 1064—1066).—The agreement between the observed and calculated values of the b. p. rise for various concentrations of resorcinol in a solution of potassium chloride are said to justify the conclusion that potassium chloride and resorcinol coexisting in solution conform to the requirements of the ideal solution. J. GRANT.

Calculation of ionic equilibria. P. M. VÈZES (Compt. rend., 1927, **184**, 943—945).—The amount of silver chloride precipitated from equal volumes of solutions of silver nitrate and hydrochloric acid of the same molecular dilution (50) agrees with the calculated amount within 0·1%. J. GRANT.

Second dissociation constants of certain dibasic acids. M. DUBOUX and J. FROMMELT (J. Chim. phys., 1927, **24**, 245—258).—The second dissociation constant K_2 for a dibasic acid partly neutralised by an alkali is given by the formula $K_2=[H^·](H^·]+K_1-a)/(2a-K_1)$, where K_1 is the first dissociation constant and a is connected with the degree of dissociation α of the alkali salt by the expression $a=K_1\{C-S(1-\alpha)\}/\{S(2\alpha-1)+[H^·]\}$, C being the total molecular concentration and S that of the salt. The velocity constant K of the hydrolysis of ethyl diazoacetate in the presence of certain partly neutralised dibasic acids has been determined, and by using an approximate value for the proportionality factor K_H of the expression $K/K_H=[H^·]$, its accurate value 36·8 has been deduced, and is independent both of concentration and of the nature of the acid. Using this value, the following second dissociation constants have been obtained: malonic acid, $K_2=1·9\times10^{-6}$; succinic, $2·8\times10^{-6}$; malic, $7·4\times10^{-6}$; tartaric, $39·4\times10^{-6}$; glutaric, $6·0\times10^{-6}$; maleic, $0·77\times10^{-6}$; fumaric, $27·3\times10^{-6}$. S. J. GREGG.

Monoalkyl carbonates. IV. Solutions of carbon dioxide in dry methyl and ethyl alcohols; monomethyl and monoethyl carbonates in dry alcoholic solution and in the solid state. C. FAURHOLT (Z. physikal. Chem., 1927, **126**, 227—237).—Solid sodium and potassium methyl carbonates have been prepared by saturating a methyl alcohol solution of the alkali metal with carbon dioxide, decanting off the solution from the precipitate, and drying. The monoethyl carbonates may be prepared similarly. Measurement of the equilibrium carbon dioxide pressure over the solid salts shows them to be very stable, in opposition to the usual statements in the literature. Sodium ethyl carbonate may be heated at 200° without any appreciable evolution of gas, but above this temperature there is a slow evolution of ethylene.

The equilibrium constant $MeCO_3^- \rightleftharpoons MeO^-+CO_2$ has been determined by potentiometric measurements of the methoxyl ion concentration in solutions of sodium methoxide in methyl alcohol. If the carbon dioxide pressure be measured in atmospheres, $K=10^{5·6}$. For potassium ethyl carbonate in ethyl alcohol solution $K=10^{6·4}$. The dissociation constant of methyl hydrogen carbonate, which is formed when carbon dioxide is passed into dry methyl alcohol, is thus $10^{-10·7}$, and of ethyl hydrogen carbonate, $10^{-12·3}$. Calculation of the carbon dioxide pressure over the system sodium ethyl carbonate–sodium ethoxide gives $P=10^{-13}$ atm., a result which accords with the observed stability of the monoalkyl carbonates. H. F. GILLBE.

Validity of the "displacement principle" for solutions. D. REICHINSTEIN (Z. Elektrochem., 1927, **33**, 122—127).—By applying Raoult's law to a solution made up of liquid components, it follows that $k_1p_1+k_2p_2+\ldots=k$, where p_1, p_2, . . . are the partial pressures of the components in the solution and k_1, k_2, . . . k are constants for the given components in the given system, independent of the actual values of p_1, p_2, . . . This forms an example of the author's "displacement principle" (cf. A., 1915, ii, 678), which can also be applied to the interpretation of the effects produced by salts in connexion with the solubility of non-electrolytes. The consideration of adsorption equations from this point of view leads to the conclusion that the action of a substance in lowering the solubility of another is in the nature of a "ballasting action" (cf. *loc. cit.*), and it is probable that substances arranged according to their poisoning action on a given catalyst will form a sequence which is independent of the nature of the reaction being catalysed. From a philosophical analysis of the Nernst parallelism it is concluded that

the displacement law for solubility does not actually follow from that of vapour pressure, but that in a comparison of the two groups of regularities, vapour pressure corresponds with solubility and lowering of vapour pressure to lowering of solubility.

H. J. T. ELLINGHAM.

Buffer action. III. Aluminium hydroxide. IV. Buffering by heated alkaloid solutions. V. Sodium fluoride. H. MOSER (Helv. Chim. Acta, 1927, **10**, 310—319, 319—322, 322—331).—III. The peptisation of "alucol," a commercial aluminium hydroxide, by hydrochloric acid is studied electrometrically. The solution eventually reaches neutrality, providing sufficient alucol is present; physical adsorption and neutralisation of the acid both take place. Similarly, alucol adsorbs hydroxyl ions from solution, although less rapidly than in the case of hydrogen ions. The sol has a greater adsorption capacity than the suspension under similar conditions. The activity of alucol is considerably diminished in Sorensen's glycine solution. Peptic digestion is hindered by large amounts of alucol, the suspension being slightly more active in this respect, but is favoured by small quantities. The hydroxyl ion of aluminium hydroxide promotes the stem growth of certain plants as compared with the roots when added to feebly acid soils.

IV. The buffering of heated alkaloid solutions may often be effected by the addition of colloids. Variations in the osmotic ratio are eliminated, and in the case of albumin the whole p_H range is covered. Comparatively small colloid concentrations suffice to counteract the increase in acidity due to hydrolysis of the alkaloid salt.

V. The buffer action of sodium fluoride in solution is investigated; the results are consistent with the supposition that the salt is at least partly polymerised to double molecules.

S. K. TWEEDY.

Relation between p_H and the reaction of aqueous solutions at various temperatures. E. I. FULMER (Iowa State Coll. J. Sci., 1926, **1**, 37—41).—The empirical equation, $\log(p_H-5{\cdot}215)=0{\cdot}3450-0\ 00422t$ closely represents values of p_H at neutrality for different temperatures. A nomogram is given for the calculation of the p_H at any temperature which is equivalent in acidity to the p_H at the given temperature. Neutrality varies from p_H 6·053 at 100° to p_H 7·428 at 0°. The relation of the medium to neutrality is expressed as "p_A."

CHEMICAL ABSTRACTS.

Abnormal change of p_H of mixtures of boric acid and sodium hydroxide with change of dilution and of temperature. I. M. KOLTHOFF and W. BOSCH (Rec. trav. chim., 1927, **46**, 180—188).—Dilution of a borate solution containing a large excess of boric acid causes the reaction to become more alkaline, whereas if the borate be in excess, dilution produces increases of acidity. The p_H of a borax solution is but little affected by dilution. The properties of the mixed solutions may be explained on the assumption that complex ions are formed between the boric acid and metaborate. Measurements of p_H at 60° indicate that the complexes break down at higher temperatures. Taking the p_H of (0·01N-HCl+0·09N-KCl) as 2·038, then $K_{H_3BO_3}=6{\cdot}2\times10^{-10}$ at 18°, and $1{\cdot}2\times10^{-9}$ at 60°. Taking $\log pa_H=-2{\cdot}093$, then $K_{H_3BO_3}=5{\cdot}5\times10^{-10}$ at 18°, and $1{\cdot}06\times10^{-9}$ at 60°.

H. F. GILLBE.

Influence of dextrose, alcohol, and carbon dioxide on the p_H values of phosphate and hydrogen carbonate solutions. E. BIILMANN and H. KATAGIRI (Biochem. J., 1927, **21**, 441—455).—Dextrose makes a phosphate mixture, p_H 6·79, more acid, whilst alcohol makes it less acid. When both are present, the influence is additive. Solutions of disodium hydrogen phosphate and sodium hydrogen carbonate were examined with the hydroquinhydrone electrode after saturation with carbon dioxide at barometric and higher pressures. The influence of dextrose on the p_H values of the liquids saturated with carbon dioxide is very feeble. Comparative measurements with and without dextrose show that the colorimetric method gives lower p_H values than the electrometric method up to 6·4; above this the colorimetric method gives higher values than the electrometric method. As a comparison electrode a hydroquinhydrone electrode in a phosphate mixture, p_H 6·79, was used in this investigation. Such an electrode is stable and its use obviates high liquid junction potentials. A hydroquinhydrone electrode in 0·01N-hydrochloric acid and 0·09N-potassium chloride is not very stable, but is stabilised by the addition of dextrose. There is a specific action of dextrose on the platinum of the quinhydrone electrode.

S. S. ZILVA.

Amphoteric behaviour of complex systems. III. Conductivity of sulphanilic acid-lysine mixtures. IV. Isoelectric point and ionisation constants of sulphanilic acid. A. E. STEARN (J. Gen. Physiol., 1927, **10**, 369—377, 379—383).—III. The conductivities of solutions of sulphanilic acid, of lysine, and of mixtures of these two compounds in presence of phosphate as buffer have been determined at various p_H values. The difference between the conductivities of the mixture and the sum of the individual conductivities of the two compounds reaches a maximum at a point corresponding with the apparent isoelectric point of the system (cf. *ibid.*, 313). The relation of the properties of systems containing two or more ampholytes to problems of cell physiology is discussed.

IV. From solubility measurements the basic dissociation constant of sulphanilic acid is found to lie between $2{\cdot}0\times10^{-15}$ and $2{\cdot}2\times10^{-15}$. The isoelectric point is at p_H 1·25. The following constants have been found for glycine: $K_a=2{\cdot}3\times10^{-10}$ and $K_b=2{\cdot}2\times10^{-12}$.

W. O. KERMACK.

Development of the Sorensen equation for the isoelectric points of ampholytes. W. R. ATKIN (Proc. Leeds Phil. Lit. Soc., Sci. Soc., 1927, **1**, 165—168).—Theoretical. Sorensen's equation for the isoelectric point of amphoteric electrolytes is applicable only to simple amino-acids, and not to proteins in which the basic and acidic groups are not necessarily equal. The following equation gives the isoelectric point of proteins:

$$h=\{-k_a(1-n)+\sqrt{k_a^2(1-n)^2+4n(K_w\times k_a/k_b)}\}/2,$$

where h is the hydrogen-ion concentration at the isoelectric point, k_a is the average dissociation constant

of the acid groups, and k_b of the basic groups, K_w is the ionic product for water, and n is the ratio of the number of acid to basic groups. When $n=1$ $h=\sqrt{K_w \times k_a/k_b}$, which is the usual formula for a simple amino-acid. M. S. Burr.

Theory of electrolytes. L. Onsager (Physikal. Z., 1927, **28**, 277—298).—The author's revision of the Debye–Huckel theory is continued (cf. A., 1926, 906). The change in molecular conductivity with dilution depends primarily on changes in ionic mobility, which in turn depend on two effects: (*a*) solvent movements analogous to electrophoresis, (*b*) deformation of ions by environmental influences. For both effects the decrease in conductivity is proportional to the square root of the concentration, in conformity with the experimental observations of Kohlrausch. The theoretical and mathematical basis of the theory of inter-ionic attractions etc. has been thoroughly revised, and a set of modified equations is advanced. The idea of a constant speed characteristic of an ion is now abandoned, and the implications of the conception of ion-atmosphere are worked out and used instead. The modified theory retains the original relation between conductivity and concentration, but the calculation of coefficients is considerably modified. The relevant conductivity data for aqueous solutions are shown to be in moderately good agreement with the new equations. R. A. Morton.

Mineral waters. I. Method of representing the composition of mineral waters. M. Betti and G. B. Bonino [in part with V. Vaglio] (Annali Chim. Appl., 1927, **17**, 89—114).—The laws which hold for ideal or infinitely dilute solutions are not applicable to mineral waters. The activity coefficients of the ions present and of the solvent must be determined, and the methods of calculating these coefficients are described and applied to the salt waters of Riolo in the province of Ravenna. T. H. Pope.

Mineral waters. II. Calculation of the f. p. of highly concentrated mineral waters. G. B. Bonino (Annali Chim. Appl., 1927, **17**, 115—129).—The cryoscopic anomalies of concentrated mineral waters depend on the unjustifiable use of formulæ which apply only to infinitely dilute solutions, and disappear when thermodynamically exact methods of calculation are employed. For instance, the fact that osmotic concentration derived from the cryoscopic behaviour by means of the reduced formulæ is higher than the actual concentration in general, signifies only that the logarithm of the coefficient of activity of the solvent is negative, and that the osmotic coefficient exceeds 1. Application of the author's methods to the water of Salsomaggiore yields satisfactory results. T. H. Pope.

System tin–cadmium in the crystalline state. A. Fedorov (Ukraine Chem. J., 1926, **2**, 69—74).—Tin dissolves 10% of cadmium, but cadmium does dissolve tin. The eutectic mixture (70% Sn, 30% Cd) crystallises at 177°. On cooling, the greatest thermal effect is observed at 120°. This is not due to chemical combination, but to the change of the cadmium–γ-tin form to β-tin and cadmium.

E. Rothstein.

Lithium. VI. Thermal analysis of the systems lithium halides–water. G. F. Huttig and W. Steudemann (Z. physikal. Chem., 1927, **126**, 105—117; cf. Huttig and Schliessmann, A., 1925, ii, 1181).—The f.-p. curves show the existence of the hydrates, $LiCl,5H_2O$ and $LiBr,5H_2O$.

G. A. Elliott.

System sulphur dioxide–*n*-octane. W. F. Seyer and A. F. Gallaugher (Trans. Roy. Soc. Canada, 1926, [iii], **20**, III, 343—345).—Determination of the mutual solubilities of *n*-octane and liquid sulphur dioxide between −50° and 27° gives no indication of compound formation. The surface tension of octane between 80° and −50° has been measured. The following data are given for octane: m. p. −58·61°; n_C^{20} 1·39578; n_D^{20} 1·39761; n_F^{20} 1·40268. R. Cuthill.

Ternary systems with iron and carbon. I. Phases "Fe_3C,Cr_4C" and $Cr_{10}C_6Fe_3$ and "physical residual analysis." F. Sauerwald, H. Neudecker, and J. Rudolph (Z. anorg. Chem., 1927, **161**, 316—320).—Iron, carbon, and chromium in the proportions required for making the compound Fe_3C,Cr_4C, which is alleged to occur in chromium steels, were melted together and the microstructure of the alloy was examined. Whether slowly cooled or annealed for a long period and quenched, this alloy invariably exhibits a duplex structure, and, after powdering finely, can be separated into a magnetic and a non-magnetic fraction. The latter has a composition corresponding with the empirical formula $Cr_{10}C_6Fe_3$, and after melting has a homogeneous structure. This substance, therefore, appears to be a chemical entity, and may be more probably formulated as $5Cr_4C_2,2Fe_3C$. A. R. Powell.

Ternary system lead–antimony–arsenic. E. Abel and O. Redlich (Z. anorg. Chem., 1927, **161**, 221—227).—The system lead–antimony–arsenic belongs to the type in which two of the constituents (arsenic and antimony) form a continuous series of solid solutions which are insoluble in the third constituent (lead), but form a eutectic with it. The eutectic melts at 252° for the alloys rich in antimony and at 294° when arsenic predominates. The line of eutectic crystallisation on the ternary diagram connects the point 20·5% Sb on the antimony side with the point 6% As on the arsenic side, and is slightly convex to the antimony side.

A. R. Powell.

Properties of bauxite. Y. Yamaguchi, T. Takebe, and T. Yazawa (Bull. Inst. Phys. Chem. Research, 1926, **5**, 735—740).—The vapour pressure of bauxite has been measured between 230° and 518°. The decomposition occurs in two stages: $Al_2O(OH)_4 \rightarrow Al_2O_2(OH)_2 - Q_1$ and $Al_2O_2(OH)_2 \rightarrow Al_2O_3 + H_2O - Q_2$. For the first (200—340°) and second (350°—450°) stages the vapour pressures are given by $\log \pi = 6{\cdot}5277 - 2206{\cdot}5/T$ and $\log \pi = 5{\cdot}2566 - 1780/T$, respectively. For comparison, the vapour pressures of aluminium and ferric hydroxides obtained by precipitation were measured, The heats of decomposition of bauxite given by the Clapeyron–Clausius formula are Q_1(200—340°)=10,100 g.-cal./mol. and Q_2(350—450°)=8100 g.-cal./mol., respectively. K. Kashima.

Diaspore. Y. YAMAGUCHI, T. TAKEBE, and T. MORIOKA (Bull. Inst. Phys. Chem. Research, 1926, **5**, 17—31).—The vapour pressure of the water produced from diaspore according to the scheme $Al_2O_3,H_2O \longrightarrow Al_2O_3+H_2O$ has been measured at various temperatures. The Clapeyron–Clausius formula is applicable to the data obtained. The heat of decomposition of diaspore at about 500° calculated from this formula is 353 kg.-cal./kg. The specific heat of diaspore is given by $c'=0{\cdot}2085+0{\cdot}000127t$ between 100° and 400°. The total energy required to convert diaspore into alumina at 502·5° is calculated to be 486·7 kg.-cal./kg. K. KASHIMA.

System zinc hydroxide, zinc oxide, sodium zincate, and sodium hydroxide. E. MULLER, J. MULLER, and A. FAUVEL (Z. Elektrochem., 1927, **33**, 134—144).—In addition to the crystalline hydroxide, $Zn(OH)_2$ [1], there exists an amorphous hydroxide, approximately $ZnO,0{\cdot}5H_2O$ [2], which may be prepared by drying over sulphuric acid the precipitate obtained in the usual manner. Determinations were made of the solubility of these hydroxides and also of amorphous zinc oxide and crystalline sodium zincate in sodium hydroxide solutions of varying concentrations. The solubility increases with the alkali concentration except for sodium zincate, where there is a sharp fall. The hydroxide [2] loses water on shaking with alkaline solutions, giving approximately $ZnO,0{\cdot}05H_2O$ [3], and has a metastable solubility curve lying slightly above that of zinc oxide, which is the stable solid phase and does not take up water from sodium hydroxide solutions. The hydroxide [1] also gives a metastable solubility curve lying considerably above that of [2], but, although its saturated solutions are strongly supersaturated with respect to zinc oxide, only those with very high zinc and alkali content become unstable and give a deposit similar to [3], or in some cases set completely to stiff pastes or crystalline masses, the nature of which it has not been possible to investigate completely. The zinc oxide solubility curve cuts that of sodium zincate at a point corresponding with 14·2*N*-sodium hydroxide and about 2·9 g.-mol. of zinc per litre, but metastable continuations of these curves into regions of higher zinc concentration can be realised. Hence, to prepare crystalline sodium zincate, sodium hydroxide solutions of at least 14*N* must be saturated with zinc oxide and, unless seeding out can be resorted to, higher concentrations of alkali (19*N*) are needed, since sodium zincate does not separate readily even from highly supersaturated solutions. A sample after washing with alcohol had a composition corresponding closely with $NaHZnO_2$. It dissolves readily in water, but hydrolyses with precipitation of zinc hydroxide. To obtain the hydroxide [1] most conveniently it is recommended that 16*N*-sodium hydroxide, which has been shaken with excess of zinc oxide and filtered, should be diluted until the alkali is about 2·5*N* (cf. Fricke and Ahrndts, A., 1924, ii, 681). A few data for solubilities in potassium hydroxide solutions are also given.

H. J. T. ELLINGHAM.

System $Al(NO_3)_3$–KNO_3–H_2O. G. MALQUORI (Atti R. Accad. Lincei, 1927, [vi], **5**, 451—452).—The data for 25° show the existence of the crystalline double salt $KNO_3,Al(NO_3)_3,9H_2O$. The results fail to confirm the existence of the double salt $Al(NO_3)_3,3KNO_3,10H_2O$, which is reported by La-Porte (A., 1921, ii, 699). R. W. LUNT.

Precipitated solids, especially strontium and calcium sulphates. P. P. VON WEIMARN (J.C.S., 1927, 929—930).—References are given to the author's systematic investigations of the precipitation of strontium and calcium sulphates prior to the work of Lambert and Hume-Rothery and of Lambert and Schaffer (A., 1926, 1209). E. S. HEDGES.

Composition of crystals from mixed solutions. E. FABRIS (Annali Chim. Appl., 1927, **17**, 197—208).—With the object of obtaining purgative salts of constant composition from the waters of Montecatini, experiments have been made on the crystallisation of solutions containing (1) sodium sulphate and chloride, (2) sodium carbonate and sulphate, (3) sodium sulphate, carbonate, and chloride, with and without small proportions of lithium salts. Investigation of the 25° isotherm for the system sodium sulphate–sodium carbonate indicates the formation of mixed crystals (cf. Dawkins, J.C.S., 1922, **121**, 776).

T. H. POPE.

Equilibrium between tin, cadmium, and their chlorides in the fused state. R. LORENZ (Annalen, 1927, **453**, 338—347).—The equilibrium $Sn+CdCl_2 \rightleftharpoons SnCl_2+Cd$ at 600° has been investigated. The equilibrium constant obtained from the new mass law formula (A., 1926, 126) is approximately constant over the whole range of concentrations examined, whereas that obtained from the classical expression varies from 1497 to 120·5. R. CUTHILL.

Ternary systems. V. Potassium hydrogen carbonate, potassium carbonate, and water. A. E. HILL and D. G. HILL (J. Amer. Chem. Soc., 1927, **49**, 1967—969; cf. this vol., 418).—The system at 25° and 36° affords no evidence of compound formation or solid solution. The normal carbonate cannot be precipitated from saturated solutions containing more than 2·21% of hydrogen carbonate at 25° and 3·88% at 36°.

S. K. TWEEDY.

System dextrose–sodium chloride–water. S. MATSUURA (Bull. Chem. Soc. Japan, 1927, **2**, 44—48).—Observations at 24° show that the only compound formed is $(C_6H_{12}O_6)_2,NaCl,H_2O$, which is decomposed by water, but can be crystallised by adding excess of sodium chloride to the solution. S. J. GREGG.

Reduction equilibrium of chromic oxide. H. VON WARTENBERG and S. AOYAMA (Z. Elektrochem., 1927, **33**, 144—147).—Pieces of chromium were heated in a current of hydrogen, the water vapour content of which had been reduced to a known, very low value by cooling to a known temperature in a freezing mixture. At a fixed partial pressure of water vapour, oxidation occurs below a certain temperature and reduction at higher temperatures. Such temperatures have been determined for partial pressures of water vapour between 10^{-2} and 10^{-6} atm., and the corresponding partial pressures of oxygen in the gas calculated from the dissociation

constant for water vapour. The heat of reaction calculated from these results agrees with the value for the heat of formation of chromic oxide from chromium, and it is inferred that chromous oxide is not an intermediate stage at these temperatures (600—1400°). Whereas iron oxides are reduced at 1100° when p_{H_2O}/p_{H_2} is about 1, this ratio must be about 0·001 for the reduction of chromic oxide. Hence, since water is produced in the reduction, an enormous excess of hydrogen would be needed to reduce any quantity of chromic oxide, and there is no possibility of such a process being used instead of the alumino-thermic process for preparing carbon-free chromium.

H. J. T. Ellingham.

Aqueous solutions of sodium silicates. VI. Heterogeneous equilibria; system sodium oxide–silica–water at 25°. VII. Silicate ions. Electrometric titrations, diffusion, and colorimetric determination. R. W. Harman (J. Physical Chem., 1927, **31**, 511—518, 616—625; cf. this vol., 415; Morey, A., 1914, ii, 202; Morey and Fenner, A., 1917, ii, 370).—VI. Observations at 25° indicate that two compounds only, sodium metasilicate and the compound $Na_2O,2SiO_2$, are stable in contact with solution. The metasilicate crystallises with 9, 6, and 2·5 mols. of water, and the compound $Na_2O,2SiO_2$ with $9H_2O$. Towards the water–silica side of the system, the solutions become colloidal, invalidating further work. The ternary diagram at 25° is given, and previous work in this field is summarised.

VII. Electrometric titrations of 0·1 and $0·2N_W$-solutions of sodium metasilicate with $0·1N$- and $1·219N$-hydrochloric acid give curves typical of dibasic acids, indicating that metasilicic acid is dibasic. The constants for the dissociations $H_2SiO_3 \quad H^+ + HSiO_3'$ and $HSiO_3' \rightleftharpoons H^+ + SiO_3''$ calculated from hydrolysis data and from the electrometric titrations are $k_1 = 4·2 \times 10^{-10}$ and $k_2 = 0·51 \times 10^{-16}$. Titration of the ratio $Na_2O : SiO_2$ 1 : 4 in $0·2N_W$-solution with $10N$-sodium hydroxide indicated that the mixture of silicate and sodium hydroxide does not reach equilibrium immediately, and that the hydroxyl-ion concentration of the ratio 2 : 1 is not much greater than that of the ratio 1 : 1 (cf. A., 1926, 907). Using the colorimetric test with sulphuric acid and ammonium molybdate as indicative of crystalloidal silica, most of the silica in $0·005N$-solutions of the ratios 2 : 1, 1 : 3, 1 : 4, and 1 : 1 is crystalloidal, but an increase in concentration and in ratio increases the colloidal content. Diffusion through collodion and parchment paper indicated that most of the silica in the ratios 1 : 1 and 1 : 2 is diffusible, and that two thirds of the silica in the ratio 1 : 4 ($0·3N_W$) and one third in N_H-metasilicic acid is crystalloidal. Silicate ions definitely exist in all the ratios up to 1 : 4, and in metasilicic acid itself.

L. S. Theobald.

System lime–alumina–silica. The composition $8CaO + Al_2O_3 + 2SiO_2$. W. C. Hansen, W. Dyckerhoff, F. W. Ashton, and R. H. Bogue (J. Physical Chem., 1927, **31**, 607—615; cf. Jänecke, A., 1912, ii, 761; Rankin and Wright, A., 1915, ii, 50).—The evidence bearing on the existence of the compound $8CaO,Al_2O_3,2SiO_2$ has been investigated. When the oxyhydrogen flame was used in preparing samples of this composition, there was obtained a crystalline phase which differed in appearance from the phases ordinarily found in mixtures of lime, alumina, and silica heated up to 1600°. The correct heat treatment, however, brought these preparations to the equilibrium found to exist in this system by Rankin and Wright (*loc. cit.*). The birefraction, mean refractive index, and *X*-ray spectrum of this phase were identical with those of the compound $3CaO,SiO_2$. High magnification and *X*-ray analysis showed the preparations to be non-homogeneous. The results obtained are opposed to the existence of the ternary compound $8CaO,Al_2O_3,2SiO_2$, and to the existence of solid solutions of the silicates and aluminates. The crystals previously reported by other workers as those of this compound are concluded to be those of the compound $3CaO,SiO_2$.

L. S. Theobald.

Thermodynamic relations. I. I. Placinteanu (Ann. sci. Univ. Jassy, 1927, **14**, 218—221).—From Laplace's theory of capillarity, the force between two molecules in a liquid may be shown to be kre^{-} where r is their relative distance apart, d their diameter, k a constant, and α the degree of association. The relation between the heat of evaporation and the surface tension previously obtained (A., 1925, ii, 39) is a particular case of this expression. From this result, the equation $C = \sqrt{r}$ (for the velocity of sound in the liquid) can be deduced. Using Grüneisen's theory of the solid state (A., 1912, ii, 1048), the longitudinal and transverse velocities of sound in a solid are found to be $\sqrt{[12(1-\sigma)\lambda/(1+\sigma)]}$ and $\sqrt{[6(1-2\sigma)\lambda/(1+\sigma)]}$, respectively, where λ is the heat of sublimation of unit mass at 0° (Abs.) and σ is Poisson's number.

R. Cuthill.

Free energy of chlorine. N. Kameyama, H. Yamamoto, and S. Oka (J. Soc. Chem. Ind. Japan, 1926, **29**, 679—686).—The *E.M.F.* of the chain $Hg|Hg_2Cl_2$—satd. soln. KCl|satd. soln. KCl|Pt,Cl_2 has been measured at 25° with various concentrations of chlorine, using nitrogen as a diluent. The cell reaction is essentially as follows: $2Hg(liquid) + Cl_2(gas) = Hg_2Cl_2(solid)$. This is accompanied by a transport of some potassium chloride through the cell from one electrode chamber to another, but this can scarcely affect the *E.M.F.*, because the activity of potassium chloride is practically the same throughout the electrolyte, so long as the solubility of chlorine is not appreciable. The *E.M.F.* should be independent of the chloride and of its concentration. The potassium chloride solution may therefore be replaced by hydrochloric acid of sufficient concentration without affecting the *E.M.F.* The influence of varying partial pressure of the chlorine should be given by $E = E_0 + 29·58 \log A_{Cl_2}$, and approximately, $E = E_{o\cdot p} + 29·58 \log P_{Cl_2}$, where E_0 and $E_{o\cdot p}$ are the *E.M.F.* in millivolts with chlorine of unit activity and at 1 atm., respectively. Two possible disturbances are represented by $Cl_2 + H_2O \rightleftharpoons H^+ + Cl^- + HClO$ and $Cl_2 + Cl^- \rightleftharpoons Cl_3^-$. Except when the mol.-fraction of the gas mixture is small, $E_{o\cdot p}$ is found to be fairly constant throughout each series, and it follows that the disturbances mentioned above are of negligible order. The mean value of $E_{o\cdot p}$ from two series of observations is

1·0902 volt. The present investigation gives 1·0903 volt for E_0, assuming the fugacity of chlorine under unit pressure at 25° to be 0·989. It is proposed to use the results for the determination of the purity of chlorine (cf. Lewis and Rupert, A., 1911, 364; Wolff, A., 1914, ii, 104). K. KASHIMA.

Intertraction. (SIR) A. E. WRIGHT (Proc. Roy. Soc., 1927, **A**, **114**, 576—591; cf. A., 1926, 901; Adam and Jessop, A., 1925, ii, 772; Adam, this vol., 16).—Experiments are described to refute the criticisms made by Adam and Jessop (*loc. cit.*) of the author's previous work on the phenomena of intertraction. L. L. BIRCUMSHAW.

Influence of temperature on neutral salt action. A. WEISSBERGER (Z. physikal. Chem., 1927, **126**, 127—132).—Theoretical. The observation that neutral salt action (cf. Grube and Schmid, A., 1926, 474) is independent of temperature is shown to be consistent with the assumptions of Hantzsch and Weissberger (this vol., 525), and with the thermodynamic considerations of Bjerrum (Z. anorg. Chem., 1920, **109**, 275). G. A. ELLIOTT.

Calculation of chemical affinity on the basis of the entropy. II. G. BOZZA and G. DEVOTO (Atti R. Accad. Lincei, 1927, [vi], **5**, 287—293; cf. this vol., 419).—According to Eucken's procedure (A., 1925, ii, 97, 98), the calculation of a chemical equilibrium requires a knowledge not only of the chemical constants, but also of certain functions $\Phi=\int_0^T dT/T^2\int_0^T c_p dT$. Since c_p is usually expressed by empirical formulæ at temperatures above the ordinary and by Debye's or Einstein's function or the sum of these at low temperatures, it is convenient to resolve the integral into two parts, one applicable to temperatures below the ordinary and the other to higher temperatures. Moreover, since the chemical constant i is calculated from the vapour-pressure curves of the components, various corrections are necessary to allow for deviations from the gas laws.

These complications may be avoided by calculating the free energy of a chemical process from the heat of reaction at 298° Abs., the entropy at 298° of the components in the physical state which they assume in the equilibrium in question, and the specific heats from 298° to the temperature considered. For a number of equilibria the results are given of calculations of ΔS_{298}. In the majority of cases the values obtained are in good agreement with those of ΣS_{298}, the few discordant results being explainable by uncertainty in the data available. T. H. POPE.

Absolute zero of the externally controllable entropy and internal energy of a substance and a mixture. R. D. KLEEMAN (Phil. Mag., 1927, [vii], **3**, 883—895, and J. Physical Chem., 1927, **31**, 747—756).—Nernst's third law of thermodynamics is shown to be only a case of a much more general result which can be deduced from results of an axiomatic character. The internal energy and the entropy of a substance or mixture can be divided into two parts, one a function of the temperature and volume only, the other independent of these quantities. Thus, the one part is externally controllable, whilst the other part is not. Following this, the specific heat at constant volume of a substance or mixture is shown to have only positive values. The coefficients $(\partial p/\partial T)_v$ and $(\partial^2 p/\partial T^2)_v$ cannot have infinite values. Using these results, it is shown that the controllable internal energy is zero when the matter is in the solid state under the pressure of its own vapour at the absolute zero. A similar result is obtained with regard to entropy. It is further shown that the specific heat of a gas at constant infinite volume is zero at the absolute zero of temperature. W. E. DOWNEY.

Analogies to the gas laws in the solid state of matter. (Electron gas laws.) G. BECK (Z. anorg. Chem., 1927, **161**, 76—84).—From the equation previously derived for the contraction in reactions between solids (A., 1926, 1211), there is deduced as the equation of state for solids the expression $kpV/M=RT$, where V is the molecular volume, p the density, M the atomic or mol. wt., R the gas constant, and T the "atomic temperature." Values of the internal pressure, P, calculated by putting $P=p/M$ in this equation agree satisfactorily with those calculated from compressibility data for a number of salts, but are much higher than Richards' calculated values (A., 1924, ii, 723). The contraction equation may also be applied to the isobaric thermal expansion of elements and compounds. The values of k so obtained are of the same order as those for chemical contraction, indicating that the forces involved in both these kinds of volume change are essentially the same. According as the exchange of electrons in the formation of a salt molecule involves an energy change or not, the heat of formation is greater than or equal to the heat effect of the physical dilatation of the compound. The equation of state for solids will fail for excessive pressures in the same way as does the gas equation. From the relations deduced, matter in the solid state is seen to have both physically and chemically the properties of a nearly ideal electron gas. The laws which are applicable have a wider range of validity than have the gas laws, presumably because the co-volume of the electrons relative to the corresponding volume of the solid is much less than the co-volume of the gas molecules relative to the total volume of the gas. Probably owing to the influence of secondary factors, the relation between the number of electrons per unit volume and the corresponding internal pressure is more complicated than Avogadro's law. The maximum value of the ratio of the volume of the reactants to that of the resultants in a reaction between solids may be shown from the contraction equation to be e. R. CUTHILL.

Surface energy and heat of dissolution of solid sodium chloride. I. S. G. LIPSETT, F. M. G. JOHNSON, and O. MAASS (J. Amer. Chem. Soc., 1927, **49**, 925—943).—An adiabatic calorimeter is described in which the temperature is measured by a "thermal"—a multiple thermo-element which measures temperatures by radiation. With its aid the heats of solution of coarse and fine sodium chloride crystals were determined at 25°, the former over a concentration range of 0·4—24·3% (a maximum occurring at 1%) and the latter at a concentration of 5·67%. Water vapour converts fine salt crystals into coarse crystals by the process of

dissolution and recrystallisation; the accompanying heat effect is measured directly in a special calorimeter. The difference in the heats of dissolution of the two types of salt, corrected for the water-vapour effect, is 12·3 g.-cal., from which the surface energy of solid sodium chloride is calculated to be 400 ergs/cm.^{2} at 25°. S. K. TWEEDY.

Heat of formation of copper hydride. A. SIEVERTS and A. GOTTA (Annalen, 1927, **453**, 289—297).—By subtracting the heat evolved when copper hydride is dissolved in cupric chloride solution acidified with hydrochloric acid, according to the equation $CuH+[aCuCl_2+bHCl+cH_2O]=2CuCl+0{\cdot}5H_2+[(a-1)CuCl_2+bHCl+cH_2O]$, from the heat effect when copper is dissolved in the same solvent by the reaction $Cu+[aCuCl_2+bHCl+cH_2O]=2CuCl+[(a-1)CuCl_2+bHCl+cH_2O]$, the heat of formation of moist copper hydride from gaseous hydrogen and precipitated copper is found to be −5120 cal./g.-mol. R. CUTHILL.

Salicylic acid as a calorimetric standard. E. COHEN, P. E. VERKADE, S. MIYAKE, J. COOPS, jun., and J. A. VAN DER HOEVE (Z. physikal. Chem., 1927, **126**, 290—296).—See A., 1926, 1103.

Temperature effects of mixing liquids. W. M. MADGIN and H. V. A. BRISCOE (J.S.C.I., 1927, **46**, 107—109T).—The rise in temperature observed on mixing equal volumes of two liquids has been determined, under adiabatic conditions, for 37 common non-aqueous liquids taken together in pairs. Of the 628 pairs thus examined, 416 give a negative heat of mixing and the remainder positive, but there is a tendency for the positive effect to be greater than the negative. M. S. BURR.

Electrical conductivities of solutions in aniline. J. R. POUND (J. Physical Chem., 1927, **31**, 547—563).—Conductivity data at 30° are given for solutions of acetic, phenylacetic, phthalic, salicylic, and benzoic acids, of acetic and phthalic anhydrides, of aniline hydrochloride, and of saccharin, as well as of aniline in acetic acid. Many substances have been investigated qualitatively. The solutions in aniline are relatively poor conductors, behaving generally as typical, non-aqueous electrolytic solutions. The molecular conductivity increases with the concentration. Specific conductance and concentration could not be connected by a simple equation. At low concentrations, certain solutions behave like aqueous solutions. The stronger acids with aniline give solutions the conductivity of which increases with time, an effect which is attributed to the formation of aniline and water from the aniline salt initially produced. L. S. THEOBALD.

Electrical conductivity of salt solutions containing agar-agar. E. IWASE (Bull. Chem. Soc. Japan, 1927, **2**, 61—65).—The conductivity of agar-agar sols containing copper sulphate, sodium chloride, or potassium sulphate, chloride, iodide, or thiocyanate increases slightly when gelatinisation occurs (cf. Hatschek and Humphry, A., 1925, ii, 34). In e case of salt-free agar-agar sols, the conductivity may either increase or decrease on gelatinisation. R. CUTHILL.

Conductivity and velocity measurements in *n*-propyl alcohol. H. GOLDSCHMIDT and L. THOMAS (Z. physikal. Chem., 1927, **126**, 24—40).—A continuation of earlier work (Goldschmidt and Mathiesen, A., 1926, 686) on solutions of the hydrogen halides in various alcohols. The conductivity data are similar to those previously recorded; *i.e.*, addition of water causes a rapid diminution, followed by an increase, whilst the conductivities of the halogen hydrides increase in the order hydrogen chloride, bromide, iodide. The conductivity of piperidine hydrochloride is small compared with that of hydrogen chloride. The anticatalytic effect of the water produced during esterification may be allowed for in the manner previously described, the constant involved being independent of the nature of the organic acid. The velocity of esterification is not proportional to the concentration of the halogen acid. In the anhydrous alcohol the addition of aniline or piperidine hydrochlorides slightly decreases the rate of esterification, but in presence of water an increase is observed. G. A. ELLIOTT.

Coefficient of ionisation of a fused salt. T. M. LOWRY (Nature, 1927, **119**, 564).—Formal values of $\alpha=\Lambda/\Lambda_\infty$ for silver chloride are computed as 1·74 and 2·35; the anomalous result is attributed to the presence of multiply-charged ionic aggregates resembling the "ionic micelle" of a colloidal electrolyte. A. A. ELDRIDGE.

Ion transference in bromine solutions of phosphorus pentabromide. W. FINKELSTEIN (Z. physikal. Chem., 1927, **125**, 229—235).—When solutions of phosphorus pentabromide in bromine are electrolysed, phosphorus moves towards the cathode. This is in accordance with the previously outlined theory of the process of ionisation obtaining in such solutions (A., 1923, ii, 534) and with the amphoteric nature of phosphorus. L. F. GILBERT.

Water transference in solutions of organic electrolytes. H. REMY and H. REISENER (Z. physikal. Chem., 1927, **126**, 161—171).—The electrolytic transference of water in normal solutions of organic bases has been determined by the diaphragm method previously employed for the inorganic halides. The results of Lorenz and Hevesy's rule connecting the charge with the radius require that salts with organic cations should exhibit smaller water transference than salts with inorganic cations of the same valency. The measurements confirm these views. The water transference in the solutions investigated has always a negative value, whereas in solutions of univalent metals of the same concentration positive values are always obtained. H. F. GILLBE.

Constitution of solid electrolytes. II. Cuprous chloride. J. N. FRERS (Ber., 1927, **60**, [*B*], 864—889; cf. A., 1924, ii, 827).—Observations on cuprous chloride, compressed or in the presence of a protective electrolyte, such as silver chloride, bromide, and iodide (cf. Tubandt, A., 1920, ii, 279; 1921, ii, 480), show that it is a true, mixed conductor in which only the cuprous ion is mobile. Below 170°, the conductivity is purely metallic, whereas at 200° electrolytic conductivity is observed to an extent of 2—10%. The proportion of current concerned with metallic

and electrolytic conduction is influenced by surface action, discharge of silver ions on cuprous chloride, discharge of lead ions, temperature, and duration of electrolysis. The mechanism of metallic conductivity is explained by the hypothesis that the conductivity electrons are united in metals to the metallic atoms, and in metallic-conducting salts only to one type of ion, so that a functional differentiation exists among the ions in the lattice. One type of ion is not concerned with the conduction of electricity, whereas the other type provides both electronic and ionic transport. The former type is firmly fixed in the lattice, whereas the latter type is mobile. The different temperature coefficient of the metals and the metallic-conducting salts is ascribed to the functional differentiation of the ions in the lattice, by which, also, the rectifying action of crystal detectors is explained. The observations afford an explanation of Baedeker's experiments with cuprous iodide (cf. A., 1908, ii, 654). H. WREN.

Potential of aluminium in aqueous solutions. L. KAHLENBERG and S. J. FRENCH (Trans. Amer. Electrochem. Soc., 1927, **51**, 491—496).—The potential of pure aluminium (99·97% Al) against the *N*-calomel electrode in a *N*-solution of potassium chloride is about 0·840 volt in air and 0·800 volt in oxygen. Displacement of the air in the electrolyte by boiling or replacement by nitrogen, hydrogen, coal gas, or carbon dioxide causes an increase in the potential to more than 1 volt. Commercial aluminium behaves in a similar manner, but its potential is always lower than that of the pure metal. These results prove that the low potential of aluminium is not due to the presence of a film of aluminium oxide on the surface of the metal, and indicate that a more probable explanation is the presence of a film of adsorbed oxygen, *i.e.*, the potential measured is that of the aluminium–oxygen electrode. Amalgamation of aluminium raises its potential to 1·73—1·79 volts, and this value is unaffected by the presence or absence of any of the above-mentioned gases. The increase is due to the action of the mercury in increasing the rate of the chemical reaction between the aluminium and the water, a reaction which takes place very slowly when both reactants are pure. A. R. POWELL.

Reduction potentials of quinones. III. Free energy of reduction referred to the gaseous state. J. B. CONANT (J. Amer. Chem. Soc., 1927, **49**, 293—297).—For benzoquinone, four chloro-derivatives, and xyloquinone the free energy of reduction (referred to the gaseous state) has been calculated from the reduction potentials (referred to the solid state) (A., 1923, ii, 839) and the vapour pressures of these substances (Coolidge, this vol., 195). The replacement of hydrogen by chlorine raises this quantity progressively and regularly, whilst substitution of two alkyl groups lowers it. The free energy referred to the gaseous state is said to be a correct measure of the affinity of quinones for hydrogen, whereas in solution and in the solid state the potentials are complicated by the affinities of the quinone and quinol molecules for each other. R. K. CANNAN.

Solutions in high-tension electric fields. Z. STARY (Z. physikal. Chem., 1927, **126**, 173—195).—The electro-osmosis of water and of a number of solutions has been measured with a view to determine whether errors in electro-endosmosis measurements may be ascribed to this cause. Two strips of blotting paper, held in metal clips and partly immersed in the solution, form the electrodes; when a high *P.D.* is maintained across the electrodes, the solution rises in the capillaries of the paper to a greater extent at one electrode than at the other, giving a qualitative measure of the extent of the osmosis. In all cases studied the quantity of liquid transported per minute from one electrode to the other by electro-osmosis falls to zero within a few minutes.

Experiments with hydrochloric acid solutions at concentrations between $N/2$ and $N/256$, and with 500—920 volts *P.D.*, show that cellulose receives a negative charge when in contact with the solution, and although it is possible to reduce this charge by depositing an electropositive precipitate such as barium sulphate in the pores of the paper, strips of silk form more convenient electrodes.

By measuring the electro-endosmotic rise of 5% methylene-blue in 0·1*N*-hydrochloric acid and potassium hydroxide solutions, it is found that the error due to electro-osmosis is negligible, and need be considered only when readings are taken before a steady value has been obtained. The error increases with increasing concentration, but may be neglected at the concentrations usually employed for electro-endosmotic measurements. The results of Gicklhorn, Fürth, and Blüh (A., 1926, 1092) for the transference of ions in high-potential fields are confirmed by measurements with ammonium iodide solutions. The apparent reversal of the direction of transference after some minutes is explained. Since in general the current through the solution increases with time, owing to heating and evaporation, the electrolytic ion transference increases, whereas the electro-osmotic effect falls rapidly to zero. The time required for this reversal must depend on the concentration, and a series of experiments with potassium permanganate and sodium chloride shows that this is the case. Since Gicklhorn, Fürth, and Blüh employed 5—20% sodium chloride solutions, and less than 0·1% potassium permanganate solutions, their anomalous results are explicable.

In order to eliminate errors due to electro-osmosis from electro-endosmosis measurements, readings should not be taken until some minutes have elapsed from the time of applying the electric field, and the concentrations of the solutions employed should not be greater than 0·1*M*. H. F. GILLBE.

Irreversible reduction of organic compounds. IV. Apparent reduction potentials of unsaturated carbonyl compounds. J. B. CONANT and R. E. LUTZ (J. Amer. Chem. Soc., 1927, **49**, 1083—1091; cf. A., 1926, 1134).—The oxidation–reduction potentials of a series of benzoquinone–quinol and dye–leuco-form systems were measured against a quinhydrone electrode in aqueous 75% acetone in presence of 0·2*M*-hydrochloric acid. The values obtained were then applied, by a method analogous to that previously described, to the determination of the "apparent reduction potential" of a series of unsaturated 1 : 4-

diketones and related substances in the same solvent. Assuming that the reduction of the grouping ·CO·C:C·CO· by soluble reducing agents takes place by the addition of a hydrogen atom at each end of the group (cf. Conant and Lutz, A., 1923, ii, 285), the process will be completely reversible when the resulting di-enol is stable, but is followed by an irreversible change if the di-enol isomerises to a saturated diketone. In the dibenzoylethylene group, the apparent reduction potential is lowered by *ortho*-substitution in the aromatic nuclei, and by replacement of α-hydrogen atoms by a variety of substituents, whilst *para*-substitution by methyl or chlorine is without effect. It is suggested that the changes are due, in the first case, to decreases in the rate of ketonisation of the enols brought about by the steric hindrance of *ortho*-substituents, but that in the latter case the potential of the reversible reduction is also affected.

*αγ-Dibromo-αγ-dibenzoyl-*n*-propane*, m. p. 115—115·5°, is obtained, together with an *isomeride*, m. p. 89°, by bromination of *αγ*-dibenzoylpropane in chloroform. When warmed with zinc dust and sodium iodide in acetone, the former yields 1 : 2-*dibenzoylcyclopropane*, m. p. 103—104°, which is reduced to dibenzoylpropane by zinc dust and boiling glacial acetic acid, but not by chromous chloride. *αδ-Dibromo-αδ-dibenzoyl-*n*-butane*, m. p. 171°, and an *isomeride*, m. p. 96°, are obtained analogously, and the former is converted as above into 1 : 2-*dibenzoylcyclobutane*, m. p. 163°. The latter is not reduced by zinc dust and acetic acid, nor by chromous chloride.

F. G. Willson.

Pyrochemical Daniell and equilibrium cells. R. Lorenz and F. Oppenheimer (Z. anorg. Chem., 1927, **161**, 183—200).—The *E.M.F.* at temperatures between 500° and 750° of Daniell cells of the type $M'|M'Cl_2|M''Cl_2|M''$ and of so-called "equilibrium" cells of the type $\begin{matrix}M'\\M''\end{matrix}\left|\begin{matrix}M'Cl_2\\M''Cl_2\end{matrix}\right|M'Cl_2|M'$ have been measured and compared with the theoretical values obtained from the equation of Lorenz and van Laar (A., 1926, 355) using the equilibria data of Lorenz and Mannheimer (A., 1926, 355, 680). The experiments were carried out in two quartz tubes connected through a quartz capillary tube, to prevent diffusion of the molten salts or salt mixtures. The *E.M.F.* of the Daniell cell $Pb|PbCl_2|CdCl_2|Cd$ at 700° is 0·1302± 0·004 volt, which is approximately equal to the sum of the *E.M.F.* of the cells $\begin{matrix}Pb\\Cd\end{matrix}\left|\begin{matrix}PbCl_2\\CdCl_2\end{matrix}\right|PbCl_2|Pb$ and $\begin{matrix}Pb\\Cd\end{matrix}\left|\begin{matrix}PbCl_2\\CdCl_2\end{matrix}\right|CdCl_2|Cd$. The *E.M.F.* of the cells $Sn|SnCl_2|PbCl_2|Pb$, $Sn|SnCl_2|CdCl_2|Cd$, and $Tl|Tl_2Cl_2|CdCl_2|Cd$ at 500—700° are, respectively, 0·031± 0·003, 0·143±0·007, 0·294±0·005 volt. In most cases the experimental results are higher than the theoretical, and this is attributed to slight errors in the thermochemical data used.

A. R. Powell.

***E.M.F.* of flames.** A. Sisojev (Ukraine Chem. , 1926, **2**, 158—162).—By allowing a flame to impinge on a piece of platinum foil after passing o r a piece platinum wire, consistent values are obtained for the *P.D.* Flames containing salts of e alkali and alkaline-earth metals have been examined under various conditions. If the platinum foil is cooled, the *P.D.* between the wire and the foil is raised, and reaches a maximum of 1·1 volts in the case of potassium carbonate. The platinum electrodes are not attacked, and maintain a constant weight. The *P.D.* increases with the area of the foil, but diminishes with increase in the diameter of the wire. The author discusses the origin of the *P.D.*, and reaches the conclusion that it is due to the production of electrons. The effect cannot be due to the condensation of the salt vapour, nor to the difference in the temperature of the two electrodes, since when these are covered with a paste of lime, or other alkaline earth, the difference of potential between them is decreased.

E. Rothstein.

Electrolysis without electrodes. O. M. Corbino (Atti R. Accad. Lincei, 1927, [vi], **5**, 377—379).—When copper sulphate solution is electrolysed using a copper anode immersed in the solution, and an aluminium cathode suspended above the solution in an atmosphere due only to the vapour pressure of the solution, finely divided copper appears in the solution as a suspension. The size of particle increases with the current. Similar results were obtained with solutions of silver nitrate and gold chloride.

R. W. Lunt.

Short-circuited cell for electro-organic reductions. C. J. Brockman (Trans. Amer. Electrochem. Soc., 1927, **51**, 383—385).—For small-scale experiments the substance to be reduced is added to a solution of sulphuric acid or sodium hydroxide contained in a porous pot which stands in a beaker of dilute sulphuric acid, at the bottom of which is an anode of zinc amalgam. On connecting this anode directly to a cathode of a relatively noble metal dipping into the solution in the porous pot, electrolytic reduction proceeds. By varying the nature of the cathode material, the area of the exposed surfaces of anode and cathode and the concentrations of the anolyte and catholyte, a wide range of reducing conditions can be realised. Examples of the application of the method are given.

H. J. T. Ellingham.

Velocity of chemical reactions. I. K. Syrkin (J. Russ. Phys. Chem. Soc., 1926, **58**, 1101—1128).—Mathematical. A critical examination of all the recent expressions for the velocity constants of homogeneous gas reactions. A modification of Kruger's formula is deduced for the velocity constant of a homogeneous gas reaction of the *n*th order: $k_n=(\sqrt{(0,(8)\pi kT\sigma^{n-1}/n_1!n_2!r)N_0{}^{n-1}}\times \sqrt{[(n_1/m_1)+(n_2/m_2)]/(n_1+n_2\dots)}e^{-q/kT}$, where $n_1, n_2\dots$ are the numbers of colliding molecules of mass m_1, m_2, etc., N_0 is Avogadro's number, and α is the sphere of action in which an effective collision takes place. For a homogeneous unimolecular reaction, $\sigma=4/3\cdot S^3$ is the sphere of action inside the molecule of the atoms of mass m_1, m_2 which constitute it and into which it decomposes. The unimolecular expression is: $K_1=(2\sqrt{-kT/3s})\sqrt{(m_1+m_2)/m_1m_2}e^{-q/kT}$.

By assuming that s is the distance between the centres of gravity of the rotating vibrating atoms m_1, m_2, ν, the resulting radiation (infra-red) is given by the expression $K_1=(4\pi/3)\sqrt{(\pi kT\nu)/nhe^{q/kT}}$. The value of this for the decomposition of nitrogen pent-

oxide is close to the experimental. The problem of activation is discussed, and the latest developments of the black body radiation theory are examined and criticised.

An expression similar to the above is deduced for bimolecular reactions, and shown to give values in agreement with experiment on the assumption that airs of molecules on collision are further activated y the impact of light quanta. In termolecular reactions, the dependence of the velocity constant on the duration of the collisions is emphasised, and the case of rapid reactions considered, where the ordinary kinetic treatment does not apply.

Bimolecular reactions which require a collision with a third molecule for activation are also mentioned.

M. Zvegintzov.

Supposed law of flame speeds. A. G. White (Nature, 1927, **119**, 674; cf. this vol., 115, 211).—Experiments with carbon disulphide–second combustible substance–air mixtures yield results at variance with the supposed law of flame speeds.

A. A. Eldridge.

Law of flame speeds. W. Payman and R. V. Wheeler (Nature, 1927, **119**, 747; cf. this vol., 317).

Gaseous explosions. IV. Rate of rise of pressure, velocity of flame travel, and the detonation wave. G. G. Brown and G. B. Watkins.—See B., 1927, 322.

Propagation of detonation across an air-gap between two cartridges of explosive. G. St. J. Perrott and D. B. Gawthrop.—See B., 1927, 350.

Burning of carbon disulphide near the limit for the propagation of flame, with remarks on the ignition point of sulphur. A. G. White (J.C.S., 1927, 793—802).—In the contraction of the propagation range through the addition of certain vapours to carbon disulphide–air mixtures, the added substance may act in three ways: (1) alteration of the thermal constants of the mixture, (2) alteration of the percentage of oxygen in the mixture, (3) introduction of a catalytic effect. Effect (1) appears with all combustibles, but (2) is not common unless the mixture is deficient in oxygen: it is exhibited to a marked extent with carbon disulphide and hydrogen sulphide, but does not appear to be connected very directly with (3). The catalytic effect is most marked with combustibles, and appears to be connected with the ease of oxidation of the added substance. When a certain minimum of a second combustible is added, carbon disulphide generally behaves as a normal combustible having a lower limit of about 4%. The normal combustion of carbon disulphide at the limit is probably catalysed, but this catalysis is inhibited by a large variety of substances. Carbon monosulphide, suggested by Dixon (A., 1925, ii, 683) as the catalyst, is not likely to be the sole catalytic agent, as sulphur shows a similar effect at its ignition point. The order of substances arranged according to their activity in raising the lower limit of carbon disulphide is not that found by Dixon for raising the ignition temperature of carbon disulphide, nor that found by Delepine (A., 1922, i, 914) for preventing the autoxidation of certain organic substances.

E. S. Hedges.

Velocity of formation of nuclei in supersaturated vapours. L. Farkas (Z. physikal. Chem., 1927, **125**, 236—242).—Kinetic considerations support the views of Volmer and Weber (A., 1926, 676).

L. F. Gilbert.

Hydrogen ions as a factor in lowering the order of a reaction. (Mlle.) M. Rosenberg (Ukraine Chem. J., 1926, **2**, 88—108).—The subject has already been studied for ferricyanide and iodide, and the permanganates and oxalates of both tin and iron (cf. *ibid.*, 1925, **1**, 19). The reaction $MnO_4' + 5C_2O_4'' + 16H^{\cdot}$ was also investigated. In order to study the mechanism of oxidation, the action of the permanganate ion on the halogen ions has been examined. The reaction with chlorine was too slow, and that with iodine too fast to yield any conclusive results, and therefore bromine ions were used. The reaction investigated was: $MnO_4' + 5Br' + 8H^{\cdot} \longrightarrow Mn'' + 5Br + 4H_2O$. The reaction was carried out in concentrations of hydrogen ions varying from $0{\cdot}3N$ to $1{\cdot}5N$. The order of the reactions was measured by means of the deflexions of a galvanometer, connected to the solutions by means of two platinum electrodes, in a manner similar to that previously used (*loc. cit.*). As the concentration of the hydrogen ions increases, the reaction tends to become unimolecular. Thus when $C_H = 1{\cdot}2—1{\cdot}5N$, the reaction is always of the first order. When $C_H — 0{\cdot}5N$, it is, in the main, of the second order. When $C_H = 0{\cdot}3N$, the reaction is of the second order for the first 2 min., and afterwards of the first order. The author discusses the mechanism whereby these results are obtained.

E. Rothstein.

Chemical kinetics in mixtures of solvents. III. G. Muchine, R. Ginsburg, and C. Moisseieva (Ukraine Chem. J., 1926, **2**, 136—152).—The velocity coefficients $K(\times 10^3)$ for the reaction of pyridine, and triethylamine with benzyl bromide in various solvents are: at 29°, ethyl alcohol, 17·0, 39·0; nitrobenzene, 32·3, 171·0; benzene, 0·73, 3·70; at 45°, 56·7, 127·5; 65·5, 369·3; 2·26, 9·2, respectively.

When the reactions were carried out in various mixtures of alcohol and benzene, a convex curve was obtained by plotting K against the concentration; K was larger, and seemed to be almost additive. In mixtures of nitrobenzene and benzene, the curve was concave, but there was still an increase in the value of K. With pyridine at 45°, the curve was S-shaped.

The form of the curve for the alcohol–benzene mixtures is stated to be due to the formation of associated alcohol molecules, the amount of association varying with the concentration and the temperature. In the case of the nitrobenzene, reaction between the latter and the pyridine is supposed to have taken place.

E. Rothstein.

Velocity of formation of quaternary ammonium salts from trimethylamine and benzyl chloride and the three mononitrobenzyl chlorides. H. McCombie, H. A. Scarborough, and F. F. P. Smith (J.C.S., 1927, 802—810).—The velocity coefficients for the formation of quaternary ammonium salts from benzyl chloride and the three mononitrobenzyl chlorides are comparable with those obtained for the interaction of the

same aryl chlorides with sodium thiosulphate and with potassium iodide, and differ from those obtained with alkaline hydrolysing agents. The relative effects of a series of solvents are considered, and the authors suggest that in the case of a reaction taking place in solution, the solvent itself activates the reacting molecules by means of its external field. Thus, the activating power of a solvent should be increased by the presence of an ethylenic linking, or nitrogen, oxygen, or halogen atoms, and this is found to be the case. The polarising action of the solvent is not its only effect, however. The solubilities of the three mononitrobenzyl chlorides were measured in a series of solvents, and there appears to be no constant relationship between the velocity coefficient and the solubility. E. S. HEDGES.

Kinetics of reaction in the presence of strong acids. A. HANTZSCH and A. WEISSBERGER (Z. physikal. Chem., 1927, **125**, 251—263).—The velocity of inversion of sucrose in moderately concentrated acid solutions increases not only with increase of acid concentration, but also with increase of sugar concentration. The latter effect is opposed to accepted ideas concerning catalytic reactions.

By plotting the equivalent activity of each of the acids against its concentration, it is found that the equivalent activities of all the acids tend to the same limiting value at low concentrations. By dividing the activity of each acid at a number of concentrations by this limiting value, a series of figures is obtained which for hydrochloric, hydrobromic, nitric, benzenesulphonic, and perchloric acids increases with increasing concentration, and for formic, acetic, and dichloroacetic acids decreases with increasing concentration. The former group are therefore classed as strong, and the latter as weak acids.

These observations may be explained quantitatively by assuming that towards the acids investigated water behaves as a weak base, not by the formation of simple hydroxonium salts, but of complex salts containing several molecules of water. If to such a solution be added another substance which is capable of combining with water, its ability to do so will be reduced with increase of the stability of the complex hydroxonium salt. The strong acids (in the above sense) form these complexes with ease, but the complex is easily ionised, and the acid is therefore catalytically active. The complexes formed by the weak acids are, however, of the nature of esters, and are catalytically inactive. In behaviour they are identical with the undissociated molecules of the classical ionisation theory, and they are therefore termed pseudo-acids.

These views are supported by measurements of the velocity of decomposition of ethyl diazoacetate in water and in a number of organic solvents, in the presence of hydrochloric and hydrobromic acids at various concentrations. H. F. GILLBE.

Monoalkyl carbonates. III. Kinetics of the decomposition of monoalkyl carbonates and of r formation from hydrogen carbonate in alkaline aqueous solution. C. FAURHOLT (Z. physikal. Chem., 1927, **126**, 211—226).—Determination of the rate of hydrolysis of sodium methyl carbonate at 0° in the presence of 0—4·0*M*-methyl alcohol and at various concentrations of hydrogen ion show that the velocity is independent of p_H, but diminishes rapidly with increasing alcohol concentration. It is postulated, therefore, that the reaction takes place in two stages, the first corresponding with the decomposition of the monomethyl carbonate into methyl alcohol and carbon dioxide, and the second the formation of carbonate. Since the velocities of these two reactions are known, the velocity of the hydrolysis may be calculated; the value obtained agrees well with the observed velocity over a wide range of acid and alcohol concentrations. The same reactions, in the reverse order, take place when monomethylcarbonate is formed from hydrogen carbonate. Skrabal's work on the hydrolysis of dimethyl carbonate is criticised. H. F. GILLBE.

Clerget-invertase hydrolysis constants of sucrose and raffinose. H. S. PAINE and R. T. BALCH (J. Amer. Chem. Soc., 1927, **49**, 1019—1028).—The Clerget-invertase hydrolysis constant for sucrose is given by the expression $131{\cdot}17+0{\cdot}073c$, where c is the number of grams of sucrose in 100 c.c. The ratio of the polarisation of raffinose after invertase hydrolysis to the original polarisation is 0·521, this value being constant over a wide range of concentrations. These constants can be applied to the determination of sucrose and of mixtures of sucrose and raffinose (cf. Paine and Balch, B., 1925, 417).
F. G. WILLSON.

Effect of foreign substances on hydrolysis of ethyl acetate under the influence of hydrogen chloride. C. D. PANA (Ann. sci. Univ. Jassy, 1927, **14**, 315—352).—The influence of varying amounts of arabinose, dextrose, galactose, lævulose, mannose, lactose, methyl alcohol, ethyl alcohol, *iso*propyl alcohol, acetone, antipyrine, and pyramidone on the rate of hydrolysis of ethyl acetate in *N*-hydrochloric acid solution at 25° has been studied. In general, the velocity coefficient, K, increases with increase in the mol. wt. of the added substance. If the effect of the foreign substance is to increase the viscosity of the reaction mixture, K is lowered, and *vice versa*. When the added substance is insoluble in ethyl acetate, the viscosity of the mixture increases with the concentration of the foreign substance, whilst if it is soluble, the reverse is true. In general, K is greater when the foreign substance is insoluble in ethyl acetate than when it is soluble. From f.-p. measurements, it appears that the f.-p. depression of a solution of one of the foreign substances in the pure hydrogen chloride solution exceeds the sum of the depressions which would be produced by each substance if present in solution alone by an amount which decreases with increase in the mutual solubility of the two solutes, and may become negative. At a high dilution, the molecular conductance of solutions of hydrochloric acid containing one of the above non-electrolytes is inversely proportional to the viscosity. In some more concentrated solutions, it increases with increase in the acid concentration. R. CUTHILL.

Effect of alkali on oxidation of sodium sulphite with air. S. MIYAMOTO (Bull. Chem. Soc. Japan, 1927, **2**, 74—78).—The rate of oxidation of a solution of sodium sulphite at 20° when air is passed through

it increases with the rate of passage of the air, but is independent of the salt concentration, possibly because the rate of dissolution of oxygen is slower than that of the oxidation. Addition of sodium hydroxide retards the oxidation, perhaps by reducing the rate of dissolution of oxygen. Raising the temperature to 30° or 40° has little effect. R. CUTHILL.

Dependence of velocity of hydrolysis of esters on constitution. H. OLSSON (Z. physikal. Chem., 1927, **125**, 243—250).—The velocity coefficients of the hydrolysis, by sodium hydroxide, of *iso*amyl acetate, diethylcarbinyl acetate, dimethylethylcarbinyl acetate, methyldiethylcarbinyl acetate, dimethyl-*n*-propylcarbinyl acetate, allyl acetate, allylcarbinyl acetate, and dimethylallylcarbinyl acetate in aqueous solution, and of benzyl acetate, ethyl benzoate, ethyl phenylacetate, and ethyl hydratropate in equimolecular mixtures of alcohol and water have been determined at 20°. Complication of the alkyl radical, in contradistinction to simple lengthening of the carbon chain (cf. A., 1926, 33), has a marked influence on the rate of hydrolysis. With unsaturated and phenyl-substituted esters there is no parallelism between rate of ester formation and rate of hydrolysis (cf. *ibid.*). L. F. GILBERT.

Instability and explosiveness of bleaching powder and calcium hypochlorite. H. KAST and L. METZ.—See B., 1927, 297.

Dissolution of lead by water. A. FARINE.—See B., 1927, 318.

Second experimental report to the Atmospheric Corrosion Research Committee (British Non-Ferrous Metals Research Association). W. H. J. VERNON.—See B., 1927, 301.

Rate of reduction of metallic oxides by gases. P. H. EMMETT (Trans. Amer. Electrochem. Soc., 1927, **51**, 259—264).—Factors determining the rate of reduction of metallic oxides by a reducing gas include: (1) the chemical nature of the oxide; it is suggested that cases in which the reduction is autocatalytic are those in which the oxide does not form solid solutions with the corresponding metal at the given temperature; (2) the method and temperature of preparation of the oxide; (3) whether the oxide is in the massive form or spread in thin layers over the surface of some supporting substance; (4) whether substances which increase or reduce the catalytic activity of the reduced metal are present in the oxide. H. J. T. ELLINGHAM.

Rate of decomposition of calcium carbonate hexahydrate. J. HUME and B. TOPLEY (Proc. Leeds Phil. Lit. Soc., Sci. Sec., 1927, **1**, 169—176).—The rate of decomposition of calcium carbonate hexahydrate to the anhydrous salt and water has been followed dilatometrically. The curve obtained by plotting "fraction decomposed" against time has a sigmoid form, the rate of change being a maximum at about 50% decomposition. Although the general form of the curve is unaltered, the rate of decomposition at all stages is reduced to a greater or less extent by the presence of small quantities of foreign substances in solid solution in the hexahydrate (cf. Kohlschütter and Egg, A., 1925, ii, 1036). The stabilising effect of different substances is very specific, and for the same adsorbed substance the retardation increases with the amount adsorbed. The form of the curve is in accordance with Langmuir's view (A., 1917, ii, 19) that in kinetic equilibria of the type Solid 1 Solid 2 + Gas the reaction occurs only at the interface between the two solids. The presence of adsorbed substances may affect the potential energy of the space-lattice, and hence may cause an increase in the energy required for the activation of molecules in the interface. M. S. BURR.

Saponification of cellulose acetate. G. KITA, I. SAKURADA, and T. NAKASHIMA (J. Cellulose Inst. Tokyo, 1927, **3**, 61—71).—Saponification with aqueous sodium hydroxide solution takes place up to 50% for solutions at rest, and up to 90% with shaking, according to the equation $dt/dx = K(a-x)$, the velocity of saponification under the former conditions diminishing suddenly when the reaction is half completed. Assuming that the heterogeneous saponification proceeds according to the equation $dt/dx = Ks(a-x)$, where s is the surface of contact of the ester with the sodium hydroxide, then s must be constant. This confirms the results of Haller and Ruperti (Leipz. Mon. Text., 1925, **40**, 353, 399). With alcoholic potassium hydroxide solution the reaction without shaking proceeds quickly at first and then slows down, no equation being yet established, whilst with shaking, if the alcohol content of the alkali solution is fairly high, the following equation is satisfied: $dx/dt = K(a-x)(b-x)$, a and b being the original concentrations of alkali and ester, and x the amount converted in time t. This equation is equally applicable to the saponification of the higher fatty acid esters. For reactions carried out at rest with alcoholic potassium hydroxide it is shown that higher concentrations of alcohol favour the swelling of the ester and increase the surface of contact, but retard the diffusion of the saponification product, sodium acetate. The authors suggest the possibility of comparing the qualities of cellulose acetate by means of the saponification velocity, as samples of different origin give different values under the same conditions. B. P. RIDGE.

Kinetics of the catalytic dehydrogenation of decahydronaphthalene. N. D. ZELINSKI and A. A. BALANDIN (Z. physikal. Chem., 1927, **126**, 267—289).—When decahydronaphthalene is passed over finely-divided platinum at a moderately high temperature it is decomposed, with the production of naphthalene and hydrogen. The reaction has been studied at 200—350° by maintaining the catalyst at a constant temperature in an electric oven and measuring the rate of evolution of hydrogen. The dehydrogenation is nearly complete at 333°, but at lower temperatures the catalyst is less active, probably owing to retention of naphthalene. By passing hydrogen over the catalyst, impregnated with naphthalene, at 160°, complete reduction occurs.

The catalyst employed is prepared by depositing finely-divided platinum upon active charcoal, and is much more active than platinised asbestos.

The course of the reaction at various temperatures agrees closely with the Arrhenius equation

$k=k_0e^{-Q/RT}$ up to 270°; above this temperature, partial poisoning of the catalyst by reaction products occurs. Greater or less activity on the part of the catalyst influences the coefficient k_0, but not the activation energy Q. This has been confirmed by studying the systems *cyclo*hexane–platinum, *cyclo*hexane–palladium, *cyclo*hexane–nickel, piperidine–platinum, and piperidine–palladium, and by comparing the values of k_0 it is inferred that for the same substrate the activation energy Q depends solely on the chemical nature of the catalyst. When different substrates are employed, Q is constant for each catalyst, viz., for platinum 18,725, for palladium 15,780, and for nickel 9850 g.-cals./g.mol. For the dehydrogenation of decahydronaphthalene with nickel as catalyst, a very similar value is found for Q, although in this case interference is caused by a side reaction, which at higher temperatures results in the formation of methane. A theory of the catalytic reaction is built up on the assumption that the carbon atoms which undergo a change of valency attach themselves to the surface of the metal. By taking the distance between adjacent carbon atoms in the decahydronaphthalene molecule as 1·53 Å., it is shown that only those metals can be catalytically active of which the distance between the surface atoms is in the neighbourhood of 2·63 Å. This agrees with the facts as far as they have been studied.

The effect of rate of flow of the substrate has been investigated; increase in the rate markedly reduces the percentage of dehydrogenation, but no simple law governing the process could be found. The presence of an excess of naphthalene reduces the extent of the dehydrogenation, whilst excess of hydrogen has no effect. The effects of the reaction products have been studied for the dehydrogenation of *cyclo*hexane in benzene solution. H. F. Gillbe.

Acid and salt effects in catalysed reactions. VII. Tridimensional co-ordination of catalytic variables. Relations between the data for pure acids and the corresponding minimum-velocity mixtures. H. M. Dawson (J.C.S., 1927, 756—761).—The spatial co-ordination of catalytic variables is considered, and the characteristic features of a model, constructed on the basis of ionic reaction velocity, and acid concentration co-ordinates, are described. A general proof is given of the equations which connect the catalytic coefficients k_h, k_a, and k_m with the hydrogen-ion concentrations and the ionic reaction velocities for the solutions of the pure acids and of the corresponding minimum-velocity mixtures. The experimental data for the catalytic effects produced by acetic acid in the acetone–iodine reaction are shown to be in close agreement with these equations over the acid concentration range $c=0·01$ to $c=0·5$. E. S. Hedges.

Molecular induction in activation by shock. Perrin and (Mlle.) Choucroun (Compt. rend., 1927, **184**, 985—987).—In the reaction between glycerol and methylene-blue, which is determined by the light which produces fluorescence in the latter, very small traces of hydroxyl ions may produce a catalytic effect. In buffered solutions the chemical activity of the glycerol is constant between the concentrations 0·5 and 0·02%. At lower concentrations the rate of reaction decreases, owing to the influence of the buffer solution. The law of mass action holds, therefore, for a substance activated by thermal means only. The same influences which act by induction when an ordinary molecule approaches an activated molecule and deactivates it with the production of kinetic energy, also act by induction in the inverse sense when two ordinary molecules approach one another and their kinetic energy is transformed into energy of activation (*i.e.*, shock). There is evidence of great selective sensitiveness to shock between two similar isochronous molecules (cf. A., 1926, 884, 885). J. Grant.

Catalytic action of traces of iron and copper on the anaerobic oxidation of sulphydryl compounds. D. C. Harrison (Biochem. J., 1927, **21**, 335—346).—Very small quantities of hydrogen cyanide produce a marked inhibition in the rate of anaerobic reduction of methylene-blue by sulphydryl compounds such as cysteine, glutathione, and thioglycollic acid. Although methylene-blue is reduced by sulphydryl compounds to an appreciable extent in the complete absence of catalytic metals, the addition of very small quantities of the order of a fraction of a mg. of iron or copper accelerates the anaerobic reduction in the presence of cysteine. With thioglycollic acid the addition of traces of iron does not appreciably increase the reduction of methylene-blue; copper, on the other hand, acts as a very powerful catalyst. The addition of 0·001*M*-hydrocyanic acid produces practically no inhibition when purified cysteine or thioglycollic acid is used. In the presence of minute traces of copper the same concentration of hydrocyanic acid inhibits the reduction of methylene-blue. Iron-free leuco-methylene-blue oxidises rapidly in the air, and there is no difference in the rate of oxidation of reduced methylene-blue by exposure to air, whether cyanide is present or not. Molecular oxygen therefore can act as a hydrogen acceptor without being previously activated by iron. S. S. Zilva.

Catalytic combustion. V. Union of carbonic oxide and other gases with oxygen in contact with a fireclay surface at 500°. W. A. Bone and A. Forshaw.—See B., 1927, 289.

Reciprocal activation and de-activation of catalysts. II. A. Quartaroli (Gazzetta, 1927, **57**, 234—242).—The effect of pairs of catalysts on the rate of decomposition of hydrogen peroxide, rendered slightly alkaline by sodium hydroxide, has been investigated. At 50° the oxides of magnesium, cadmium, and nickel precipitated by the addition of sodium hydroxide solution to hydrogen peroxide solution containing salts of these metals act as anti-catalysts. Lead oxide alone acts as a positive catalyst. The oxides of nickel, magnesium, cadmium, and zinc, precipitated as described, diminish the action of lead oxide. At 20° the decomposition of the peroxide in the presence of silver oxide is exceedingly slow; the addition of small amounts of the oxides of magnesium, nickel, copper, cobalt, cadmium, and zinc to the solution containing silver oxide greatly increases the rate of decomposition, whilst thallium

oxide still further retards the action, and the hydroxides of iron and manganese are without action.
R. W. LUNT.

Mechanism of catalysis of hydrogen peroxide. L. PISARSHEVSKI and V. ROITER (Ukraine Chem. J., 1927, 2, 75—87).—See A., 1926, 917.

Oxidation of dextrose at the ordinary temperature by oxides of manganese. C. D. INGERSOLL (Ann. physiol. physicochim. biol., 1926, No. 3, 1—14).—The compounds MnO_2, Mn_2O_3, Mn_3O_4, and MnO, in order of decreasing activity, cause the oxidation of dextrose to carbon dioxide at the ordinary temperature in a solution through which air is passed. The rate of oxidation is a linear function of the time except with manganese dioxide, with which the rate increases more rapidly. CHEMICAL ABSTRACTS.

Kinetic activity, oriented adsorption, and molecular deformation as factors in catalysis. J. ALEXANDER (Science, 1927, 65, 62—63).—The function of a catalyst is pictured as follows: (*a*) the catalyst binds or adsorbs a reacting constituent and holds it relatively immobile, (*b*) the bound particles are held in oriented fashion (oriented adsorption) so that they present to the other reacting particles fields most favourable to adherence or combination with them, (*c*) the electromagnetic or electrostatic fields of the reacting particles thus joined react on each other in such a way that the linking between the inner particle and the catalyst is broken, whilst that between the two reacting particles persists (synthesis). The remaining charges on an adsorbed molecule are redistributed so that it can then make attachments not possible previously. Rise of temperature may increase, and then diminish, the number of successful encounters. A. A. ELDRIDGE.

Measurement of radiation intensity by photographic methods. E. A. BAKER (Nature, 1927, **119**, 707).—Variations of individual plates may be due to the sensitiveness of the emulsion to slight changes in the composition of the developer.
A. A. ELDRIDGE.

Photochemical action of intermittent light. IV. Intermittent light of different frequency combinations. M. PADOA and (SIGNORINA) N. VITA (Gazzetta, 1927, **57**, 187—194).—The oxidation of hydriodic acid by oxygen (exothermic) and the oxidation of ferrous iodide by iodine have been examined under the action of intermittent visible light. Light from an arc, after passing through alum solution to remove infra-red frequencies, is allowed to fall on the reaction mixture after passing through a rotating disc of variable speed. This disc is fitted with slots into which coloured glass sectors of two colours are placed alternately. The reaction mixture is thereby illuminated alternately with the corresponding transmitted colours. In some experiments white light has been used alternately with a coloured light; in others only one colour, the alternate sectors being blocked. In each reaction a maximum velocity is attained, depending on the rate of rotation of the disc. These maxima are in some cases greater than those obtained by continuous illumination with white light, and the majority occur in the range 0—50 interruptions per min.(?). It is suggested that the light-sensitive substance absorbs energy which is effective in producing chemical change during the one period of illumination and, according to the colour of the succeeding period, this change is accelerated or retarded. The results are to held be in agreement with Einstein's law of photochemical equivalence.
R. W. LUNT.

Photochemical equilibrium in nitrogen peroxide. I. R. G. W. NORRISH (J.C.S., 1927, 761—775).—Illumination of nitrogen peroxide by means of the mercury-vapour lamp produces a slow increase in pressure, which is too great to be ascribed to a heating effect. A subsequent return to the normal pressure occurs, at first rapidly and then slowly, in the dark. The suppression of the effect by the addition of excess of nitric oxide or oxygen, coupled with the fact that nitric oxide is the more effective agent, points to the establishment of a photochemical equilibrium $2NO_2 \rightleftharpoons 2NO+O_2$. Since no atomic oxygen could be detected in the reaction mixture, the reaction appears to be bimolecular, probably by collision between a photoactive and an inactive molecule of nitrogen peroxide. A heating effect, due to the recombination of nitric oxide and oxygen and to the absorbed radiation, is also involved. Mathematical expressions are deduced theoretically for both the photochemical and the heating effects. A simple mechanism is proposed for the photochemical decomposition of nitrogen pentoxide in presence of nitrogen peroxide (cf. Daniels and Johnston, A., 1921, ii, 249). E. S. HEDGES.

Kinetics of the addition of bromine to cinnamic acid and to stilbene under the influence of light. A. BERTHOUD and J. BERANECK (Helv. Chim. Acta, 1927, **10**, 289—299, and J. Chim. phys., 1927, 24, 213—237).—The velocities of the above irreversible reactions in carbon tetrachloride solution under the influence of blue light are practically independent of the concentration of the acceptor, *A*, and are almost proportional to the square root of the intensity of the light source. For feeble and total absorption the respective order of the reactions is 1·5 and 1 with reference to bromine. The following scheme explains the observations: $Br_2+h\nu=2Br$; $A+Br=ABr$; $ABr+Br_2=ABr_2+Br$; $2ABr=A_2Br_2$. Prolonged repetition of the second and third stages accounts for the high quantum yield; the latter is 36 for violet light and 10 for green. The thermal coefficients (10—20°) are 2·42 and 2·08 for cinnamic acid and stilbene, respectively (cf. Padoa and Vita, A., 1926, 1014). S. K. TWEEDY.

Action of light on the ferrous-ferric : iodine-iodide equilibrium. G. B. KISTIAKOVSKI (J. Amer. Chem. Soc., 1927, **49**, 976—979).—The reaction $2Fe^{\cdot\cdot}+I_3'=2Fe^{\cdot\cdot\cdot}+3I'$ is sensitive to the radiations 5460, 4360, and 3660 Å. in the mercury spectrum, contrary to the results of Rideal and Williams (A., 1925, ii, 416). The Einstein law of photochemical equivalence is obeyed.
S. K. TWEEDY.

Photochemical action of the mercury-vapour arc on a formaldehydic liquid covered with olive oil. E. ROUSSEAU (Compt. rend., 1927, **184**, 1007—1009; cf. this vol., 429).—The production of reducing

sugars, after exposure to the mercury arc, in an aqueous solution containing freshly-prepared commercial "formalin" (1 c.c.), crystalline monocalcium phosphate (1 g.), and 0·8 c.c. of a 50% solution of pure ammonium nitrate in 100 c.c. has been tested in the presence and absence of a layer of olive oil 3 mm. thick, which acts as a screen absorbing the ultra-violet, but not the unknown photochemically active rays. Almost parallel sinusoidal curves were obtained when the sugars produced were plotted against the time of exposure in the presence of quartz and the oil, the curve corresponding with the latter being the higher. Maxima were obtained after 2 and 4 hrs. and minima after 3 and 5 hrs., corresponding with the photocatalytic effect of the total or of the unknown radiation, and with the photolytic effect due to the continuity of the radiant action, respectively.

J. GRANT.

Photochemical reactions of colouring matters. I. Reversible photochemical reaction of malachite-green. T. ARIGA (Bull. Chem. Soc. Japan, 1927, **2**, 65—73).—The rate of decolorisation of malachite-green solutions when alkali is added to them has been followed with the aid of the spectrophotometer, and is found to obey the unimolecular law, the velocity coefficient being approximately proportional to the hydroxide concentration. When the colourless solution is exposed to the light from a mercury-vapour lamp, it regains its colour, the same law being obeyed, but the velocity coefficient is independent of the alkali concentration, is the same at 35° as at 25°, and is proportional to the light intensity. Finally, if the coloured solution is kept in the dark, it loses its colour again, the process obeying the same law as the decolorisation with alkali. It appears probable that the coloured substance formed in the light is Hantzsch and Osswald's unstable ammonium base (A., 1900, i, 256), which in the dark passes into the stable ψ-form. The light reaction appears, from the fact that the temperature coefficient is zero, to be a purely photochemical effect. Intense direct sunshine has the same effect as the light from a mercury lamp.

R. CUTHILL.

Surface constitution and spectral sensitivity of silver bromide and chloride precipitates. W. STEINER (Z. physikal. Chem., 1927, **125**, 275—306; cf. A., 1923, ii, 109, 614).—The spectral sensitisation of silver bromide in presence of excess silver ions (*e.g.*, the "silver-body") takes place also in acid solution, thus excluding the possibility that the sensitisation is due to adsorbed hydroxyl ions. The sensitivity of the "bromide-body" (*e.g.*, silver bromide in presence of excess bromine ions) is the same in neutral and acid solutions, with ethylene as acceptor. The silver- and chloride-bodies behave similarly to silver bromide. The decrease in sensitivity of the chloride-body persists over a wider range than that of the silver-body. As previously observed for silver bromide, the chloride-body of silver chloride is sensitised to wave-lengths longer than 15 mμ by treatment with sodium carbonate, *i.e.*, hydroxyl ions. Phenylpropiolic and sulphurous acids sensitise the bromide-body of silver bromide, owing apparently to the formation of adsorbed films of the corresponding and slightly soluble silver salts, as these salts have the same spectral sensitivities as those imparted to the bromide-body by the acids. Lead ions do not sensitise silver bromide. Thallium ions sensitise the bromide-body of silver bromide to wave-lengths greater than 615 mμ, but have no influence on the chloride-body of silver chloride.

L. F. GILBERT.

Spectral sensitisation of silver bromide and silver chloride by adsorbed ions. K. FAJANS and W. STEINER (Z. physikal. Chem., 1927, **125**, 307—320; cf. preceding abstract).—Theoretical. The spectral sensitisation of silver bromide or chloride is due to the adsorption of ions on the halide lattice. It is considered that the sensitising effect is not due to the ions functioning as halogen acceptors, but to their direct influence on the primary photochemical change. With silver and thallium ions this influence is evinced in a deformation of the electronic orbits of the halogen ions at the lattice surface. The effect of anions consists in the formation of an adsorbed layer of the corresponding silver salt, which decomposes in the presence of light of suitable wave-length.

L. F. GILBERT.

Hydrogen. VI. Compounds of hydrogen with sodium. G. F. HUTTIG and F. BRODKORB (Z. anorg. Chem., 1927, **161**, 353—362; cf. A., 1926, 809).—Sodium hydride prepared by the passage of hydrogen over heated sodium has the composition NaH, and appears in the form of colourless needles, which, however, belong to the regular system. *X*-Ray examination by the Debye and Scherrer method indicates that the sodium ions are arranged in a face-centred cubic lattice with a parameter 5·53 Å. These results provide an essential experimental basis for the previous calculations (*loc. cit.*) of the electron affinity of the hydrogen atom. The hydrogen ions are probably arranged in such a way that the complete crystal lattice is similar to that of rock-salt. The hydride has ^{20} 0·9206; the value calculated from the *X*-ray data is 0·927. The dissociation of the hydride at reduced pressures and at the ordinary temperature is such as would be expected from a solution of hydrogen in sodium rather than from a definite compound. At higher temperatures, however, the dissociation is accompanied by the separation of sodium, free or almost free from hydrogen; the heat of formation of the hydride is about 20 kg.-cal. A similar value is obtained by a study of the dissociation of products of metallic appearance with a very low hydrogen content. The value for the lattice energy of calcium hydride given previously (*loc. cit.*) should be 500 kg.-cal. (not 229 kg.-cal.).

G. A. ELLIOTT.

Reaction of iodine with potassium chlorate in presence of acid, and preparation of the normal iodate. N. PUTOCHIN (Trans. Inst. Pure Chem. Reagents, Moscow, 1927, 59—68).—Experiment shows that the principal part in the acceleration of the interaction of iodine with potassium chlorate, expressed by the equation $10KClO_3+6I_2+6H_2O=6KIO_3,HIO_3+4KCl+6HCl$, by addition of acid is played by the chlorine liberated by the acid; hence hydrochloric acid, which liberates chlorine the most readily from the chlorate, exerts a greater accelerating effect than sulphuric acid, and this greater than that

of nitric acid. As regards their influence on the reaction, such acids may be completely replaced by a stream of chlorine. The chlorine reacts with the iodine to form iodine monochloride, which immediately enters into double decomposition with the potassium chlorate, giving the iodate and chlorine, this again reacting with iodine, and so on. Potassium chlorate and iodine alone also react, but extremely slowly. In presence of water, the chlorine liberated gives hydrochloric and hypochlorous acids, the latter oxidising iodine to iodic acid and being itself converted into hydrochloric acid. This oxidising action of the chlorine explains the necessity of using excess of iodine, which should be taken in the proportion $6I_2 : 10KClO_3$.

The preparation of normal potassium iodate consists of two stages: the preparation of the acid iodate, and the neutralisation of the latter. The method of preparation varies according to whether the aim is to utilise completely the chlorine of the potassium chlorate or to obtain the final product rapidly. The procedure to be followed in each case is described. T. H. POPE.

Miethe and Stammreich's work on gold from mercury. E. DUHME and A. LOTZ (Z. anorg. Chem., 1927, **161**, 180—182).—Polemical. Further work by the authors has confirmed their previous opinion that the more carefully the apparatus and materials used are freed from gold the smaller is the gold content of the mercury after the experiment, showing that in all probability the gold in the mercury has been derived from the apparatus (cf. Miethe and Stammreich, Naturwiss., 1924, **12**, 597, 744; Duhme and Lotz, A., 1926, 930). A. R. POWELL.

Behaviour of sparingly soluble metal oxides in solutions of their salts. II. Magnesium oxide cements. W. FEITKNECHT.—See B., 1927, 301.

Surface film of aluminium. H. SUTTON and J. W. W. WILLSTROP (Nature, 1927, **119**, 673—674).—The existence of surface films on aluminium is directly proved by exposing strips cut from thin sheet to hydrogen at 300°, and then to dry hydrogen chloride, when the exposed metal at the edge sublimes as the chloride, leaving a thin, continuous surface film. A. A. ELDRIDGE.

Preparation and properties of aluminium perchlorate containing fifteen molecules of water. D. DOBROSERDOV (Ukraine Chem. J., 1926, **2**, 109—118).—When aluminium hydroxide is added to perchloric acid, dissolution proceeds slowly at the ordinary temperature, and soon stops. The liquid when kept deposits colourless needles having a composition $Al(ClO_4)_3,26HClO_4,73H_2O$. When the filtrate is heated on a water-bath wth excess of aluminium hydroxide, further dissolution occurs, the liquid depositing crystals of aluminium perchlorate, $Al(ClO_4)_3,15H_2O$. The filtrate, after being evaporated to half its volume, deposits crystals having the composition $Al(ClO_4)_3,23HClO_4,64H_2O$. The compound $Al(ClO_4)_3,15H_2O$ is not hygroscopic at the ordinary temperature. When kept in a vacuum desiccator over sulphuric acid, the dodecahydrate is formed; in a steam oven, the hexahydrate is formed, m. p. 100° without decomposition. The solubility of the quindecahydrate in water is 6·86% at 18·5° (the solution having $d_{15}^{19\cdot7}$ 1·0535) and 42·27% at 90°. E. ROTHSTEIN.

Perchlorates of aluminium with nine and six molecules of water. Solubility, dehydration, and influence of heat. D. DOBROSERDOV (Ukraine Chem. J., 1926, **2**, 119—135; cf. preceding abstract).—Excess of aluminium hydroxide was added to aqueous perchloric acid heated on a water-bath; a cloudy solution was obtained which on cooling set to a jelly, having a composition corresponding with $Al(ClO_4)_3,Al(OH)_3$. To this a quantity of perchloric acid, equal to that originally taken, was added, and the solution evaporated considerably. Crystals of the compound $Al(ClO_4)_3,9H_2O$ were deposited. The latter compound is very hygroscopic, and in a few minutes is converted into the perchlorate with $15H_2O$. In a vacuum desiccator over sulphuric acid, 3 mols. of water are lost. In a steam oven, the compound melts, but does not lose water to form the hexahydrate, as is the case with the quindecahydrate. At 150—160°, the compound is only partly decomposed. When heated in a platinum crucible, it is decomposed, $4Al(ClO_4)_3 \longrightarrow 2Al_2O_3+6Cl_2+21O_2$. One hundred parts of water dissolve 462·75 g. of the nonahydrate at 0°, 564·13 g. at 14·3°, and 3064·6 g. at 96°. The densities of the solutions in the first two cases are, $d_{15}^{18\cdot5}$ 1·5746 and $d_{15}^{18\cdot5}$ 1·6078. The constitution of the various hydrates is discussed. E. ROTHSTEIN.

Lower valency compounds of the rare-earth elements. I. Samarous chloride. G. JANTSCH, H. RUPING, and W. KUNZE (Z. anorg. Chem., 1927, **161**, 210—216).—For the preparation of samarous chloride from samaria the latter is heated at 640—650° in a current of chlorine saturated with sulphur monochloride, to convert it into trichloride, which is then carefully dehydrated in a current of hydrogen chloride at 300° and reduced at 750° in a stream of anhydrous ammonia containing half its volume of hydrogen. The product is a dark reddish-brown mass of fine needles (m. p. 740°), and dissolves readily in water, but the solution is unstable, evolving hydrogen and depositing an insoluble oxychloride on keeping. Alkali sulphates produce a light orange-coloured precipitate in the solution, and liquid ammonia gives an additive product with the anhydrous chloride. The intense colour of samarium dichloride serves as a means of detecting the element in the presence of large quantities of the other rare earths when the chlorides are heated in hydrogen and ammonia. A. R. POWELL.

Thallous carbonates. R. DE FORCRAND (Compt. rend., 1927, **184**, 987—990).—The chemical role of thallium has been fixed by direct and indirect measurements of the heats of formation of thallous carbonate and hydrogen carbonate. The values for the heats of neutralisation by carbon dioxide of TlOH and 2TlOH indicate the place of thallium among the alkali metals, whereas if the thallium is taken as the metal, and not as the base, the values for both carbonates agree with those of the heavy metals, particularly of lead. The values for thallous oxide place thallium between the alkali metals and the heavy metals, *i.e.*, after

potassium and before lead or copper, and show it to be the limit of these two groups. The heat of formation of the hydrogen carbonate from the carbonate indicates the gradual passage from the alkaline-earth metals to the heavy metals. Thallous carbonate is obtained in long, colourless, anhydrous needles by evaporation of a solution of the hydroxide saturated with carbon dioxide. A small yield of hydrogen carbonate results when a concentrated solution of the carbonate is saturated with carbon dioxide at 0°, and twice the volume of alcohol saturated with carbon dioxide added at 0°. It forms small, pulverulent, hard, brilliant crystals, stable in the cold.

J. GRANT.

Decomposition of carbon monoxide in the corona due to alternating electric fields. II. R. W. LUNT and R. VENKATESWARAN (J.C.S., 1927, 857—867; cf. *ibid.*, 1925, 2052).—Carbon monoxide has been subjected to the discharge in a Siemens ozoniser, the gas being circulated (at pressures over the range 20—69 cm.) and continuously freed from the carbon dioxide produced in the reaction (*loc. cit.*). The discharge was excited by alternating electric fields of the order of 20,000 volts per cm. at 250 cycles per sec. Under these conditions a brown solid was deposited, which, on removal from the ozoniser, had the composition C_5O_3,xH_2O. This substance was very hygroscopic, and reacted with water, forming carbon dioxide (approximately 1 mol. of CO_2 was obtained per mol. of C_5O_3), a brown solution containing oxalic acid and colloidal particles, and a dark insoluble residue. The amount of oxalic acid formed was equivalent to 1 mol. for every 3 mols. of C_5O_3 decomposed.

G. A. ELLIOTT.

Phenomena arising from the addition of hydrogen peroxide to the sol of silicic acid. H. A. FELLS and J. B. FIRTH (Proc. Roy. Soc., 1927, A, 114, 517—521).—On addition of hydrogen peroxide to a mixture of equal volumes of sodium silicate solution (d 1·15) and hydrochloric acid ($3N$) there is no evolution of gas until the sol has almost set to a firm gel. This initial time lag was shown by the measurement of the pressure developed when the mixture was contained in a closed vessel, and independently by measurements of the rate of evolution of the dissolved gases. The latter proved to be oxygen with a certain amount of chlorine. A few minutes after the initial evolution of gas, the bubbles become fixed, owing to the high viscosity of the gel, after which they increase in size and pass gradually from a spherical to a lenticular form. Two possible explanations for the period of induction are given, one of which, involving the primary fixation of the hydrogen peroxide as a compound of the nature SiO_2,xH_2O_2,yH_2O, is preferred.

L. L. BIRCUMSHAW.

Surface devitrification of glass. III. Devitrification of alkali silicates. IV. Devitrification of lead silicates. K. TABATA.—See B., 1927, 501.

Weathering of glasses. I. K. TABATA, K. EGAMI, and S. MORIYASU (Res. Elec.-Tech. Lab. Japan, 1926, No. 179, 1—11).—The crystals formed during weathering are, in general, alkali metadisilicates; the degree of weathering action depends on the amount of alkali (particularly potassium) silicate present. Flint glasses are regarded as mutual solutions of alkali metadisilicates, lead metadisilicates, and silica.

CHEMICAL ABSTRACTS.

Vanadic acid. J. MEYER [with A. PAWLETTA] (Z. anorg. Chem., 1927, **161**, 321—336).—Vanadium pentoxide dissolves in water on addition of hydrogen peroxide to produce a yellow solution which rapidly evolves oxygen and gradually again deposits the pentoxide. The stability of the solution is a function of the vanadium concentration and of the temperature. A study of conductivity and colour changes during the process of dissolution (cf. this vol., 326) shows that the assumption previously made that the solution contains hexavanadic acid, $H_4V_6O_{17}$, is not correct. The vanadium goes into solution first as peroxyorthovanadic acid, $H_3(V(O)_2O_3)$, which is an acid of approximately the same strength as orthophosphoric acid. Oxygen is then evolved with the formation of vanadic acid. During this decomposition the solution becomes red, owing to the formation of a peroxyvanadyl salt of vanadic or peroxyvanadic acid, which subsequently decomposes with loss of oxygen to form yellow vanadyl vanadate. Quinquevalent vanadium is colourless as anion and yellow as cation; peroxide formation causes a deepening of these colours to yellow and red, respectively. Owing to the amphoteric character of vanadium, the vanadyl vanadates have a strong tendency to polymerise, and finally the solution precipitates the resulting product, $(V_2O_5)_n$, almost free from combined water. The catalytic decomposition of hydrogen peroxide by small quantities of vanadic acid is attributed to the formation of an intermediate peroxyorthovanadic acid, which loses oxygen more readily than hydrogen peroxide; the vanadium retains its quinquevalent character throughout.

G. A. ELLIOTT.

Reactions and complex compounds of thiocyanic acid. B. ORMONT (Z. anorg. Chem., 1927, **161**, 337—352).—When sulphuric acid is added to a concentrated solution of potassium or ammonium thiocyanate (1 : 2) the solution becomes yellow in a few minutes. The reagent containing 40—45% of sulphuric acid, obtained in this way, differs essentially from a neutral solution of thiocyanate; *e.g.*, with ferric salts it gives a red colour which rapidly disappears, and with silver, lead, and mercury salts white precipitates are obtained (as with potassium thiocyanate), which, however, slowly become yellow. Cobalt nitrate gives a green precipitate consisting of perthiocyanogen ($HC_3N_3S_3$), with traces of cobalt salts and of perthiocyanic acid ($H_2C_2N_2S_3$). Addition of hydrochloric acid to a solution of thiocyanate does not essentially alter its properties. Rapid addition of hydrogen peroxide to the concentrated thiocyanate solution produces a violent, usually explosive, reaction. When acids (preferably nitric acid) are added to a solution containing two or more thiocyanates, precipitation of a complex thiocyanate of definite composition may result. The precipitate must be collected immediately; otherwise a violent reaction may take place after a few minutes, with decomposition of the precipitate and evolution of oxides of

nitrogen, sulphur dioxide, hydrogen cyanide, etc. The *compounds* HgCo(CNS) (blue), $PbBi(CNS)_5$ (red), and possibly $CdHgBi(CNS)_7$ (red) have been obtained by this method. The formation of the mercury–cobalt complex may be used as a qualitative test for mercuric mercury, and it will indicate the presence of 0·0002 g. per c.c. of solution. G. A. Elliott.

Colour of selenium dioxide. J. Meyer (Ber., 1927, **60**, [*B*], 990).—A reply to Weller (this vol., 432). H. Wren.

Preparation of selenium trioxide. J. Meyer and A. Pawletta (Ber., 1927, **60**, [*B*], 985—989).—Repetition of the experiments of Worsley and Baker (J.C.S., 1923, **123**, 2870) fails to confirm the production of selenium trioxide. Dissolution of selenium in selenium oxychloride results in the formation of selenous chloride, which is precipitated with selenium dioxide when ozone is passed into the solution. The white sublimate observed by Worsley and Baker is considered to be selenous chloride. Substitution of glacial acetic acid or carbon tetrachloride for selenium oxychloride does not lead to the separation of selenium trioxide. H. Wren.

New fluorides of selenium. E. B. R. Prideaux and C. B. Cox (J.C.S., 1927, 928—929).—*Selenium oxyfluoride* has been prepared by acting on selenium oxychloride with dry silver fluoride in a platinum bottle. *Selenium tetrafluoride* was obtained similarly, using selenium tetrachloride and silver fluoride. Both compounds are colourless fuming liquids. The latter contains a red liquid in the first portion of the distillate, which may be a lower fluoride, Se_2F_2.
E. S. Hedges.

Preparation of sodium phosphomolybdate. A. S. Schakov (Trans. Inst. Pure Chem. Reagents, Moscow, 1927, 74—78).—Pure sodium phosphomolybdate may be conveniently prepared from commercial molybdic acid by a modification of Sonnenschein's method (Annalen, 1857, **104**, 45). The acid (600 g.) is converted into its ammonium salt, which is treated in aqueous solution with sodium phosphate (100 g.) and subsequently with hydrochloric acid (400 c.c.). The precipitated ammonium phosphomolybdate, washed free from chloride, is dissolved in a solution of 200 g. of sodium hydroxide in a small quantity of water, the liquid evaporated to dryness, and the residue heated to expel the residual ammonia. The salt is then crystallised from water, the final yield being 115—120% of the molybdic acid taken. The proportions of water of crystallisation and of sodium present vary in different preparations.
T. H. Pope.

Industrial preparation of fluorine. P. Lebeau.—See B., 1927, 297.

Comparability of the fluorosulphonates with perchlorates in chemical and crystallographical relationship; a fluorophosphate. W. Lange (Ber., 1927, **60**, [*B*], 962—970).—The salts of fluorosulphonic acid are analogous chemically and, in part, crystallographically with the corresponding perchlorates and permanganates. Mixed crystals of the fluorosulphonates and perchlorates of cæsium, potassium, lithium, tetraethylammonium, and of the copper tetrapyridinium complex can be prepared, and of the fluorosulphonates and permanganates of cæsium, potassium, and tetraethylammonium. The salts of fluorosulphonic acid with heavy metals are generally freely soluble in water and too easily hydrolysed to permit their isolation; they become stable and crystalline when the size of the cation is increased by complex formation with ammonia or other amine. The following fluorosulphonates are described: *cæsium*, m. p. about 292°; *nitrosyl*, $NO{\cdot}SO_3F$, m. p. 118—140° (mixed with nitrosylsulphuric acid); *tetramethylammonium*; *o-toluenediazonium*; *benzenediazonium*; *pyridinium*; *nitron*; *strychnine*; *brucine*; *morphine*; *cocaine*, and the complex *salts*, $Cu(SO_3F)_2,4NH_3,2H_2O$, m. p. 55·6° (also anhydrous); $Cu(SO_3F)_2,2\,en,0{\cdot}5H_2O$; $Cu(SO_3F)_2,4C_5H_5N$. The crystallographic constants and solubilities in water of the above salts are recorded.

Hydrolysis of phosphoryl fluoride by water reaches a well-defined stage with the production of the acid $POF_2{\cdot}OH$, of which the *nitron* salt, $C_{20}H_{16}N_4,HPO_2F_2$, m. p. 230·5—232·5°, is described. The compound is more readily obtained by fusing phosphoric oxide with ammonium fluoride, dissolving the residue in water, and adding nitron to the solution. The corresponding *ammonium* salt has been obtained. The ions of fluorophosphoric acid are also contained in the solution of phosphoric oxide in aqueous hydrofluoric acid.
H. Wren.

Preparation and chemical properties of rhenium. I. Noddack and W. Noddack (Z. physikal. Chem., 1927, **125**, 264—274).—The minerals in which rhenium is most likely to have been deposited during the cooling of the earth's crust are considered, on the basis of the probable chemical properties of the oxides. A large number of minerals have been subjected to *X*-ray analysis for rhenium. Gadolinite had a rhenium content of 10^{-6}. Others, such as many niobium and tantalum minerals, contained only about one tenth as much. Monazite was quite free from rhenium.

About 2 mg. of rhenium have been separated from these minerals, by manipulation of the sulphides of the metals present in them. When heated in hydrogen, the sulphide yields a black powder, consisting of the metal or a lower sulphide. This residue on combustion in oxygen yields an oxide which dissolves to a colourless solution in dilute hydrochloric acid. The solution gives no precipitate with alkalis, sulphuric acid, or hydrogen sulphide. Ammonia and hydrogen sulphide do not precipitate the sulphide, but on acidifying the solution strongly, a grey precipitate is produced. The spectrum of the element has been observed, but no measurements are given.
S. Barratt.

Decomposition of iron carbide by acids. R. Schenck and R. Stenkhoff (Z. anorg. Chem., 1927, **161**, 287—303).—Pure iron carbide, prepared by dissolving pearlite in cold dilute sulphuric acid, dissolves readily in the same acid, benzenesulphonic acid, or acetic acid at temperatures above 60°, according to one or other of the following equations: (*a*) $Fe_3C+6H^{\cdot}=3Fe^{\cdot\cdot}+CH_4+H_2$, (*b*) $Fe_3C+6H^{\cdot}=3Fe^{\cdot}+3H_2+C$. The higher the hydrogen-ion concentration of the acid the greater is the proportion of carbide

decomposed according to (*a*), and the higher the concentration of ferrous ions the greater is the proportion of free carbon obtained. The incomplete hydrogenation of the carbon under experimental conditions with acids of medium strength is due to the reduction of the hydrogen-ion concentration by the acid anion and the simultaneous ennoblement of the iron owing to the presence of ferrous ions. A. R. Powell.

Preparation of liquid nickel carbonyl. F. W. Laird (Rec. trav. chim., 1927, **46**, 177—179).—Nickel carbonyl may be prepared by passing dry carbon monoxide over freshly-reduced nickel at 90°, and condensing the resulting vapour in a vessel immersed in liquid air. With a rate of flow of gas of one litre per 3—5 min., 35 c.c. of the liquid carbonyl may be roduced per day. A more active nickel is obtained y heating freshly-precipitated nickelous hydroxide at 250° in a current of hydrogen; the high temperature necessary if the nitrate be employed renders the product less active.

Three new uses are suggested for nickel carbonyl: a nickel mirror may be produced by allowing the vapour to impinge on a glass surface maintained at 125°; by a modification of this method, thin nickel foil may be prepared; and by filling glass apparatus with the vapour, the interior wall may be rendered electrically conducting at any desired place by gentle heating. H. F. Gillbe.

Valency of ruthenium. E. Zintl and P. Zaimis (Ber., 1927, **60**, [*B*], 842—844).—Potentiometric observation of the reduction of ruthenium trichloride by chromous sulphate or titanous sulphate confirms the conclusion of Remy and Wagner (this vol., 328) that the blue coloration is due to the univalent metal (contrast Gall and Lehmann, this vol., 123).

H. Wren.

Compound RuS_2 and its structure. W. F. de Jong and A. Hooe (Rec. trav. chim., 1927, **46**, 173—176).—Analysis of the substance produced when the precipitate formed by hydrogen sulphide from a solution of ruthenium chloride is heated at 500° in an atmosphere of carbon dioxide shows it to consist entirely of RuS_2. This result is confirmed by a study of the *X*-ray spectrum, which is of the pyrites type. The same substance may be prepared by heating ruthenium trichloride with sulphur for three days at about 400°.

Laurite is probably chiefly ruthenium disulphide, containing about 3% of osmium, but if it be assumed that the latter directly replaces ruthenium, the calculated density does not agree with the observed value. H. F. Gillbe.

Use of mercury as a cathode in electroanalysis. H. S. Lukens (Trans. Amer. Electrochem. Soc., 1927, **51**, 133—138).—The current density at the mercury cathode should not exceed 30 amp./dm.^{2} In etermining cobalt by electrolysis of solutions of the nitrate, a black deposit of cobalt oxide may be formed on the mercury surface owing to the presence of ammonia produced by cathodic reduction. This difficulty may be avoided by slight acidification. It does ot arise with the nitrates of nickel and more noble metals.

Tarnishing of mercury sometimes produced by washing with ether or by contact with glass vessels which have been washed with ether is attributed to a strongly oxidising substance, which is formed when purified ether is kept in contact with air and exposed to light. Attempts were made to isolate this substance.

H. J. T. Ellingham.

Calibration of flasks, burettes, and pipettes; density determinations with the Westphal balance. J. P. Jacobsen (Dansk Tidsskr. Farm., 1927, **1**, 335—347).—A paper dealing with the calibration of graduated volumetric apparatus by the usual method of weighing their water content. Attention is directed to the errors caused by variations of temperature and pressure, and correction tables are given for these. A detailed account of the accurate determination of the density of liquids by means of the Westphal balance is also included, and the sources of error are discussed. H. F. Harwood.

Differential potentiometric titration. W. A. Roth (Z. Elektrochem., 1927, **33**, 127—129).—The method of potentiometric titration described by MacInnes and Jones (this vol., 35) is simplified by using a glass filter crucible for keeping the solution around one electrode separate from the bulk of the solution while the titrating agent is being added. Satisfactory electrical connexion is made through the sintered glass bottom of the crucible. The system can be used for titrations with electrodes of any type. Results are given for the titration of silver nitrate solutions with chloride solutions and of acids with alkalis. H. J. T. Ellingham.

Todt's simplified colorimetric method for measuring the hydrogen-ion concentration of small quantities of strongly coloured or turbid liquids. Rossée and von Morgenstern (Chem.-Ztg., 1927, **51**, 302—303).—To a few drops of the liquid in a depression in a white porcelain tile, is added a drop of a suitable indicator, and the colour compared with a chart showing the colour of various indicators over a p_H range of 2·8—9·8.

F. R. Ennos.

Permanent standards for the determination of hydrogen-ion concentration. A. Taub (J. Amer. Pharm. Assoc., 1927, **16**, 116—122).—An attempt to secure a complete set of standards for the Clark and Lubs indicators. Seventy-three permanent standards consisting of mixtures of 1% hydrochloric acid solutions of cobalt, iron, and copper chlorides (cf Arny and Taub, *ibid.*, 1923, **12**, 839) with Lovibond comparative readings and the corresponding standard buffer solutions have been made. The standards cover a range of 1·2—9·0 with a limit of accuracy of 0·1 p_H, are easily prepared, and, owing to the preserving action of the hydrochloric acid, are very stable. The two-coloured indicators recommended in the International Critical Tables, 1926, 13, were used in 20% alcoholic solution, the tendency for mould formation thus being inhibited and the permanency increased. They may also be used in buffered and unbuffered solutions. E. H. Sharples.

Measurement of the hydrogen-ion concentration in solutions poor in buffering power by the quinhydrone electrode. I. M. Kolthoff and W. Bosch (Biochem. Z., 1927, **183**, 434—443).—In solu-

tions the buffering power of which is not too small, quinhydrone preparations give excellent results. When quinhydrone, prepared by oxidation of quinol with ferric ammonium alum and washing, is stored, acid oxidation products arise, the preparation then giving with solutions poor in buffer a much too acid reaction. Such preparations give good results if they are carefully washed, or if fresh amounts of solution are used until the potential becomes constant. Quinhydrone prepared by Valeur's method gives readily reproducible results, and is to be recommended for solutions poor in buffer. P. W. CLUTTERBUCK.

Protein error in determining p_H with neutral red and phenol-red. E. H. LEPPER and C. J. MARTIN (Biochem. J., 1927, **21**, 356—361).—The protein errors with neutral-red and phenol-red for pseudoglobulin and serum-albumin of the horse and for egg-albumin and egg-white in varying concentrations have been determined. With both these indicators the colorimetric error due to the presence of this pseudoglobulin is in the opposite direction to that caused by serum-albumin. In either case the errors with neutral-red are in the opposite sense to those with phenol-red. Pure egg-albumin up to 7% does not cause any colorimetric error with either neutral-red or phenol-red. S. S. ZILVA.

Determination of water in concentrated sulphuric acid by thermometric titration. T. SOMIYA. —See B., 1927, 329.

Standards and standard methods of examining chemical reagents. Standards for sulphuric, hydrochloric, and nitric acids as reagents. A. V. RAKOVSKI (Trans. Inst. Pure Chem. Reagents, Moscow, 1927, 5—24).—Permissible limits for the proportions of impurities in these acids are suggested, and methods of analysis and the results obtained with a large number of samples during 1922—1925 are given. T. H. POPE.

Iodometric analysis of a mixture of sulphide, sulphite, and thiosulphate. A. KURTENACKER and R. WOLLAK (Z. anorg. Chem., 1927, **161**, 201—209).—The method previously described by Kurtenacker and Bittner (A., 1925, ii, 239) has been found to give erroneous results, owing to adsorption of thiosulphate by the zinc sulphide precipitate and to the rapidity with which the sulphide is oxidised by the air. These objections have been overcome in the following modification. The solution is treated with 10 c.c. of glycerol and 20 c.c. of a suspension of zinc carbonate and diluted to 200 c.c. in a graduated flask. After vigorous shaking, a portion is filtered through a dry paper and two aliquot parts are measured out; one is treated with an excess of iodine, acidified with acetic acid, and titrated with thiosulphate to obtain the sum of the sulphite and thiosulphate, and the other is treated with 5 c.c. of 40% formaldehyde solution, acidified with acetic acid, and titrated directly with iodine to obtain the thiosulphate content. The sum of the three anions, sulphide, sulphite, and thiosulphate, is obtained by treating another portion of the original solution with iodine and titrating the excess with thiosulphate. The zinc carbonate suspension is made by precipitating a solution of 40 g. of zinc sulphate crystals in 200 c.c. of water with 200 c.c. of a cold 10% solution of sodium carbonate while stirring vigorously. A. R. POWELL.

Volumetric determination of selenium and tellurium in the same solution. Z. LITTMAN (Chem.-Ztg., 1927, **51**, 323).—The substance is dissolved in hot dilute sulphuric acid, with the addition of the minimum quantity of nitric acid for complete oxidation of all the constituents. Nitrous fumes are removed by passing a current of air through the boiling solution after dilution, and any insoluble material is filtered off. The cold filtrate is diluted to a definite volume and an aliquot part treated with an excess of exactly 0·1*N*-permanganate at 50°, whereby the selenium and tellurium dioxides are oxidised to the trioxides. By titrating the excess of permanganate with 0·1*N*-oxalic acid, the sum of the two elements is found. A second aliquot portion is treated with a quantity of 0·1*N*-dichromate solution exactly equivalent to the permanganate consumed in the first titration, whereby only the tellurium dioxide is oxidised to trioxide; on adding potassium iodide to this solution, the selenium dioxide is reduced to the element and the excess of dichromate to chromic salt with the liberation of iodine. Then one third of the volume of 0·1*N*-thiosulphate required to titrate this iodine corresponds with the selenium content of the material; the tellurium content is calculated from the difference between the permanganate consumption and one third of the thiosulphate used. A. R. POWELL.

Determination of nitrate-nitrogen by reduction to ammonia. C. J. VAN NIEUWENBURG and G. P. DE GROOT (Chem. Weekblad, 1927, **24**, 202—203).—Reduction is effected by use of aluminium shavings in presence of copper sulphate, instead of Devarda's alloy. S. I. LEVY.

Detection of nitric acid and nitrates. D. BUZNEA and R. CERNATESCO (Ann. sci. Univ. Jassy, 1927, **14**, 302—304).—One part of nitric acid in 300,000 parts can be detected by the red coloration produced when there is added to the solution a fresh solution prepared by dissolving diaminophenol hydrochloride a little at a time in concentrated sulphuric acid until a faint violet colour is produced. Hydrochloric, hydrobromic, and hydriodic acids interfere, and should first be removed with mercurous sulphate. Permanganates, chromates, dichromates, chlorates, and some other oxidising agents give the test, but, unlike nitrates, also give a similar reaction with a solution of the hydrochloride in concentrated hydrochloric acid. R. CUTHILL.

Volumetric determination of phosphate and magnesium. F. L. HAHN and H. MEYER (Ber., 1927, **60**, [*B*], 975—977).—Phosphate may be determined by addition of standard magnesium solution to a solution of the phosphate containing ammonia and ammonium chloride in presence of an indicator prepared by dissolving 10 g. of crystalline sodium acetate and 0·2 g. of 1 : 2 : 5 : 8-tetrahydroxyanthraquinone in alcohol (cf. A., 1924, ii, 784). Mechanical agitation of the mixture is advisable. The colour change is from pink to pale blue in the turbid liquid.

Magnesium is determined by precipitation with an excess of standard phosphate and titration of residual phosphate with standard magnesium solution.

H. WREN.

Micro-determination of metals in salts. H. J. COOMBS (Biochem. J., 1927, **21**, 404—406).—A modification of Pregl's method. A few mg. of the salt are moistened with sulphuric acid in a boat placed in a platinum cylinder which retains any material lost by spitting or creeping. The combustion is carried out in a silica tube in a current of air. The boat is weighed together with the platinum cylinder.

S. S. ZILVA.

Separation of silver and lead. H. BRINTZINGER (Z. anal. Chem., 1927, **70**, 448—452).—The silver and lead are precipitated from the boiling solution of their nitrates by the addition of a cold saturated solution of oxalic acid, avoiding excess. By addition of *N*-ammonium hydroxide until the liquid just smells of it, the silver oxalate is dissolved. The lead oxalate is then either dried at 125° and weighed, or is treated several times with warm 2*N*-sulphuric acid, and the oxalic acid liberated is titrated with permanganate. The solution is acidified with nitric acid, and the silver determined either volumetrically by Volhard's method, or gravimetrically by precipitation as the chloride. Alternatively, the silver in an aliquot portion of the solution of the two nitrates may be determined by Volhard's method, and the lead in another portion separated and determined as the oxalate.

R. CUTHILL.

Use of oxygen in determination of calcium and magnesium. R. CERNATESCO and (MLLE.) E. VASCAUTAN (Ann. sci. Univ. Jassy, 1927, **14**, 305—307).—When calcium is precipitated as oxalate and weighed as oxide, and when magnesium is weighed as pyrophosphate, the time taken by the ignited precipitate to attain constant weight is much reduced if the heating is carried out in a current of oxygen.

R. CUTHILL.

Determination of magnesium and calcium. A. TERESCHENKO and M. NECRITCHE (Ukraine Chem. J., 1926, **2**, 163—172).—An examination of methods for determining magnesium in the presence of other metals. The precipitation of magnesium as the pyrophosphate is not always quantitative. Whilst in the presence of citric acid calcium pyrophosphate is not precipitated, in the presence of magnesium, some is precipitated together with the magnesium salt, and the results are too high. On the other hand, when other metals are not present, the weight of precipitated magnesium pyrophosphate is too small, as is the case if too much citric acid is present. Ammonium chloride, however, assists the precipitation of the pyrophosphate, whilst diluting the solution prevents the precipitation of calcium pyrophosphate, within certain limits. In general, the method is accurate, unless only small quantities of magnesium are present. When magnesium is precipitated as magnesium ammonium arsenate, and the latter determined by its reaction with potassium iodide, the results obtained are too low, owing to the fact that the theoretical quantity of iodine is not liberated because the above reaction never goes to completion. This difficulty may be avoided by first reducing the arsenate to the arsenite, which reacts completely with potassium iodide. This method is accurate unless other cations are present.

E. ROTHSTEIN.

Application of electrometric titration to the determination of the solubility of sparingly soluble oxides. W. BUSCH (Z. anorg. Chem., 1927, **161**, 161—179).—Strong acids and bases may be determined by conductometric titrations in dilutions as great as 0·001*N* with errors not exceeding 0·3—0·5$\times10^{-3}$ g.-equivalent, using Muller's apparatus ("Die Elektrometrische Massanalyse," Leipzig, 1923). The method is applicable to the determination of the solubility of oxides of magnesium, zinc, aluminium, and the rare-earth metals if an excess of acid is added to the saturated solution and the mixture then titrated with 0·001*N*-alkali; the results for the three first-named oxides agree closely with those obtained by Kohlrausch by conductivity measurements. The solubility of the various rare earths in g.-mol./litre of water at 29° is as follows: lanthana, 12·3$\times10^{-6}$; praseodymia, 0·61$\times10^{-6}$; neodymia, 5·75$\times10^{-6}$; erbia, 12·8$\times10^{-6}$, and yttria 8·00$\times10^{-6}$. The solubility of black praseodymium oxide (Pr_6O_{11}) is 3·9$\times10^{-6}$ g.-mol./litre. The temperature at which the oxide has been ignited has an appreciable effect on the solubilities of the rare earths and of magnesia, the higher the ignition temperature the smaller being the solubility.

A. R. POWELL.

Gravimetric determination of magnesium and phosphoric acid. F. L. HAHN, K. VIEWEG, and H. MEYER (Ber., 1927, **60**, [*B*], 971—975).—Crystalline magnesium ammonium phosphate is the most sparingly soluble of all magnesium phosphates, and hence is precipitated pure if a few nuclei of the salt are present in solution and the precipitate is allowed to increase slowly. This is achieved by "precipitation at infinite dilution," for which the solutions of magnesium salt and sodium ammonium phosphate are slowly added from separate burettes to a hot solution of ammonium chloride and ammonia. The method is accurate even in the presence of very large amounts of ammonium salts.

In a second method, the concentration of the magnesium ions is sufficiently reduced by the addition of ammonium hydrogen tartrate. The solution of magnesium salt, phosphate, and hydrogen tartrate is heated at 100°, and ammonia is added. After remaining at 100° for 1 hr., a further portion of ammonia is added and the solution is preserved overnight, or the precipitate may be filtered immediately it is cold if mechanical agitation is used during cooling. In the presence of considerable amounts of alkali salt, the precipitated phosphate is amorphous and the values for magnesium are high. After re-precipitation, satisfactory results are obtained. The method is applicable to the determination of phosphates.

H. WREN.

Direct titration of zinc with potassium ferrocyanide, using diphenylamine or diphenylbenzidine as indicator. I. M. KOLTHOFF (Chem. Weekblad, 1927, **24**, 203—205; cf. Cone and Cady, this vol., 331).—The titration using diphenylamine is best effected at 60° in presence of sulphuric acid and

ammonium sulphate. The colour change from blue to greenish-yellow is permanent at the end-point. Lead does not interfere. S. I. Levy.

Solubility of lead sulphate in water and solutions of electrolytes. M. Huybrechts and H. Ramelot (Bull. Soc. chim. Belg., 1927, **36**, 239—260).—An investigation of the most favourable conditions for the gravimetric determination of lead as sulphate. Lead sulphate is soluble in water at 18° and 30° to the extent of 34 and 44 mg./litre, respectively. In presence of sulphuric acid, sodium sulphate, or ammonium sulphate, the solubility decreases rapidly with increasing concentration of sulphate ion, is minimal (3—4 mg./litre at 18°) at 0·01—0·05*M* added electrolyte, and then slowly rises. In presence of potassium sulphate, however, the solubility decreases regularly to a lower limiting value of 0·23 mg./litre at 18° at a salt concentration of 0·17*M*. Lead sulphate is rather more soluble at 18° than at 30° in solutions of sodium sulphate more concentrated than 0·05*M*. In presence of nitric acid, the solubility increases almost linearly with the acid concentration. In 0·89*M* solutions, the solubility at 18° is 1·437 g./litre. The enhanced solubility in solutions containing nitric acid is rapidly diminished in presence of sulphuric acid or soluble sulphates, the solubility decreasing regularly with increasing concentration of sulphate ion. The solubility in 0·89*M* solutions of nitric acid at 18° is reduced to 20·4 mg./litre in presence of 0·51*M*-sulphuric acid. The evaporation of a mixture of lead salt and sulphuric and nitric acids until white fumes are freely evolved does not completely remove nitric acid; complete removal, although desirable, is not essential. The solubility at 18° for hydrochloric acid solutions, in consequence of the decreased solubility of lead chloride with increasing concentration of chloride ion, is maximal (1·02 g./litre) at 0·7*M*-acid. As with nitric acid, the increased solubility in solutions of hydrochloric acid is diminished on addition of sulphuric acid or sulphates.

In the analytical determination of lead as sulphate the concentration of sulphuric acid after evaporation of the lead salt–nitric acid–sulphuric acid mixture and subsequent dilution should be of the order 0·3%. The precipitate should be washed with a solution of sulphuric acid of this concentration, or with a 0·3% solution of ammonium sulphate if the presence of this salt in the filtrate is not undesirable. If the solution contains salts having a tendency to form basic compounds, the washing should be carried out with a rather more concentrated solution of acid. J. S. Carter.

Electrolytic determination of copper in bronze. R. A. F. Hammond.—See B., 1927, 301.

Determination of copper in presence of other metals by potentiometric titration with chromous chloride. E. Zintl and G. Rienacker (Z. anorg. Chem., 1927, **161**, 374—384).—Chromous chloride is used to determine copper by reduction in hot acetic acid solution containing chlorides. It is a stronger and more rapid reducing agent than titanium chloride, which was used previously (A., 1926, 929) for the determination of mercury. G. A. Elliott.

Potentiometric determination of mercury in presence of other metals. E. Zintl and G. Rienacker (Z. anorg. Chem., 1927, **161**, 385—392).—A detailed description of the application of the method described in the preceding abstract to the determination of mercury. G. A. Elliott.

Examples of induced precipitation. W. Bottger and K. Druschke (Annalen, 1927, **453**, 315—331).—When copper is precipitated as sulphide with hydrogen sulphide from an acidified solution containing iron, the precipitate frequently contains appreciable amounts of iron, which cannot readily be removed by washing with hydrochloric acid. The result is the same whether the solution be acidified with nitric, sulphuric, or hydrochloric acid, but if the concentration of nitric acid exceeds about 4*N*, the co-precipitation does not occur. The effect appears to be a specific action of the copper sulphide. If hydrogen sulphide is passed into a solution containing 0·2 g. of zinc per 100 c.c. and 0·6*N* with respect to sulphuric acid, no precipitation occurs, but if copper is present, the copper sulphide precipitated contains zinc, whilst if the solution is saturated with hydrogen sulphide and shaken for some time with added copper sulphide, zinc passes into the solid phase. Zinc can be removed from the mixed precipitate by shaking with *N*-hydrochloric acid, and its precipitation can be prevented initially by increasing the acid concentration to *N*. When mercury and cadmium are precipitated together as sulphides, the cadmium cannot be completely removed from the mixture by boiling with dilute acid. F.-p. determinations with solutions containing cadmium chloride and mercuric chloride, both separately and together, indicate that the mixed solution contains some complex molecules. This does not, however, seem to be the cause of mixed sulphide formation, since solutions of the nitrates, which probably dissociate normally, give the same abnormal precipitate. The properties of the precipitate are altered if ammonia or potassium cyanide is present in the solution before precipitation. The *X*-ray spectrogram of the mixed sulphide gives no indication of the presence of any compound other than the two simple sulphides. The only explanation of the observed phenomena seems to be that the crystals of the two sulphides grow into one another in a way similar to that in which isomorphous substances form mixed crystals. R. Cuthill.

Determination of cerium. T. Lindeman and M. Hafstad (Z. anal. Chem., 1927, **70**, 433—443).—If the sulphuric acid concentration used in the oxidation of a cerous salt by ammonium persulphate in von Knorre's method for determining cerium (A., 1898, ii, 311) is greater than 4·6 g./100 c.c. of solution, hydrogen peroxide is liberated from the persulphate, whilst if it is less than 2·7 g./100 c.c., basic salts are precipitated. When cerium is to be determined by this method in presence of other metals, it is necessary that the solution shall contain at least 5 g. of magnesium, as the sulphate, per 1 g. of cerium, as otherwise the ceric ions tend to pass spontaneously into the cerous state. In the gravimetric determination of the cerite metals by precipitation of the oxalate according

to Gibbs' method, the water of crystallisation of the dried oxalate must be taken as 2 mols., not 3 mols.
R. CUTHILL.

Determination of manganese as pyrophosphate. D. BALAREV and N. DESEV (Z. anal. Chem., 1927, **70**, 444—447).—In the method of Gooch and Austin for the precipitation of manganese as pyrophosphate in the separation of manganese and iron, the presence in the solution of considerable quantities of acetate, sulphate, potassium, or sodium ions causes the result to be too high. The error caused by sodium acetate cannot be eliminated by dissolving the precipitate and then reprecipitating it. Boiling the solution for more than 5 min. also leads to incorrect results. The precipitated pyrophosphate appears to undergo change in contact with air.
R. CUTHILL.

Spectrophotometric investigation of complex compounds and its application to analysis. A. USPENSKI and K. TSCHIBISOV (Trans. Inst. Pure Chem. Reagents, Moscow, 1927, 32—49).—Spectrophotometric examination of cobalt complexes of the tetrammine and ethylenediamine series shows that, when the complexes have outer colourless spheres, the absorption spectrum in the visible region is determined by the inner sphere. Absorption spectra of complex compounds with equally coloured cations and different colourless anions are similar. The character of the spectrum is determined by the composition and the chemical and stereochemical structure of the complex, but the concentration of the solution exerts only a slight quantitative influence. The molecular extinction coefficient increases with this concentration.
T. H. POPE.

Micro-titration of chromic and barium ions based respectively on the disappearance or the appearance of the yellow colour due to chromic ions. R. F. LE GUYON (Compt. rend., 1927, **184**, 945—947).—If a standard solution of potassium chromate is run into a known volume of a solution of a barium salt, barium chromate is precipitated, and the end-point corresponds with the first appearance of the yellow colour due to the chromate ions. This, and the disappearance of the yellow colour with the converse reaction, is used for the micro-determination of the ions concerned. Using the centrifugo-volumetric method (A., 1926, 927), 0·5 and 1·33 mg. of chromium and barium, respectively, may be determined in 1 c.c. of liquid.
J. GRANT.

Analysis of cassiterite, SnO_2. P. WENGER and (MLLE.) E. ROGOVINE.—See B., 1927, 301.

Micro-determination of platinum in ores and minerals. G. LUNDE.—See B., 1927, 302.

Metal calorimeter for determination of the specific heats of metals, oxides, and slags. W. GROSSE and W. DINKLER.—See B., 1927, 336.

Lovibond colour system. I. Spectrophotometric analysis of Lovibond glasses. K. S. IBSON, F. K. HARRIS, and I. G. PRIEST (U.S. Bur. Standards, Sci. Paper 547, 1927, **22**, 1—46).—The spectral transmission of the glasses supplied with Lovibond's "tintometer" has been analysed by means of the spectrophotometer. If is the transmission for a given wave-length by the glass with the number N of the red, yellow, or blue set, it is found that $-\log T_\lambda = kN + b$, where k and b are constants. This is taken to be the ideal relation for the purpose of calibrating the glasses, and glasses which vary erratically from this equation are to be regarded as wrongly numbered. The integral transmission for sunlight is not, in general, a linear function of N.
R. CUTHILL.

Comparative examination of different colorimeters. M. J. VAN TUSSENBROEK (Chem. Weekblad, 1927, **24**, 240—247).—The Krüss colorimeter, the Lovibond tintometer, the Hilger spectrophotometer, the Keuffel and Esser colour analyser, and the Moll extinctometer are described, and compared for examination of picric acid solutions of various concentrations.
S. I. LEVY.

Efficient gas scrubber. H. W. SOUTHGATE (Biochem. J., 1927, **21**, 347—348).—The gas or mixture of gases and vapours is aspirated through the pores of a glass filter plate, and consequently emerges into the trapping liquid in small bubbles. A small tube through the centre of the porous plate coming from the bottom of the bubbler ensures an efficient circulation of the trapping liquid.
S. S. ZILVA.

Apparatus for filtering saturated liquids at a constant temperature. P. WEBER and H. L. DUNLAP (Ind. Eng. Chem., 1927, **19**, 481).—A condenser is sealed to the ground-glass stopper of a wash-bottle, the outlet tube of which passes into a Soxhlet thimble within the flask. The whole is placed in a thermostat. By applying air pressure to the outlet tube, the filtered solution is brought into contact with the solute in the flask. The sample is then drawn from the thimble by applying pressure to the condenser end.
C. IRWIN.

Mercury compressor [for gases] evolved from Archimedes' screw pump. J. G. DE REMER (Ref. Eng., 1926, **13**, 156—162). CHEMICAL ABSTRACTS.

Lecture experiments. H. VON WARTENBERG (Z. Elektrochem., 1927, **33**, 147—149).—A description of lecture experiments relating to weighing, the law of multiple proportions, Brownian movement, the formation of hydrogen bromide, the law of mass action, a protective film on aluminium, and a transition point of nickel.
H. T. J. ELLINGHAM.

"Discovery" of aluminium. M. TOSTERUD and J. D. EDWARDS (Trans. Amer. Electrochem. Soc., 1927, **51**, 109—112).—Experiments on the production of aluminium by heating potassuim amalgam with aluminium chloride support the claims of Oersted to be regarded as the first to produce metallic aluminium (1825).
H. J. T. ELLINGHAM.

Mineralogical Chemistry.

Origin of the earth's surface structure. J. Joly and J. H. J. Poole (Nature, 1927, **119**, 674; cf. this vol., 439).

Weissite—a new mineral. W. P. Crawford (Amer. J. Sci., 1927, [v], **13**, 345—346).—Weissite occurs as small lenses in veins of pyrite (with native tellurium, sylvanite, petzite, and rickardite as associated minerals) in Colorado. The mineral is massive, bluish-black to black in colour; it has a black streak, a metallic lustre, hardness 3, d about 6. It contains Cu 45·85%, Te 53·97%, and the formula is therefore Cu_5Te_3, corresponding with a new type of telluride. The powdered mineral gives a violet colour in warm concentrated sulphuric acid. R. A. Morton.

Phosphorus and arsenic compounds of sea-water. W. R. G. Atkins and E. G. Wilson (J. Marine Biol. Assoc., 1927, **14**, 609—614).—Arsenic is present in sea-water, principally in the form of arsenite, in amount equal to or greater than that of phosphate; it follows that previous determinations of phosphates in sea-water by methods involving preliminary treatment with nitric acid have included also the arsenic, since arsenates react with the reagents used in the determination of phosphates. The arsenic content of sea-water varies with the depth, owing to its absorption by algæ.

C. R. Harington.

Organic Chemistry.

Application of fluorescence spectrography to the examination of organic compounds. A. Andant (Compt. rend., 1927, **184**, 1068—1070).—Characteristic curves of the fluorescence produced by certain paraffins and oils under ultra-violet radiation (3650 Å.) may be used to examine small amounts of rare substances. Examples show that photographic methods must be used to distinguish between fluorescences which appear identical to the unaided eye, but are produced by different substances. J. Grant.

Effect of temperature and solvent on nitrogen trichloride additions. Acetylene hydrocarbons. G. H. Coleman, C. N. Owen, and J. A. Rodriguez (Proc. Iowa Acad. Sci., 1925, **32**, 325—326).—The yield of the additive product of nitrogen trichloride and β-butylene is maximal at −20°; carbon tetrachloride is the best solvent. Acetylene hydrocarbons and nitrogen trichloride afford nitrogen and ammonium chloride, with only traces of an amine.

Chemical Abstracts.

Mechanism of reaction between aluminium, iodine, ethyl alcohol, and water. Preparation of ethyl iodide. A. O. Jones and G. M. Green (J.C.S., 1927, 928; cf. A., 1926, 1224).—The main products of the reaction between aluminium, iodine, ethyl alcohol, and water are ethyl iodide, aluminium iodide, and hydrogen, the hydrogen iodide produced by the hydrolysis of aluminium iodide distributing itself between the ethyl alcohol and the aluminium in a ratio depending on the concentration of water in the alcohol used. E. S. Hedges.

Reactivity of halogenated hydrocarbons. II. Reactions with unsaturated alkyl halides. J. Loevenich, J. Losen, and A. Dierichs (Ber., 1927, **60**, [*B*], 950—957).—The sole reaction between ethylenic alkyl halides with the halogen atom united to doubly linked carbon and sodium alkoxides consists in the elimination of halogen acid with production of acetylenes. Aniline behaves similarly, but less energetically, whereas silver acetate, silver benzoate, and benzamide are inactive. The only reagent which effects replacement of the halogen atom is sodium mercaptide, which gives thioethers. Potassium hydrogen sulphide, potassium xanthate, and potassium thiocyanate are inactive. Bromoacetylene could not be caused to react, whereas α-bromo-Δ$^{\alpha}$-propinene gives allylene with sodium ethoxide or mercaptide. The reactions of vinyl bromide, α-bromo-Δ$^{\alpha}$-propene, and α-chloro- and α-bromo-Δ$^{\alpha}$-heptenes are described. The following compounds are described: *ethyl vinyl sulphide*, b. p. 91·5—92°, d^{22} 0·8691, 1·4631; *ethyl* Δ$^{\alpha}$-*propenyl sulphide*, b. p. 125—130°; *ethyl* Δ$^{\alpha}$-*heptenyl sulphide*, b. p. 196—202°. Δ$^{\alpha}$-*Bromopropinene*, b. p. 65°, d_0^{25} 1·35015, is prepared by the action of alcoholic potassium hydroxide on ααβ-tribromopropane in an atmosphere of hydrogen. αααββ-*Pentabromopropane*, m. p. 212° (corr.), αβ-*dichloro*-α-*bromo*-Δ$^{\alpha}$-*propene*, b. p. 62°/20 mm., ααββ-*tetrachloro*-α-*bromopropane*, m. p. 208° (corr.), and α-*bromo*-αβ-*diiodo*-Δ$^{\alpha}$-*propene*, m. p. 52°, are described. Ethylidene dibromide and sodium ethoxide afford acetylene and vinyl bromide, whereas with sodium mercaptide ethyl vinyl sulphide (from primarily-formed vinyl bromide) and αα-diethylthiolethane are produced. With aniline and ethyl malonate, respectively, ethylidene bromide gives vinyl bromide and *ethyl ethylidenemalonate*, b. p. 116—118°/20 mm. H. Wren.

Reaction between phenol and *n*-propyl alcohol at high temperatures and pressures. W. Ipatiev, N. Orlov, and A. Petrov (Ber., 1927, **60**, [*B*], 1006—1008; cf. this vol., 239).—Phenol and *n*-propyl alcohol at 380—400° and a maximal pressure of 125—130 atm., in presence of aluminium oxide, afford a mixture of saturated and unsaturated gaseous hydrocarbons, phenyl -propyl ether, alkylphenols, among which *o*-*n*-propylphenol is identified, *o*-*n*-propylphenyl *n*-propyl ether, di-*n*-propyl ether, and polymethylene hydrocarbons; the two last-mentioned compounds are formed by dehydrogenation and condensation of *n*-propyl alcohol. The production of an analogue of xanthene could not be established.

H. Wren.

***iso*Propyl- and butyl-trichloromethylcarbinols.** J. W. Howard (J. Amer. Chem. Soc., 1927, **49**, 1068

1069).—Condensation of chloral with magnesium *iso*propyl bromide and magnesium butyl bromide, respectively, in ethereal solution, affords *trichloromethylisopropylcarbinol*, b. p. 105°/674 mm. (*propionate*, b. p. 163—164°/685 mm.; *butyrate*, b. p. 176—177°/685 mm.; *benzoate*, b. p. 180—181°/685 mm.), and *trichloromethylbutylcarbinol*, b. p. 108°/673 mm. (*propionate*, b. p. 166—167°/684 mm.; *butyrate*, b. p. 177—178°/684 mm.; *benzoate*, b. p. 182—183°/684 mm.). F. G. WILLSON.

New synthesis of mannitol. E. PACE (Arch. Farm. sperim. Sci. aff., 1926, 42, 167—173).—Mannitol is obtainable by the following steps: acetylene⟶acetaldehyde⟶ethyl acetate⟶ethyl acetoacetate⟶ethyl sodioacetoacetate⟶ethyl diacetosuccinate⟶ acetonylacetone⟶βε-dihydroxyhexane⟶βε-dibromohexane⟶dipropenyl⟶*βγδε-tetrabromohexane* (m. p. 181°; changes readily in light)⟶hexabromohexane⟶*i*-mannitol. T. H. POPE.

Pyridine content of glucophosphates prepared by the pyridine method. S. SABETAY (Bull. Soc. chim., 1927, [iv], 41, 438—440).—Calcium glucophosphates prepared by the pyridine method (A., 1926, 1123) contain traces of pyridine which are not removed on distillation at 40° over calcium hydroxide in a vacuum. It is undecided whether this pyridine is strongly adsorbed or whether it is present as a quaternary base (cf. Fischer and Raske, A., 1900, i, 503). R. BRIGHTMAN.

Synthesis of the phosphoric acid esters. III. Synthesis of some hexosemonophosphoric esters and their behaviour towards yeast. R. NODZU (J. Biochem. [Japan], 1926, 6, 31—47).—The *barium* salt of dipropylideneglucose-γ(or δ)-phosphoric ester, $C_{12}H_{19}O_9PBa,3H_2O$, $[\alpha]^{20}$ −2·85°, is hydrolysed by 0·4*N*-sulphuric acid to barium glucose-γ(or δ)-phosphate, $[\alpha]_D^{25}$ +30·7° after 1 hr. Phosphorus oxychloride and lævulose in presence of pyridine yield lævulose-ζ-phosphoric ester, $[\alpha]_D^{18}$ −17·6° in water after 30 min. α-Dipropylidenelævulose-ζ-phosphoric ester has [α] −84·7° and yields a lævulose-ζ-phosphoric ester having [α] −19·4°, whereas β-dipropylidenelævulose yields a lævulose-β, γ, or δ-phosphoric ester having [α] −40·5°. Glucose-γ-(or δ)-phosphoric ester is fermented by yeast or zymin, after an initial delay, as rapidly as lævulose. The variable rate of fermentation indicates that the ester prepared from α-dipropylidenelævulose is a mixture of isomerides. CHEMICAL ABSTRACTS.

Hydrolysis of the dipropylidenehexosemonophosphoric acid esters. R. NODZU (J. Biochem. [Japan], 1926, 6, 49—53; cf. preceding abstract).—Hydrolysis at 40° with 0·4*N*-sulphuric acid rapidly (24 hrs.) removes the propylidene radicals from α- and β-dipropylidenelævulose monophosphoric esters, but the phosphoric acid radical is only slowly removed. The reaction is unimolecular; the velocity coefficients for α- and β-lævulose and glucose esters are, respectively, 0·01400, 0·00510, and 0·00059. CHEMICAL ABSTRACTS.

Monoalkylcarbonates. I. Formation of monoalkylcarbonates from sodium hydrogen carbonate in aqueous solutions of alcohols. Equilibrium between alcohol, monoalkylcarbonate, carbonate, and carbon dioxide in aqueous solutions. II. Formation of monoalkylcarbonic acids and their salts by solution of carbon dioxide in aqueous solutions of alcohols at different acidities. C. FAURHOLT (Z. physikal. Chem., 1927, 126, 72—84, 85—102).—I. The relative amounts of $CH_3{\cdot}CO_3'$, $CH_3{\cdot}HCO_3$, H_2CO_3, HCO_3', CO_3'', and CO_2 present in equilibrium when sodium methylcarbonate is added to water have been determined for various degrees of acidity and alcohol concentrations from measurements of the velocity and equilibrium constants of the reaction $CH_3{\cdot}CO_3' + H_2O \rightleftharpoons CH_3{\cdot}OH + HCO_3'$. It was assumed that the ionisation constant of the monomethylcarbonate is identical with the first ionisation constant of carbonic acid. Experiments in alkaline solution showed that the decomposition and recombination of monomethyl carbonate are unimolecular. The reaction velocities are constant over a wide range of acidities, but decrease with increasing alcohol concentration.

II. Addition of carbon dioxide to a solution containing sodium hydroxide and methyl alcohol gives considerable quantities of monomethylcarbonate despite the rapidity with which hydroxyl ions convert the former into carbonate. The monomethylcarbonate slowly decomposes almost completely. The proportion of carbon dioxide converted into alkylcarbonate is independent of the hydroxyl-ion concentration. It is concluded that in alkaline solution carbon dioxide reacts almost exclusively with methoxide ions and that these attain an appreciable concentration. An investigation of the decomposition and formation of monoalkylcarbonates in acid solution is included. G. A. ELLIOTT.

Dependence of velocity of hydrolysis of esters on constitution. H. OLSSON.—See this vol., 526.

Catalytic oxidation effects that resemble the specific dynamic effect. E. J. WITZEMANN (J. Amer. Chem. Soc., 1927, 49, 987—992).—In neutral or acid solution, the oxidation of butyric acid by hydrogen peroxide is catalysed by glycine, ammonium and alkali glycollates and lactates, and gelatin, in a manner similar to that previously observed with ammonia solution (cf. A., 1922, i, 6). It is concluded that this result provides a chemical interpretation of the "specific dynamic effect" associated especially with glycine and alanine. F. G. WILLSON.

Higher fatty acids. II. Some branched chain fatty acids. G. T. MORGAN and E. HOLMES (J.S.C.I., 1927, 46, 152—154T).—In the course of an investigation of the physical properties of certain fatty acids having a methyl branching in the α-position, the following acids have been synthesised: *α-methylpentadecoic acid*, m. p. 48°; *α-methylpalmitic acid*, m. p. 54°; *α-methylmargaric acid*, m. p. 51—51·5°, and *α-methylstearic acid*, m. p. 58°. These acids, which appear amorphous to the unaided eye, are, however, crystalline, and resemble sugar candy when viewed under the microscope. It is deduced that the length of the unbroken chain, rather than the total number of carbon atoms present, governs the alternating effect noticeable in the m. p. of acids

of this series. In the condensation of magnesium methyl iodide with α-bromomargaric acid, an unsaponifiable by-product was obtained and identified as *methyl α-methylmargaryl ketone*, m. p. (indef.) 40°, b. p. 212—217°/0·0001 mm. Certain *X*-ray data concerning these products are given. It is concluded that the naturally occurring acids which have m. p. below those of their normal isomerides, and invariably crystallise in pearly flakes, are certainly not α-methyl acids, but that, if this isomerism is due to branching of the chain, such branching occurs at a point remote from the carboxyl group.

Preparation and properties of the margarins. W. F. THOMSON (Trans. Roy. Soc. Canada, 1926, [iii], **20**, III, 445—458).—The five margarins and the various mixed triglycerides containing margaric with palmitic or stearic acid residues have been synthesised and their solubilities and other properties determined. *α-Monomargarin*, obtained by the method of Fischer (A., 1920, i, 805), had m. p. 76·4°, n_D^{80} 1·4412, the intermediate product being *margaryl-isopropylideneglycerol*, m. p. 35·5°, n_D^{80} 1·4268, whilst *β-monomargarin*, m. p. 75·7°, n_D^{80} 1·4413, was synthesised by the method of Grün (A., 1910, i, 356) by way of *β-margaro-αγ-dichlorohydrin*, m. p. 26·5°, n^{80} 1·4387. αγ-Dichlorohydrin and αβ-dibromohydrin when heated with potassium margarate gave, respectively, *αγ-dimargarin*, m. p. 71·8°, n_D^{80} 1·4388, and *αβ-dimargarin*, m. p. 70·1°, n_D^{80} 1·4385. Trimargarin, obtained by direct esterification, had m. p. 62·7°, n_D^{80} 1·4382. The symmetrical mixed triglycerides, prepared by the method of Whitby (A., 1926, 819), were *β-palmito-αγ-dimargarin*, m. p. 58·3°, n_D^{80} 1·4368, *β-stearo-αγ-dimargarin*, m. p. 63·1°, 1·4392, *β-margaro-αγ-dipalmitin*, m. p. 59·5°, n_D^{80} 1·4374, and *β-margaro-αγ-distearin*, m. p. 66·4°, n_D^{80} 1·4387. The unsymmetrical mixed triglycerides prepared by the method of Fischer (*loc. cit.*) include *α-margaro-βγ-dipalmitin*, m. p. 57·8°, n_D^{80} 1·4382, *α-margaro-βγ-distearin*, m. p. 63·8°, n_D^{80} 1·4389, *α-palmito-βγ-dimargarin*, m. p. 57·3°, n_D^{80} 1·4364, and *α-stearo-βγ-dimargarin*, m. p. 62·5°, n_D^{80} 1·4377. *γ-Margaro-αβ-dibromohydrin*, m. p. 35·5°, n_D^{80} 1·4574, was also prepared. The lead salts are preferable to the silver salts in these syntheses. E. HOLMES.

Unsaturated acids. G. FLORENCE (Bull. Soc. chim., 1927, [iv], **41**, 440—444).—Owing to migration of the double linking, the preparation of normal αβ-unsaturated acids by the methods of Crossley and Le Sueur (J.C.S., 1899, **75**, 161), Barbier and Leser (A., 1905, i, 628), or Fittig and Mackenzie (A., 1895, i, 204) affords mixtures from which the αβ-acid is separated in poor yield. Knoevenagel's modification of the latter method (A., 1899, i, 144) is unsatisfactory with members of the series lower than valeraldehyde. The following method is general: a solution of acetaldehyde (from paracetaldehyde) in anhydrous ether and malonic acid are allowed to react for 48 hrs. at 0° in presence of dry pyridine. After 24 hrs. at the ordinary temperature to complete the evolution of carbon dioxide, the ether is evaporated, the product acidified with hydrochloric acid, and the αβ-acid is extracted with dry ether. With higher aldehydes or for the preparation of aromatic unsaturated acids, the condensation is effected at the ordinary temperature. R. BRIGHTMAN.

Ill-defined acids of the oleic series. I. Hypogæic acid of ground-nut oil. II. Petroselic acid and the composition of English parsley-seed oil. T. P. HILDITCH and (I.) N. L. VIDYARTHI, (II.) E. E. JONES (J.C.S.I., 1927, **46**, 172—174T, 174—177T).—I. The mixed fatty acids of ground-nut oil have been separated into solid and liquid portions and the most volatile fractions of the methyl esters of these have been hydrolysed and then submitted to alkaline oxidation. θι-Dihydroxystearic acid, m. p. 130°, was the only dihydroxy-acid detected, showing that "hypogæic" or other acid, $C_{16}H_{30}O_2$, does not occur in ground-nut oil. It is suggested that the terms "hypogæic acid" and "physotoleic acid" be deleted from the literature and that the acid $C_{16}H_{30}O_2$, found in quantity in various marine animal oils, be termed palmitoleic acid (Δ⁹-hexadecenoic acid).

II. The fatty oil in the seed of English sheep's parsley (*Petroselinum sativum*) contains the following acids: palmitic, 2%; petroselic, 76%; oleic, 15%, linoleic, 6%; higher saturated acids, 1%. Oxidation of methyl petroselate by potassium permanganate in acetone solution affords good yields of lauric and adipic acids, thus indicating that petroselic acid is Δ⁶-octadecenoic acid (cf. Vongerichten and Kohler, A., 1909, i, 454). The free acid and its elaidic form have m. p. 30° and 52—53°, respectively. Oxidation of petroselic acid by permanganate in ice-cold solution yields εζ-dihydroxystearic acid, m. p. 122°, whilst treatment of methyl petroselate in acetic acid with concentrated hydrogen peroxide furnishes the *methyl* ester, m. p. 65°, of the isomeric εζ-dihydroxystearic acid, m. p. 114—115°.

The non-fatty oil of English parsley seed consists largely of the allyl phenolic ether, myristicin, and contains little if any apiole; some petroselane, $C_{20}H_{42}$, and non-volatile substances of undetermined character are also present. The English oil thus resembles the French oil rather than the German variety, in which apiole usually predominates.

Reduction of linolenic and linoleic bromides and rebromination of the free acids. F. L. SMITH and A. P. WEST (Philippine J. Sci., 1927, **32**, 297—312).—Philippine lumbang oil consists mainly of the glycerides of linolenic, linoleic, and oleic acids (cf. Santiago and West, B., 1927, 304). The mixed acids obtained by hydrolysis of the oil yielded on bromination crystalline α-linolenic hexabromide. The product obtained by reduction and re-bromination of this substance contained 46·8% of α-hexabromide (m. p. 180—182°) and 53·2% of the liquid β-linolenic hexabromide, a behaviour which has previously been observed in the case of linolenic acid from linseed oil (Erdmann and Bedford, A., 1909, i, 357), indicating that the molecular rearrangement occurs during the reduction of the hexabromide and not during rebromination. Four isomeric linoleic tetrabromides were prepared from lumbang oil (Santiago and West, *loc. cit.*): linoleic tetrabromide (m. p. 112·3—114·3°), γ-linoleic tetrabromide (liquid), and a mixture (m. p. 59·6°) containing β- and δ-tetra-

bromides. Reduction and re-bromination of this mixture gave no β-tetrabromide, but only α- and γ-tetrabromides in the proportion 1 : 2. The α-tetrabromide gave, on reduction and re-bromination, a mixture containing 48% of α- and 48% of γ-tetrabromide, whilst γ-tetrabromide was recovered unchanged after the same treatment. These results are not in agreement with those obtained by Takahashi with linoleic acid from soya-bean oil (A., 1919, i, 468). The two linolenic and the four linoleic acids are regarded as geometrical isomerides, and configurations are tentatively assigned to them in accordance with the m. p. of the corresponding bromide. A special apparatus used for the reduction of bromo-derivatives of unsaturated acids is described. W. J. Powell.

Synthesis of compounds similar to chaulmoogric acid. II. *dl*-Chaulmoogric acid. G. A. Perkins and A. O. Cruz (J. Amer. Chem. Soc., 1927, **49**, 1070—1077; cf. this vol., 359).—κ-Bromoundecoic acid, m. p. 51°, is obtained in good yields by passing hydrogen bromide through a cooled solution of undecenoic acid in a mixture of aqueous 90% acetic acid and light petroleum. Treatment of the sodium salt with aqueous methyl-alcoholic sodium cyanide yields κ-cyanoundecoic acid, m. p. 57° (cf. Walker and Lumsden, J.C.S., 1901, **79**. 1191). Phosphorus trichloride in toluene converts the latter into the *acid chloride*, which, when condensed with ethyl sodioacetoacetate in toluene, followed by conversion of the product into the sodium derivative, treatment with Δ^2-*cyclo*pentenyl chloride, and hydrolysis, yields dl-λ-*ketochaulmoogric acid*, m. p. 76° (*semicarbazone*, m. p. 123°; *acid amide*, m. p. 108°). Reduction of the sodium salt of the latter with hydrazine and sodium ethoxide at 195—200° yields dl-*chaulmoogric acid*, m. p. 68·5°. This m. p. is not depressed by admixture of natural *d*-chaulmoogric acid, indicating that the *d*- and *l*-isomerides form mixed crystals.

F. G. Willson.

[Chaulmoogra oil.] I. T. Hashimoto (J. Amer. Chem. Soc., 1927, **49**, 1119—1120; cf. A., 1925, i, 1234).—A reply to Power.

F. G. Willson.

Oxidative decomposition of dextrose. II. Oxidation of pyruvic acid. B. Bleyer and W. Braun (Biochem. Z., 1927, **183**, 310—314).—Pyruvic acid in alkaline solution is quantitatively oxidised by chloroamine to acetic and carbonic acids, two equivalents of oxygen being used. This supports the view that oxidation of dextrose by chloroamine which gives similar products, proceeds by way of pyruvic acid (cf. this vol. 341). P. W. Clutterbuck.

Lactones with large rings—the carriers of vegetable musk aroma. M. Kerschbaum (Ber., 1927, **60**, [*B*], 902—909; cf. A., 1913, i, 739).—Lactones with many-membered rings are responsible for the musk aroma of vegetable oils, whereas cyclic ketones with large rings function similarly in animal products (cf. Ruzicka, A., 1926, 614, 615). Musk kernel oil is treated with ice-cold sodium hydroxide to remove free fatty acids and the neutral oil is hydrolysed. The higher fatty acids are liberated from the solution by carbon dioxide, whereby a mixture of much palmitic and little ambrettolic acid is derived, from which the latter acid is isolated by crystallisation from light petroleum followed by crystallisation of the barium salt from water. *Ambrettolic acid* (ω-*hydroxy*-Δ^{ω}-*hexadecenoic acid*), m. p. about 25° (*barium* salt), passes when preserved into the odoriferous lactone and the non-odoriferous lactide. It is converted by water, acetic and hydrochloric acids into a mixture of lactone and *dihydroxyhexadecoic acid*, m. p. 83—84°. Treatment with ozone followed by decomposition of the ozonide converts ambrettolic acid into a mixture of the semialdehyde of pimelic acid (*oxime*, m. p. 111—112°, converted by treatment with acetic anhydride and subsequent hydrolysis into pimelic acid) and a volatile hydroxyaldehyde, $C_9H_{18}O_2$, m. p. 53—56° (*semicarbazone*, m. p. 93—94°; *oxime*, m. p. 100—101°), oxidised to a *hydroxy-acid*, $C_9H_{18}O_3$, m. p. 49—50°, and further to a mixture of azelaic acid and the semialdehyde of azelaic acid (*semicarbazone*, m. p. 162—163°). Reduction of ambrettolic acid in presence of spongy platinum affords dihydroambrettolic (ω-hydroxyhexadecoic) acid, m. p. 92—93° (*acetate*, m. p. 62—63°), identical with the juniperic acid of Bougault and Bourdier (A., 1909, i, 82). Oxidation of the dehydro-acid affords tetradecanedicarboxylic acid, m. p. 124°. *Ambrettolide*, $\begin{matrix}CH\text{-}[CH_2]_5\text{-}CO\\ \|\\ CH\text{-}[CH_2]_7\text{-}CH_2\end{matrix}\!\!>O$, b. p. 185—190°/16 mm., is isolated from neutral musk kernel oil by distillation under reduced pressure, whereby a mixture of fatty esters, farnesol and its acetate, and ambrettolide is derived. Cautious treatment of the mixture with alcoholic sodium hydroxide yields mainly farnesol and ambrettolide, from which the former substance is removed by phthalic anhydride. Catalytic reduction of ambrettolide gives *dihydroambrettolide*, b. p. 175—180°/13 mm., which also has a very pronounced odour of musk. ζ-Hydroxypentadecoic acid is obtained from angelica oil by the method of Ciamician and Silber, and its constitution is established by its oxidation to tridecanedicarboxylic acid, m. p. 113—114°. The hydroxy-acid is transformed into the corresponding bromo-acid, the silver salt of which when heated in xylene affords, in modest amount, a lactone with a strong odour of musk. H. Wren.

Cork. I. F. Zetzsche and G. Rosenthal (Helv. Chem. Acta, 1927, **10**, 346—374).—Hydrolysis of cork with alkali to remove fatty acids involves the simultaneous decomposition of the suberin, the essential constituent of cork, which is avoided by the use of hydrogen peroxide. Crude cork was first treated, in succession, with 0·1% potassium hydroxide solution at the ordinary temperature for 1 day, then 0·1% hydrochloric acid to remove a portion of the phlobaphens (loss of weight 1—2%), and then with a boiling mixture of alcohol and benzene (1 : 1) for 8 hrs. (loss of weight 17—20%). The residual "pure cork" (ash content 0·62—0·91%) was left for several weeks in contact with 2·3—3% hydrogen peroxide in acetic acid solution. This removes all the nitrogenous substances. The resulting product was washed with acetic acid, then with water, treated with a 3% solution of sodium sulphite for 3 days at 25—30° (loss 5—7%), warmed with alcohol

and ether (loss 2—2·5%), and the residue dried over phosphoric oxide. The resulting product, "oxidised cork" (ash content 1·26—1·30%), is a voluminous, slightly yellow substance which possesses the characteristic elasticity and insolubility of the original cork, and is completely free from nitrogen. Hydrolysis of this oxidised cork with boiling *N*-barium hydroxide solution for 4—6 hrs. yields 91·7% of fatty acids and 8·3% of unhydrolysable residue. Similar hydrolysis is effected by water alone at 160° or 180°. Glycerol could not be detected. Treatment with alcoholic hydrogen chloride at the ordinary temperature completely esterifies the fatty acids. Hydrolysis with acids is very slow and incomplete, heating with 83% phosphoric acid for 3 months leaving a considerable portion unattacked. Phellonic acid was isolated after alkaline hydrolysis of this residue. Heated with aniline in a stream of carbon dioxide at 120°, anilide formation occurs, water being evolved, the product containing 15% of the anilino-group; the percentage of nitrogen in the undecomposed portion decreases with increasing percentage decomposition, that obtained by brisk boiling for 5 hrs. being nitrogen-free. "Pure cork" behaves in a similar manner, and both specimens are readily attacked by alcoholic or even aqueous ammonia at the ordinary temperature. Acetylation of the unhydrolysable residue of oxidised cork (ash content 10%, mainly silica) with acetic anhydride and sulphuric acid yields cellobiose octa-acetate corresponding with 50—57% of the ash-free residue, representing a cellulose content of 3·3—4% in oxidised cork, a value higher than that obtained by Zemplen (A., 1913, i, 708; cf. Karrer, A., 1923, i, 276). Treatment with acetic anhydride and zinc chloride converts the cellulose into its triacetate (corresponding with 3·8% of cellulose), but at the same time acetolysis of the oxidised suberin occurs. At 55°, considerable acetylation occurs, but little decomposition; at 65—70°, acetylation of the cellulose is almost complete, whilst at 100° the acetolysis reaches its maximum value. Pure cork behaves similarly, the amount of cellulose isolated, either as such as its acetate, or as cellobiose octa-acetate, being 2·2—2·7%, according to the method employed. Both with pure cork and its unhydrolysed residue when the method of Karrer and his collaborators is employed, the largest portion of the cellulose remains insoluble in the residue and must be determined separately, unless previous oxidation of the cork has been carried out. Treatment of the oxidised cork with ammoniacal copper oxide solution at the ordinary temperature for 17 hrs. yields 3% of cellulose, but simultaneously 85·5% decomposition of the suberin occurs. Pure cork and oxidised cork behave similarly towards hydrolytic and acetylating agents, the chief difference being in the nature of the fatty acids isolated. Those from the former soften at 35° and have iodine value 58, whilst those from the latter soften at 60° and have iodine value 8—12. In neither case was glycerol or other hydroxyl compound isolated, and hence the conversion of suberin into oxidised suberin merely involves the oxidation of unsaturated acids to saturated hydroxy-acids without any fundamental change in structure. The bearing of these results on the constitution of suberin is discussed. The authors consider that the cellulose acts purely as a lattice substance of the cork cells, whilst suberin and oxidised suberin consist of high molecular polymerides of, respectively, unsaturated and saturated oxy-acids, mainly hydroxy-acids. The hypothesis of Schmidt (A., 1910, i, 540) that they are present as anhydrides is unlikely, since on heating oxidised cork with *o*-chlorobenzyl alcohol in pyridine at 80° for several days the sample is recovered unchanged and contains only a trace of halogen. Oxidised cork treated with syrupy phosphoric acid for 1 year was not then attacked by acetic anhydride, but acetylated cork is completely deacetylated by treatment with phosphoric acid for 3 months, 21·8% decomposition occurring simultaneously. J. W. BAKER.

Preparation of ethyl hydrogen oxalate and ethoxalyl chloride. E. FOURNEAU and S. SABETAY (Bull. Soc. chim., 1927, [iv], **41**, 537—540).—Ethyl oxalate (1 mol.) when heated with oxalic acid (1·0—1·03 mols.) at 130° for 3 hrs. affords 60—65% of ethyl hydrogen oxalate, from which ethoxalyl chloride is obtained (yield 70%) on heating with thionyl chloride. Formic acid and acetic acid similarly afford ethyl hydrogen oxalate in lower yield; with acetic acid, the reaction can proceed to the formation of ethyl acetate. Heating under pressure does not afford higher yields. The failure of Contzen-Crowet (A., 1926, 938) to obtain ethyl hydrogen oxalate in this way is due to the lower temperatures employed (cf. also Barré, this vol., 228). R. BRIGHTMAN.

Vanadylmalonic acid and its salts. W. SCHRAMM (Z. anorg. Chem., 1927, **161**, 231—286).—Solutions of ammonium metavanadate are reduced to the vanadyl condition when heated with malonic acid on the water-bath, and after partial neutralisation with ammonium carbonate the solution deposits blue *ammonium vanadylmalonate*, $(NH_4)_2[VO(C_3H_2O_4)_2],4H_2O$, which readily loses water and is converted into the violet *trihydrate*, which is converted by alcohol into the violet to rose-coloured *monohydrate*, yielding the pale violet anhydrous salt at 100—105°. *Vanadylmalonates* of the following organic bases are obtained as sparingly soluble, crystalline precipitates by addition of a suitable salt of the base to a solution of the above ammonium salt: *ethylenediamine* ($1H_2O$), *propylenediamine* (1 and $0·5H_2O$), *guanidine* ($1H_2O$), *triphenylguanidine* (anhydrous), *pyridine* ($2H_2O$), *quinoline* ($2H_2O$), *γ-pyridone* ($1H_2O$), *piperidine* ($4H_2O$), *caffeidine* ($2H_2O$), *cinchonine* ($2·5H_2O$), and *strychnine* (5 and $1H_2O$). *Vanadylmalonates* of the following metals have been prepared in an analogous manner: *silver* ($1H_2O$), *calcium* (5, 4, and $0·5H_2O$), *strontium* (5, 1·75, and $0·5H_2O$), *barium* (6, 5, 0·5, and $0·25H_2O$), *thallium* ($1H_2O$), and *lead* (6, 2·5, and $1·5H_2O$). The alkali metal salts are much more soluble, and can be prepared by neutralisation of the free acid or by double decomposition with the barium or silver salts; the following are described: *lithium* (5 and $0·5H_2O$), *sodium* (2, 1·5, and $0·75H_2O$), *potassium* (4 and $0·5H_2O$), *rubidium* ($3H_2O$), and *cæsium* ($3H_2O$). *Vanadylmalonic acid*, $H_2[VO(C_3H_2O_4)_2]$,aq., may be prepared as bluish-violet, deliquescent crystals by treating a solution of the barium salt with sulphuric

acid and evaporating over sulphuric acid in a vacuum. Digestion of the crystals with alcohol removes 1 mol. of malonic acid from 2 mols. of the complex, yielding *divanadylmalonic acid*, $H_2[(VO)_2(C_3H_2O_4)_3]$aq., the *ammonium* salt of which has been prepared as a deliquescent heptahydrate. *Hydrogen vanadylmalonates* of *ammonium*, *potassium*, *rubidium*, and *cæsium* have been obtained in a more or less pure form. Electrolytic reduction of solutions of ammonium or potassium vanadylmalonates yields emerald-green solutions containing *trimalonatovanadites*, *e.g.*, $K_3[V(C_3H_2O_4)_3]$,aq. Oxidation of barium vanadylmalonate by exposure to the air yields readily soluble yellow needles of *barium hydrogen vanadatomalonate*, $BaH[VO_2(C_3H_2O_4)_2]$aq. A. R. Powell.

Preparation of ethyl adipate and esters in general. R. Locquin and F. Elghozy (Bull. Soc. chim., 1927, [iv], **41**, 445–448; cf. Wahl, A., 1925, i, 880).—Esterification with ordinary alcohol in toluene in presence of hydrogen chloride as catalyst affords 85—88% of the theoretical yield of ethyl adipate, b. p. 134°/177 mm. (cf. Rysselberge, A., 1926, 1238). The mixture is heated (1 hr.) until the azeotropic mixture of alcohol–toluene–water (b. p. 75—78°) no longer distils, a further addition of alcohol and toluene being then made. A third addition affords a quantitative yield of ester. The latter is distilled over direct in a vacuum. The alcohol–toluene mixture can be dehydrated with potassium carbonate and used repeatedly. Glutaric, succinic, decoic, and stearic acids, but not cinnamic acid, are readily esterified in the same way. Adipic acid is obtained in 68% yield by oxidising *cyclo*hexanol with boiling nitric acid, *d* 1·33 (cf. A., 1908, i, 393). R. Brightman.

Pyrogenic reactions for malic, tartaric, and citric acids. J. A. Sanchez (Anal. Asoc. Quím. Argentina, 1926, **14**, 356—365).—Malic acid on being heated cautiously in a test-tube yields a white microcrystalline sublimate of fumaric acid, which gives, on dissolving it in ammoniacal water, boiling to remove excess of ammonia, and adding a few drops of 5% silver nitrate solution, a dense white precipitate insoluble in the cold but soluble on heating. The reaction takes place equally in presence of citric and tartaric acids. Both tartaric and citric acids on being heated yield a sublimate of pyruvic acid, which can be recognised by dissolving in water, adding a few drops of 30% sodium hydroxide solution, and then *o*-nitrobenzaldehyde, when indigotin is formed on warming. Citric acid may be distinguished from tartaric acid by the fact that the sublimate from its pyrogenic decomposition yields a precipitate with silver nitrate in the same way as the sublimate from malic acid, from which, however, it may be distinguished by not being microcrystalline. Citric acid may be demonstrated in a mixture of the three acids by heating the solution with a few drops of 2% potassium permanganate solution, acidifying if necessary with acetic acid, adding Imbert's reagent, consisting of equal volumes of 10% sodium nitroprusside solution and glacial acetic acid, and then pouring aqueous ammonia down the side of the inclined test-tube, when a violet ring is produced which changes subsequently to green. Malic and tartaric acids also give the violet ring, but the colour changes to yellow instead of green. The pyrogenic reactions described are not shown by salts. These should be decomposed by addition of a mineral acid.
G. W. Robinson.

Polariscopy of molybdatomalates. L. W. Andrews (Proc. Iowa Acad. Sci., 1925, **32**, 267—298).—The optically active complex in mixtures of malic acid and molybdates is a monobasic acid containing a six-membered ring. The positive rotation acquired by a mixture of a malate and an alkali molybdate on acidification is maximal when acetic acid is used; the effect is a specific character of the acid employed, and is not in the order of the relative "avidities." When the mixture is strongly acid, the effect is a nearly linear function of the malic acid concentration. The reaction can be applied to the determination of malic acid. The reaction between a malate and a molybdate is not instantaneous, but the rotation attains a constant value in about 1 day. Citrates enhance the rotation of molybdatomalic complexes in presence of free acid; this fact can be applied to the determination of citrates, either alone or in presence of malate.
Chemical Abstracts.

Uranatomalate complex. L. W. Andrews (Proc. Iowa Acad. Sci., 1925, **32**, 299—320).—The uranatomalate complex, to which the enhancement of the optical activity of malic acid by uranyl salts is due, probably has the composition $(O{\cdot}UO_2{\cdot}CO_2{\cdot}CH_2{\cdot}CH{\cdot}CO_2M)_2$ or $0{\cdot}5H_2O$ (*barium* salt). The optical activity of a mixture of solutions of uranyl acetate and sodium malate attains a maximum value in 3—10 hrs.; at great dilution, there is a diminution of the specific rotatory power due to hydrolytic dissociation of the complex. The complex has $M[\alpha]$ 4038° Ventzke in a 200-mm. tube at 20°. The relation between the rotatory power and the concentration of malic acid is tabulated. The densities of uranyl acetate solutions are approximately expressed by $P=179{\cdot}2(d^{25}-1)/d^{25}$, when P=g. per 100 c.c.

The results are applied to the determination of malic acid, in presence and absence of citric acid, and to that of uranium. Chemical Abstracts.

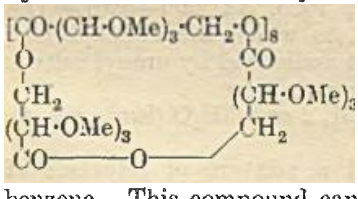
Alkali cuprotartrates. P. Gabiano (Compt. rend., 1927, **184**, 1059—1062).—From the maximum rotations of solutions containing cupric hydroxide and tartaric acid in varying proportions, the existence of the compound $CuT,3H_2O$ (where T represents $H_4C_4O_6$) has been established. Similarly, the existence of the compounds $CuNH_4T,H_2O$ and $CuNaT,2H_2O$ in solutions of $CuT,3H_2O$ in ammonia and sodium hydroxide, respectively, has been demonstrated. They form violet and deep blue solutions, and needle- and plate-shaped crystals, respectively. The existence of $CuNa_2T$ is also indicated. The three cuproalkaline compounds show a circular dichroism, and a relation appears to exist between its magnitude and that of the rotatory power. J. Grant.

Oxonium derivatives of carbopyrotritartaric acid. I. Trefiliev and A. Aisenberg (Ukraine Chem. J., 1926, **2**, 173—181).—It has been shown (*ibid.*, 1925, **1**, 215) that in carbon disulphide solution

bromine reacts with diethyl carbopyrotritartrate with the formation of a product, m. p. 79—80°; iodine similarly affords a *compound*, (?)$C_{12}H_{16}O_5I_4$, m. p. 102—103°. This compound is not decomposed by benzene, but yields iodine and the original ester on treatment with water, or when preserved in a desiccator. Concentrated hydrochloric acid yields ethyl hydrogen carbopyrotritartrate with the diethyl ester. Hydrobromic acid behaves similarly. Hydriodic acid, on the other hand, gives a green *compound*, (?)$C_{12}H_{16}O_5$,2HI, m. p. 93—94°, stable in air and in a desiccator, but decomposed by benzene. Owing to their instability, the tetrahalogenated compounds are believed to be oxonium compounds.

E. Rothstein.

Polymerisation. I. βγδ-Trimethyl *l*-arabonolactone. H. D. K. Drew and W. N. Haworth (J.C.S., 1927, 775—779).—Trimethyl methylarabinoside on hydrolysis with 3% hydrobromic acid, followed by oxidation at 65—70° with bromine, yields crystalline βγδ-trimethyl *l*-arabonolactone, m. p. 45° after softening, $[\alpha]_{}^{21}$ +179·5° (cf. A., 1925, i, 365), $[\alpha]_{6789}^{21}$ +183·5°, $[\alpha]_{5461}^{21}$ +206·3°⟶+17° (after 4 hrs. in water), $[\alpha]_{5461}^{21}$ (benzene) +203·5°. Traces of hydrochloric acid or acetyl chloride cause polymerisation of the lactone to a crystalline *compound* (annexed formula proposed), m. p. 135—138° after sintering at 130°, mol. wt. 1900—2100, $[\alpha]_{5461}$ +39° in benzene. This compound can be converted into the original lactone by heating at 175°/0·03 mm., or by successive treatment with sodium hydroxide solution and hydrochloric acid.



H. Burton.

Synthesis of α-ketogluconic acid. C. Neuberg and T. Kitasato (Biochem. Z., 1927, **183**, 485—488).—Glucosone (20 g.) oxidised with bromine water gives α-keto-*d*-gluconic acid, which can be separated as the calcium salt (yield 18 g.). Aqueous solutions of the acid reduce alkaline copper solutions. The free acid has $[\alpha]_D^{23}$ −75·5°, and the *brucine* salt, m. p. 171° (decomp.), $[\alpha]_D^{20}$ −50·8°.

P. W. Clutterbuck.

Preparation of bismuth thiolacetamide. W. C. Harden and F. Dunning (J. Amer. Chem. Soc., 1927, **49**, 1017—1018).—Antimony thiolacetamide (cf. Rowntree and Abel, J. Pharmacol., 1910, **2**, 108) can be obtained in a crystalline condition by dissolving the oily product (200 g.) in boiling water (1 litre), filtering, and keeping the filtrate at 0° over-night. It has m. p. 139°. *Bismuth thiolacetamide*, $Bi(SCH_2{\cdot}CO{\cdot}NH_2)_3$, m. p. 144·5°, is obtained by treating moist ethyl thiolacetate with bismuth oxide by the method of Rouiller (A., 1919, i, 310), followed by treatment with ammonia, the dark red, viscous product being finally crystallised from water at not above 80°.

F. G. Willson.

Nitrosyl chloride and ketones. E. V. Lynn and F. A. Lee (J. Amer. Pharm. Assoc., 1927, **16**, 309—312).—The action of nitrosyl chloride on undiluted acetone leads to the formation of oximinoacetone and phorone, which is subsequently converted into *phorone mononitrosochloride*, m. p. 175—176°, and an uncrystallisable yellow oil, possibly *phorone dinitrosochloride*, which gradually resinifies. Rheinboldt and Schmitz-Dumont (A., 1925, i, 1131) record the formation of chloro-oximinoacetone, which is not produced unless the acetone is diluted with carbon tetrachloride before treatment with nitrosyl chloride. Methyl ethyl ketone and di-*n*-propyl ketone yield oximino-derivatives only. The production of benzoic acid from acetophenone by oxidation with nitrosyl chloride (cf. Rheinboldt and Schmitz-Dumont, *loc. cit.*) is not confirmed.

W. J. Powell.

Action of hypochlorous acid on αβ-unsaturated ketones and the corresponding tertiary alcohols. J. Pastureau and J. Bader (Rocz. Chem., 1927, **7**, 87—109).—See A., 1926, 382, 1227. In the first abstract quoted, *γ-chloro-β-keto-δ-methylheptan-δ-ol* should be *γ-chloro-β-keto-ζ-methylheptan-δ-ol*.

Preparation of dimethylglyoxime by the action of nitrous and sulphurous acids on ethyl methylacetoacetate. V. Rekschinski (Trans. Inst. Pure Chem. Reagents, Moscow, 1927, 51—57).—After giving a summary of the literature dealing with the preparation of dimethylglyoxime, the author shows that this preparation may be reduced to three simple operations: the dissolution of ethyl methylacetoacetate in sodium hydroxide solution, mixing of the liquid with sodium nitrite solution, and the passage of sulphur dioxide through the mixture. Experiment confirms the preparation of dimethylglyoxime in this way, the process consisting of a number of successive reactions, expressible by the equations

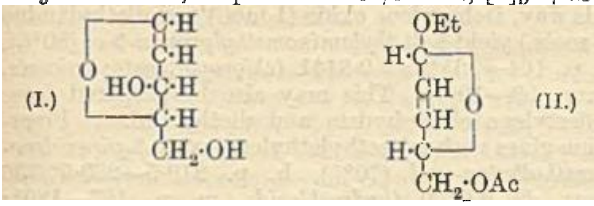
$CHMeAc{\cdot}CO_2Et+2NaOH=CNaMeAc{\cdot}CO_2Na+EtOH+H_2O$; $CNaMeAc{\cdot}CO_2Na+SO_2+H_2O=CHMeAc{\cdot}CO_2H+Na_2SO_3$; $2NaNO_2+SO_2+H_2O=2HNO_2+Na_2SO_3$; $CHMeAc{\cdot}CO_2H+HNO_2=CMeAc{:}NOH+CO_2+H_2O$; $Na_2SO_3+SO_2+H_2O=2NaHSO_3$; $NaNO_2+NaHSO_3+SO_2=OH{\cdot}N(NaSO_3)_2$; $OH{\cdot}N(NaSO_3)_2+2H_2O=NH_2OH,H_2SO_4+Na_2SO_4$; $CMeAc{:}NOH+NH_2OH=NOH{:}CMe{\cdot}CMe{:}NOH+H_2O$.

Dimethylglyoxime may be obtained also by nitrosation of methyl ethyl ketone, separation of the nitrosoketone from the amyl alcohol, and treatment with sulphur dioxide in presence of sodium nitrite.

T. H. Pope.

Arabinal. M. Gehrke and F. X. Aichner (Ber., 1927, **60**, [*B*], 918—922).—Arabinose is converted by the action of acetic anhydride and sodium acetate into *l*(+)-arabinose tetra-acetate, m. p. 96—97°, $[\alpha]_D^{20}$ +42·7° in chloroform, which is transformed by hydrogen bromide in glacial acetic acid into *l*(+)-acetobromoarabinose, m. p. 139° (decomp.), $[\alpha]_D$ +283·6° in chloroform; *d*(−)-*acetobromoarabinose* has $[\alpha]^{22}$ −283·4° in chloroform. Treatment of the latter compounds with zinc dust and acetic acid affords d(+)- and l(−)-*diacetylarabinal*, b. p. 78—82°/0·3—0·4 mm., $[\alpha]_D^{22}$ +266·2° and $[\alpha]_D^{15}$ −266·7° in chloroform (unstable *dibromide*), which are hydrolysed by barium hydroxide to d(+)- and l(−)-*arabinal* (I), b. p. 73—75°/0·1—0·3 mm., m. p. 51—52°, $[\alpha]_D^{23}$ +100·5° and $[\alpha]_D^{20}$ −100·9° in water. Oxidation of *d*(+)-arabinal with perbenzoic acid gives a product yielding a phenylbenzylhydrazone identical with that obtained from *d*(−)-ribose, whilst ribonolactone is derived from *l*(−)-arabinal. Diacetylarabinal is catalytically

hydrogenated in presence of palladium to *diacetyl-dihydroarabinal*, b. p. 122—123°/3 mm., $[\alpha]_D^{22}$ +43·1°



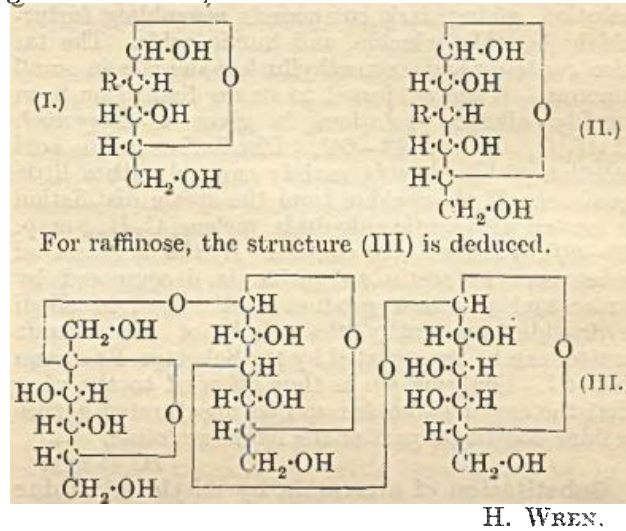
in chloroform, and is converted by successive treatment with boiling water and ammonium chloride, ethyl orthoformate, and anhydrous alcohol into the cyclic *semiacetal* of *monoacetyl-ψ-arabinal* (II), b. p. 77—79°/1 mm., $[\alpha]_D^{22}$ −146·8° in benzene. Arabinodeose, obtained by the action of dilute acids on arabinal, could not be obtained homogeneous; it is oxidised by bromine to the corresponding acid isolated as the *barium* salt, $C_{10}H_{18}O_{10}Ba$. During the distillation of diacetylarabinal, a second fraction, b. p. 117—119°/0·3—0·5 mm., $[\alpha]_D^{22}$ +26·1° in chloroform, is obtained, apparently an *arabinose triacetate*, since it is further acetylated to the tetra-acetate. In the preparation of acetobromoarabinose, a *compound*, $C_{22}H_{30}O_{14}Br$, m. p. 104—105°, $[\alpha]^{18}$ +207·6° in chloroform, is obtained in varying amount.

l(+)- and d(−)-*Arabinose tetrabenzoate*, m. p. 153°, $[\alpha]_D$ +300·8°, and $[\alpha]_D$ −301·1°, are incidentally described. H. WREN.

Reducing power of sugars. P. N. VAN ECK (Pharm. Weekblad, 1927, **64**, 400—406).—Salts of gold, platinum, rhodium, iridium, copper (even as chromate), mercury (in the mercuric state), silver, tungsten, and iron (ferric) are all reduced by dextrose in presence of sodium pyrophosphate; palladium, thallium, nickel, cobalt, bismuth, lead, manganese, zinc, and cadmium salts are not reduced under these conditions. Chromates are reduced to chromic salts. Ferric salts dissolved in excess of the pyrophosphate, and boiled with an aldehydic or a ketonic hexose give a black solution, probably of colloidal iron. Gold salts in presence of pyrophosphate are reduced by lævulose in the cold, by dextrose on boiling; the two sugars may be distinguished by this means in urine. A colorimetric determination of dextrose by reduction of potassium chromate in presence of sodium pyrophosphate is described, and the reducing effects of dextrose, lævulose, sucrose, lactose, maltose, and arabinose are tabulated. S. I. LEVY.

Oxidation of dextrose at the ordinary temperature by oxides of manganese. C. D. INGERSOLL.—See this vol., 528.

Degradation of reducing bioses. V. Constitution of melibiose and raffinose. G. ZEMPLEN (Ber., 1927, **60**, [*B*], 923—930).—Melibiose, obtained by fermentation of raffinose by top yeast, is converted into the corresponding *oxime*, m. p. about 186° (decomp.) after darkening at 184°, $[\alpha]_D^{18}$ +95° in water, which is transformed by acetic anhydride and sodium acetate into a mixture containing about 63% of octa-acetylmelobiononitrile, which could not be further purified economically. Degradation of the crude product by sodium methoxide gives melibioseoxime and melibiononitrile, corresponding with 37% and 16% of the octa-acetyl derivative, and *d*-galacto-*d*-arabinose, corresponding with 40%. Attempts to isolate the latter product were unsuccessful. If the reaction mixture is treated with phenylhydrazine, melibioseoxime is removed as melibiosephenylosazone, and the product contains *d*-galacto-*d*-arabinose as the phenylhydrazone; treatment of the latter compound with benzaldehyde followed by hydrolysis gives a strongly lævorotatory mixture of *d*-arabinose and *d*-galactose. After hydrolysis of the biose, approximately the same amount of arabinose is obtained as the diphenylhydrazone as is derived when hydrolysis precedes removal of melibiosazone. It therefore appears that *d*-galacto-*d*-arabinose is unable to yield an osazone, and hence has the constitution (I) and melibiose the formula (II) (R—galactose residue).



H. WREN.

Aucubin. M. BERGMANN and G. MICHALIS (Ber., 1927, **60**, [*B*], 935—942; cf. Bourquelot and Herissey, A., 1904, i, 606).—The glucoside, aucubin, obtained from the seeds of *Plantago lanceolata* by a modification of the process of Bourdier (A., 1907, i, 864), has m. p. 181° (corr.), (hydrated) $[\alpha]_D^{21}$ −171·4° (anhydrous), $[\alpha]_D^{3}$ −179·1° in aqueous solution. Analyses of the glucoside and its derivatives indicate the composition $C_{15}H_{22}O_8,H_2O$ for the glucoside, but determinations of mol. wt. in various solvents indicate a tendency to dissociation into smaller fragments, so that the formula must at present be regarded merely as a record of atomic proportions. In aqueous solution, aucubin absorbs almost exactly 2 mols. of bromine and evolves 2 mols. of hydrogen bromide. With acetic anhydride and pyridine, anhydrous aucubin affords the *acetyl* derivative, $C_{15}H_{16}O_9Ac_6$, m. p. 128° (corr.), $[\alpha]_D^{18}$ −154·9° in *s*-tetrachloroethane, which is converted by bromine in methyl-alcoholic solution into a mixture of *monobromoaucubin hexa-acetate* A and B, m. p. 181·5°, $[\alpha]^{20}$ −64·4° in *s*-tetrachloroethane, and m. p. 127°, $[\alpha]^{20}$ −122·7° in *s*-tetrachloroethane, respectively; in chloroform solution, *aucubin hexa-acetate dibromide*, decomp. 111°, is obtained. H. WREN.

Hemicellulose. E. HEUSER (Papierfabr., 1927, **25**, 238—243).—Polemical. On treating an alkaline solution of hemicellulose with cupric sulphate, a

complex copper–alkali–cellulose compound is precipitated which rapidly absorbs carbon dioxide, forming a depolymerised cellulose derivative, $(C_6H_{10}O_5)_2,Cu(OH)_2,Na_2CO_3$. Xylan and mannan under the same conditions form complex compounds of similar composition. W. J. Powell.

Thermal fission of pine lignin. I. Silver distillation of technical Willstatter lignin. W. Fuchs (Ber., 1927, 60, [*B*], 957—962).—Dry distillation of a mixture of technical Willstatter lignin and silver powder at 280—300° gives about 10% of distillate consisting of an aqueous and a tarry layer. The former contains pyrocatechol, a little guaiacol and organic acid, and 5-hydroxymethylfurfuraldehyde. The last-named substance readily condenses with pyrocatechol and its derivatives in faintly alkaline solution, giving dark compounds resembling furfuraldehyde, phloroglucide, and humic acids. The tar also contains hydroxymethylfurfuraldehyde in small amount. When subjected to steam distillation from weakly alkaline solution, it gives a *compound*, $C_{15}H_{14}O_2$, m. p. 63—64°. Distillation from acid solution yields phenols, mainly eugenol with a little guaiacol. If the residue from the steam distillation is treated with acetic anhydride, melene, $C_{30}H_{60}$, m. p. 59—60°, remains undissolved. If the solution of substances in acetic anhydride is decomposed by water and the dark product is dissolved in alkali hydroxide, practically the whole of the organic matter can be benzoylated by the Schotten–Baumann method. Confirmation is thus afforded to the view that the eugenol complex and an unsaturated hexose residue constitute part of the lignin molecule.

H. Wren.

Substitution of ammonia by ethylenediamine in complexes in solution. P. Job (Compt. rend., 1927, 184, 1066—1068; cf. A., 1926, 791; this vol., 205).—The existence of the complex $[Cu\ en_2]^{\cdot\cdot}$ in a stable form has been demonstrated and its equilibrium constant (k) determined from measurements of the absorption of mixtures of copper nitrate and ethylenediamine. Similarly, $[Tl(NH_3)]^{\cdot}$ and $[Tl\ en]^{\cdot}$ have been shown to exist, and the values of k verified by solubility measurements in water and in ammonia of various strengths. The latter complex is the more stable. Contrary to the rule established for copper, but not for silver complexes (A., 1923, i, 902), ethylenediamine replaces ammonia molecule for molecule.

J. Grant.

Reaction between α-oxides and ammonia or amines. K. Krassusky [with A. Stepanoff, K. Kossenko, and T. Kussner] (J. pr. Chem., 1927, [ii], 115, 315—334).—The view of Knorr (A., 1899, i, 461) that water facilitates combination between α-oxides and bases by increasing the ionisation of the latter is confirmed by the observation that the stronger a base is the more readily it reacts. The nature of the ions formed and the mode of addition to the α-oxide are discussed. The intermediate formation of a glycol cannot be assumed, since glycols are found not to react with bases under these conditions.

When dry mixtures of the following amines and α-oxides are heated together, only small amounts of amino-alcohols are formed even on prolonged treatment, but in approximately 33% aqueous solution the reaction proceeds readily in a sealed tube at 100°. In this way, *iso*butylene oxide (1 mol.) and diethylamine (2 mols.) yield β-*diethylaminomethylpropan-β-ol* (80%), b. p. 164—165°, d_0^{20} 0·8441 (*chloroplatinate*; *picrate*, m. p. 99—100°). This may also be prepared from *iso*butylene chlorohydrin and diethylamine. Piperidine gives with trimethylethylene oxide β-*piperidino-γ-methylbutan-γ-ol* (70%), b. p. 219·5—220·5°/756 mm., d_0^{20} 0·9200 (*hydrochloride*, m. p. 187—189°; *chloroaurate*, m. p. 73—74°; *picrate*, m. p. 122—123·5°); with *iso*butylene oxide, β-*piperidinomethylpropan-β-ol* (80%), b. p. 202—202·5°/753 mm., d_0^{20} 0·9114 (*hydrochloride*, m. p. 191—192°; *chloroaurate*, m. p. 118—119°; *picrate*, m. p. 111·5°), and with *iso*safrole oxide, α-3 : 4-*methylenedioxyphenyl*-β-*piperidinopropan-α-ol*, m. p. 76° [*hydrochloride*, m. p. 219—220°; *chloroplatinate* ($+2H_2O$, one of which is given off at 100°), m. p. 157—160° (decomp.); *picrate*, m. p. 158—159°]. H. E. F. Notton.

Organic catalysts. I. Isatin and its derivatives as catalysts for the dehydrogenation of amino-acids. W. Langenbeck (Ber., 1927, 60, [*B*], 930—934).—The decomposition of *dl*-alanine, *l*-asparagine, or glutamic acid into aldehyde, carbon dioxide, and ammonia in 50% acetic acid solution in an atmosphere of carbon dioxide in presence of isatin is accompanied by the separation of isatide. Since the isatide is readily converted into isatin by air, the oxidation of several molecules of the amino-acid by 1 mol. of isatin with access of oxygen is simply explained. Similar results are obtained with *N*-methylisatin and potassium isatin-5-sulphonate, the latter substance being particularly useful, since it permits operations in aqueous solution. Dehydrogenation can be effected in absence of air if methylene-blue is used as hydrogen acceptor, since isatide is able to convert the dye into its leuco-derivative with regeneration of isatin. H. Wren.

Separation of arginine and histidine. II. Separation of silver compounds at p_H 7·0. H. B. Vickery and C. S. Leavenworth (J. Biol. Chem., 1927, 72, 403—413).—If a solution containing a mixture of histidine and arginine, together with excess of a soluble silver salt, be brought to p_H 7·0, the silver compound of histidine is completely precipitated; adjustment of the filtrate to p_H 10—11 by addition of barium hydroxide causes quantitative precipitation of the silver compound of arginine; complete saturation of the solution with barium hydroxide at this stage is undesirable. The silver salts can be decomposed with hydrochloric acid and the amino-acids recovered as dinitronaphtholsulphonates.

C. R. Harington.

Basic choline derivatives. S. Frankel and K. Nussbaum (Biochem. Z., 1927, 182, 424—433).—Choline dichloride, prepared by keeping trimethylamine and dichloroethane in alcoholic solution [*chloroplatinate*, m. p. 250—260° (decomp.)], is converted by ammonia into α-*amino*-β-*chlorotrimethylaminoethane* (*chloroplatinate*), by methylamine into α-*methylamino*-β-*chlorotrimethylaminoethane* (*compound* with cadmium chloride, m. p. 80°, decomp. 200°; *chloroplatinate*, m. p. 80°, decomp. 225°), by trimethyl-

amine into αβ-*dichlorotrimethylaminoethane* (*compound* with cadmium chloride; *chloroplatinate*, m. p. 80°, decomp. 220°; *chloroaurate*, m. p. 165°).

P. W. CLUTTERBUCK.

Amino-derivatives of the sugars. II. [Addendum.] H. VON EULER and E. BRUNIUS (Ber., 1927, **60**, [*B*], 992—997, 997—999; cf. A., 1926, 714).—The cryoscopic method indicates the occurrence of a condensation between serum-albumin and lævulose, the extent of which is much smaller than that indicated by Pringsheim and Winter (Ber., 1927, **60**, 278). Witte's peptone behaves similarly to glycine in that it causes an immediate but slight diminution in the total number of molecules when mixed with lævulose, whereas with dextrose a gradual effect is observed which increases with increasing alkalinity between 7·08 and 7·90. Combination does not appear to occur between dextrose and blood-serum. In all cases, the cryoscopic method indicates less complete condensation than the reduction method.

[*Addendum.*]—Pringsheim and Winter's results with regard to the condensation of Witte's peptone with dextrose, as judged by Bertrand's method, are confirmed, but polarimetric observation of solutions of the components singly and after admixture does not give any indication of chemical union between them. Egg-albumin appears to condense with dextrose according to the reduction method, but the polarimetric method is not applicable, since sufficiently definite readings cannot be obtained. H. WREN.

Condensation between sugars and proteins. S. P. L. SORENSEN and L. LORBER (Ber., 1927, **60**, [*B*], 999—1006).—Bertrand's method is not suitable for the detection of combination between sugars and proteins, since it is not established that free sugar in presence of proteins can be determined quantitatively by oxidation with Fehling's solution. The constancy of relationship between protein and sugar observed by Pringsheim and Winter (*ibid.*, 278) could not be confirmed, since with casein and dextrose the proportion of " combined sugar " per gram of protein is found to increase with increase in amount of the sugar. Maltose and lactose do not appear to require the lapse of time before maximal concentration is attained. The use of ammonium sulphate for the removal of proteins is unsatisfactory; the presence of small amounts of ammonium sulphate does not influence the reduction of Fehling's solution, but reduction is inhibited if the amount of the salt is equivalent to that of the alkali hydroxide in the solution. Egg-albumin can be removed quantitatively by coagulation at the optimal hydrogen-ion concentration or by saturation of the solution with potassium or sodium sulphate, whilst casein can be eliminated by means of zinc sulphate or sodium potassium sulphate with or without addition of acid; in the filtrates from such solutions, the whole of the sugar is found analytically.

Attempts to obtain evidence concerning the condensation between sugars and proteins by polarimetrio methods have not yielded definite results. Experiments on the diffusion of solutions of egg albumin and dextrose separated by a collodion membrane indicate a slight condensation. H. WREN.

Diaminododecanedicarboxylic acid from caseinogen. S. FRÄNKEL and M. FRIEDMANN (Biochem. Z., 1927, **182**, 434—441).—From the filtered solution obtained by prolonged digestion of caseinogen with pancreatin was obtained an acid, $C_{12}H_{26}O_5N_2$, m. p. 255·4°, containing two amino- and two carboxyl groups which corresponded with the diaminotrihydroxydodecoic acid of Fischer and Abderhalden (A., 1904, i, 1066), but not with Skraup's caseic acid, $C_{12}H_{26}O_5N_2$ (A., 1904, i, 539, 955). This acid, whilst not decreasing in weight by heating at 120°, lost 1 mol. of water by heating above this temperature, yielding the pure diaminodicarboxylic acid, $C_{12}H_{24}O_4N_2$, m. p. 261·5°, which sublimes unchanged and gives a diester hydrochloride, m. p. 120·5°, which readily yields the diester, m. p. 210°. The diaminotrihydroxydodecoic acid of Fischer and Abderhalden is therefore $C_{10}H_{18}(NH_2)_2(CO_2H)_2,H_2O$.

P. W. CLUTTERBUCK.

Imide chlorides and imide bromides of aliphatic acids. II. J. VON BRAUN, F. JOSTES, and W. MÜNCH (Annalen, 1927, **453**, 113—147).—The halogenation of imide chlorides and bromides (cf. this vol., 231) is greatly simplified by using phosphorus pentachloride or pentabromide in place of free halogen. By this method, a halogenated imide halide can be obtained from an acid amide in one operation and the risk of halogenating aromatic residues in the compound is diminished. Amides of the type $CR_3{\cdot}CO{\cdot}NHR'$ (R = hydrocarbon residue or halogen) are converted into imide halides when warmed with these reagents, but are not further attacked, whilst amides $CHR_2{\cdot}CO{\cdot}NHR'$, $CH_2R{\cdot}CO{\cdot}NHR'$, and $CH_3{\cdot}CO{\cdot}NHR'$ react with 2, 3, and 4 mols. of phosphorus pentahalogenide, respectively, with introduction of 1, 2, and 3 atoms of halogen in the α-position. Partial halogenation of the two last-named types, using smaller quantities of reagent, affords a single product only when R' is an aryl or aralkyl group; for instance, chloroacetethylamide and 2 mols. of phosphorus pentachloride give, after decomposition of the product with water, a mixture of mono-, di-, and tri-chloroacetethylamides, whilst chloroacetanilide is quantitatively converted by similar treatment into dichloroacetanilide. Hydrolysis of the new amides by means of concentrated halogen acids proceeds smoothly except in the case of those of the type $CHClBr{\cdot}CO{\cdot}NHR'$, when substitution can be avoided only by using an equimolecular mixture of hydrobromic and hydrochloric acids. α-Bromopropionethylamide and phosphorus pentachloride give *αα-chlorobromopropionethylimide chloride*, b. p. 72—86°/15 mm., from which *αα-chlorobromopropionethylamide*, m. p. 54°, b. p. 105°/16 mm., is obtained. The latter is hydrolysed by concentrated hydrochloric acid at 115—120° to a mixture containing much dichloropropionic acid; only with the mixed acids can pure *αα-chlorobromopropionic acid*, b. p. 101°, $d_4^{22\cdot5}$ 1·694 (*β-phenylethylimide chloride*, b. p. 164—167°/11 mm.; *β-phenylethylamide*, m. p. 78°), be obtained. Amides, $CH_2R{\cdot}CCl_2{\cdot}CO{\cdot}NHR'$, in which R is a heavy radical, tend to lose hydrogen chloride on hydrolysis with formation of unsaturated acids. *δ-Phenylvalerethylamide*, b. p. 200—202°/12 mm., gives successively *αα-dichloro-δ-phenylvalerethylimide chloride*, b. p. 178°/

12 mm., and *αα-dichloro-δ-phenylvalerethylamide*, m. p. 53°, b. p. 195°/12 mm. This is hydrolysed to a *product*, b. p. 155—160°/1 mm., which probably contains mainly α-chloro-δ-phenyl-Δ^{α}-butene-α-carboxylic acid. Attempts to chlorinate a series of acid chlorides with phosphorus pentachloride under various conditions showed that these substances react much less readily than the imide chlorides and always yield mixtures of products. The new reaction affords a rapid and convenient method of determining the number of hydrogen atoms in the α-position to a carboxyl group. The following compounds were also prepared: the *methylamide*, b. p. 150—152°/16·5 mm., and *methylimide chloride*, b. p. 125—127°/15 mm., of campholic acid; *fencholic phenylimide chloride*, b. p. 165°/11 mm.; *α-chloroisobutyrphenylimide chloride*, b. p. 115—117°/15 mm.; *hexahydrobenzethylamide*, m. p. 95°; *α-chlorohexahydrobenzoic acid*, b. p. 138—140°/13 mm. (*acid chloride*, b. p. 83—85°/13 mm.; *amide*, m. p. 110°; *ethylamide*, m. p. 53°, b. p. 131—132°/13 mm.; *ethylimide chloride*, b. p. 96—105°/13 mm.); *dichloroacetphenylimide chloride*, b. p. 127—129°/14 mm.; *trichloroacetphenylimide chloride*, m. p. 35—37°, b. p. 136—138°/14 mm.; *dichloroacet-p-tolylimide chloride*, m. p. 52°, b. p. 145°/15 mm.; *trichloroacet-p-tolylimide chloride*, m. p. 64—65°, b. p. 155—157°/15 mm.; *trichloroacet-p-toluidide*, m. p. 111°, b. p. 180—182°/13 mm.; *αα-dichloropropionic acid*, b. p. 90—92°/14 mm., d_4^{28} 1·389 (*acid chloride*, b. p. 68—73°/88—90 mm.; *amide*, m. p. 117—118°; *ethyl* ester, b. p. 83—85°/53 mm.; *ethylamide*, m. p. 51—52°; *ethylimide chloride*, b. p. 66—67°/17 mm.; *anilide*, m. p. 101°; *phenylimide chloride*, b. p. 128—130°/14 mm.; *αα-dichloro-n-butyric acid*, b. p. 107—110°/14 mm. (*acid chloride*, b. p. 48—50°/16 mm.; *amide*, m. p. 51°; *ethyl* ester, b. p. 71°/16 mm.; *anilide*, b. p. 165—168°/16 mm.; *ethylimide chloride*, b. p. 72—75°/14 mm.; *ethylamide*, b. p. 98—100°/14 mm.; *phenylimide chloride*, b. p. 145—150°/13 mm.); *palmitethylamide*, m. p. 72°; *αα-dichloropalmitic acid*, m. p. 35—37° (*ethylamide*, m. p. 40—41°; *anilide*, m. p. 49—52°); *stearethylamide*, m. p. 78°; *αα-dichlorostearic acid*, m. p. 51—53° (*ethylamide*, m. p. 45—49°; *anilide*, m. p. 54°); *γ-phenylbutyrethylamide*, b. p. 190—192°/13 mm., m. p. 36°; *αα-dichloro-γ-phenylbutyric acid*, m. p. 90° (*ethylamide*, b. p. 187—188°/12 mm.; *ethylimide chloride*, b. p. 170—172°/16 mm.); cyclo*hexylacetethylamide*, m. p. 72°, b. p. 163°/13 mm.; *αα-dichlorocyclohexylacetic acid*, solid, b. p. 155°/12 mm. (*ethylamide*, m. p. 93—94°; *ethylimide chloride*, b. p. 140—145°/16 mm.); the *benzylimide chloride*, b. p. 144—147°/15 mm., *β-phenylethylimide chloride*, b. p. 155—160°/17 mm., and *β-phenylethylamide*, m. p. 78°, of dichloroacetic acid; the *benzylimide chloride*, b. p. 148—153°/11 mm., *benzylamide*, m. p. 90—91, *β-phenylethylimide chloride*, b. p. 160—170°/12 mm., and *β-phenylethylamide*, m. p. 112—113°, of trichloroacetic acid; *bromoacetethylamide*, m. p. 49°; *αα-chlorobromoacetphenylimide chloride*, b. p. 145°/14 mm., and *αα-chlorobromoacetanilide*, m. p. 119—120°.

H. E. F. Notton.

Interaction between guanidine and nucleic acid. F. D. White (Trans. Roy. Soc. Canada, 1926, III, **20**, [v], 321—329).—The inhibition of the precipitation of guanidine as the picrate by nucleic acid (cf. White and Cameron, A., 1926, 1180) is due to the formation of a complex picrate containing phosphorus, the exact nature of which has not been determined. The method of Vines (Brit. Med. J., 1923, **2**, 559) for standardising parathyroid preparations is, therefore, of no value. Small amounts of a compound of creatine and nucleotides have been isolated, but the amount was too small for a complete analysis. These last compounds may have a bearing on the combination of creatine in muscle. A. Wormall.

Formation of nitriles by the diazo reaction. A. Korczynski and B. Fandrich (Rocz. Chem., 1927, **7**, 110—111).—See A., 1926, 1037.

Carbimides. IV. 1 : 3 : 5-Oxdiazines. K. H. Slotta and R. Tschesche.—See this vol., 578.

Carbimides. V. Condensations of methylcarbimide, particularly with hydrocyanic acid. K. H. Slotta and R. Tschesche (Ber., 1927, **60**, [*B*], 1021—1025; cf. this vol., 346).—Methylcarbimide does not condense with hydrogen sulphide, phenylthiocarbimide, acetonitrile, nitromethane, acetylene, ethylene, or amylene. With aldehydes, aldoketens, carbon suboxide, and cyanic acid, polymerisation occurs so much more readily than condensation that only their polymerides and trimethyl *iso*cyanurate are obtained. Dimethyl- and diphenyl-keten do not condense with methylcarbimide. With diazomethane, *methyl methylcarbamate*, b. p. 61°/10 mm., is produced, which is not necessarily derived from a condensation product. Azoimide and methylcarbimide afford methylaminoformazide, m. p. 46°, whereas, in presence of triethylphosphine, the *compound*

(?) NHMe·CO·N$<^{\mathrm{NMe}}_{\mathrm{N=N}}>$C:NH, decomp. 228°, is obtained. With anhydrous hydrocyanic acid in ethereal solution in presence of triethylphosphine, methylcarbimide gives *methylaminoformyl cyanide*, m. p. 80°, which is also obtained when the carbimide is passed through a tube filled with glass beads heated to dull redness. It is converted by alkali hydroxide into ammonia, methylamine, and oxalic acid, by hydrogen sulphide into methylthio-oxamide, NHMe·CO·CS·NH_2, m. p. 127°, and by hydrogen peroxide into methyloxamide, m. p. 235°. Methylcarbimide (2 mols.) and hydrocyanic acid (1 mol.) in presence of triethylphosphine give *NN′-dimethylallophanyl cyanide*, NHMe·CO·NMe·CO·CN, m. p. 113—115°, converted by acids into dimethylparabanic acid and by sodium carbonate solution into dimethyloxamide. The open-chain constitution of the compound is supported by its conversion into the *amidoxime*, NHMe·CO·NMe·CO·C(NH_2):NOH, decomp. 125°.

H. Wren.

Synthesis of bromovinylarsines. E. Schmidt (Rocz. Chem., 1927, **7**, 136—137).—See this vol., 233.

Mechanism of the reaction between chromic chloride or chromous chloride and magnesium phenyl bromide. Univalent chromium. F. Hein, J. Reschke, and F. Pintus (Ber., 1927, **60**, [*B*], 749—753).—Treatment of the products formed by the action of magnesium phenyl bromide on chromic chloride with water results in the evolution

of large amounts of hydrogen supplemented by further quantities after subsequent addition of acid. The initial production of hydrogen cannot be ascribed to chromous chloride, since it is also induced by concentrated sodium acetate solution, which transforms bivalent chromium into the sparingly soluble acetate. The formation of metallic chromium is rendered improbable by the observation that the reaction product, after purification from excess of Grignard's reagent and chromium phenyl compounds by repeated treatment with ether or a concentrated ethereal solution of diphenyl, does not evolve hydrogen when treated with sodium acetate, and yields only small amounts of gas after subsequent addition of acid. Successive additions of sodium acetate and acid to the product obtained from chromous chloride and magnesium phenyl bromide cause in each case very marked evolution of hydrogen. The primary phase of the action on chromic chloride is probably $3CrCl_3 + 4MgPhBr \longrightarrow CrPh_4Cl + 2MgBr_2 + 2MgCl_2 + 2CrCl_2$, followed by the change $4CrCl_2 + 4MgPhBr \longrightarrow CrPh_4Cl + 3CrCl + 2MgCl_2 + 2MgBr$ the initial evolution of hydrogen being attributed to the unknown chromium monochloride. With magnesium phenyl bromide, a portion of the liberated hydrogen is utilised in hydrogenating the aromatic complex; evolution of hydrogen is therefore much more pronounced when magnesium *cyclo*hexyl bromide is employed.

H. WREN.

Relationship between complex-constitution and formation of organo-metallic derivatives in the case of chromium salts. F. HEIN, J. RESCHKE, and F. PINTUS (Ber., 1927, **60**, [*B*], 679—687).—The additive compound of chromic chloride and pyridine and the salt $[CrCl_3(ClK)_2OH_2]$ appear to be more readily converted by magnesium phenyl bromide into chromium phenyl compounds than is chromic chloride itself (cf. A., 1919, i, 232; 1921, i, 826; 1922, i, 76, 77). On the other hand, the salts $[Cr(NH_3)_6]Cl_3,H_2O$ and $[Cr\,en_3]Cl_3,3\frac{1}{3}H_2O$ do not yield organo-chromium derivatives under similar conditions, and may be almost quantitatively recovered. Equal indifference is shown by the compounds $[Cr(NH_3)_5Cl]Cl_2$ and $[CrCl_2\,en_2]Cl$, whereas the substance $[CrCl_2(OH_2)_4]Cl,2H_2O$ appears to yield small amounts of chromium phenyl derivatives, possibly owing to transformation into the non-electrolyte, $[Cr(OH_2)_3Cl_3]$. Anhydrous chromic bromide reacts more readily than chromic chloride with magnesium phenyl bromide, whereas the compounds $[Cr(NH_3)_6]Br$, $[Cr\,en_3]Br_3$, and $[Cr\,en_3]I_3$ are completely passive. It appears, therefore, that replacement of the halogen atoms of complex derivatives of chromium chloride and bromide by organic residues is possible only when at least three halogen atoms are in direct, non-ionic union and masking ions are not present in the outer sphere. Chromium fluoride, on the other hand, does not yield a trace of organo-chromium compounds, whereas its additive compound pyridine appears to be reduced by magnesium phenyl bromide, as indicated by almost quantitative conversion of the latter into diphenyl (cf. Turner, J.C.S., 1914, 105, 1057). Similar behaviour is shown by the compounds $[CrF_3(OH_2)_3]OH_2$ and $[CrF_6](NH_4)_3$. The abnormal behaviour of fluorine compounds is further illustrated by the indifference of lead difluoride towards magnesium phenyl bromide under conditions which, with lead dichloride, afford lead and lead tetraphenyl. Anhydrous chromic sulphate is not attacked, whereas chromic thiocyanate reacts with magnesium phenyl bromide without producing chromium phenyl derivatives; similar results are obtained with the compounds $[Cr(NH_3)_2(SCN)_4]K$ and $[Cr(NH_3)_2(SCN)_4]Cu$. Anhydrous chromous chloride and acetate are converted by magnesium phenyl bromide into organo-chromium compounds, and hence are regarded as pseudo-salts. H. WREN.

Reduction of organic halogen compounds. VIII. ββγγ-Tetrachloro-αxδδ-tetra-*p*-tolylbutane and its derivatives. IX. Catalytic reduction of ααα-trichloro-ββ-diarylethanes. K. BRAND [with G. WENDEL and O. HORN] (J. pr. Chem., 1927, [ii], **115**, 335—350, 351—378).—Catalytic hydrogenation of ααα-trichloro-ββ-di-*p*-tolylethane in pyridine–alcohol solution, using palladised calcium carbonate, gives *ββγγ-tetrachloro-αxδδ-tetra*-p-*tolylbutane*, m. p. 178°, and small amounts of 4 : 4′-dimethylstilbene and two stereoisomeric *βγ-dichloro-αxδδ-tetra*-p-*tolyl*-Δ^{β}-*butenes*, m. p. 164—165°, and m. p. 193—194°, respectively. The last three are also obtained in small yield when a boiling solution of trichloroditolylethane in aqueous alcohol (*d* 0·815) is reduced with Devarda's or Arnd's alloy. When the tetrachlorotetratolylbutane is reduced with zinc dust and alcohol or glacial acetic acid, the principal product is the dichlorotetratolylbutene, m. p. 164—165°, which does not react with bromine, but palladium and hydrogen give mainly the isomeride of m. p. 193—194°. When either form is boiled with alcoholic potassium hydroxide, it yields yellow *αxδδ-tetra*-p-*tolyl*-$\Delta^{\alpha\beta\gamma}$-*butatriene* (I), m. p. 242°, and a reddish-brown *oil* (? 2-*hydroxy*-1-p-*tolyl*-5-*methyl*-3-*di*-p-*tolylmethylindene*), converted by boiling glacial acetic acid into 1-p-*tolyl*-5-*methyl*-3-*di*-p-*tolylmethylene*-*indene*, $Me\cdot C_6H_4\cdot C(C_6H_4\cdot Me)_2$ / $C_6H_3\cdot CH$ / $C\cdot C_6H_4\cdot Me$ m. p. 192—193°; (I) is oxidised by chromic acid mixture to di-*p*-tolyl ketone and carbon dioxide, and hydrogenated in presence of palladium to *αxδδ-tetra*-p-*tolyl*-Δ^{α}- or -Δ^{β}-*butene*, m. p. 151°, as well as the corresponding butane and $\Delta^{\alpha\gamma}$-butadiene (Brand and Matsui, A., 1913, i, 1170). ααα-Tribromo-ββ-di-*p*-tolylethane, m. p. 132° (Harris and Frankforter, this vol., 139, give m. p. 104°), is reduced by Devarda's or Arnd's alloy in boiling alcohol to *ββγγ-tetrabromo-αxδδ-tetra*-p-*tolylbutane*, m. p. 233°. With zinc dust and glacial acetic acid, this gives the αxδδ-tetra-*p*-tolyl-Δ^{β}-butmene, m. p. 123° (of Matsui and Brand), the constitution of which is, therefore, confirmed, and with sodium and alcohol, αxδδ-tetra-*p*-tolyl-$\Delta^{\alpha\gamma}$-butadiene. *βγ-Dibromo-αxδδ-tetra*-p-*tolyl*-Δ^{β}-*butene*, m. p. 175—176°, obtained by hydrogenation of tribromoditolylethane in alcohol and pyridine, gives the butatriene (I) with alcoholic potassium hydroxide.

ααα-Trichloro-ββ-diphenylethane when hydrogenated using a palladised calcium carbonate catalyst gives 60% of the theoretical amount of ββγγ-tetrachloro-αxδδ-tetraphenylbutane and small amounts of the two stereoisomeric βγ-dichloro-αxδδ-tetraphenyl-

Δ^{β}-butenes; ααα-trichloro-ββ-di-*p*-anisylethane gives 26·6% of ββγγ-tetrachloro-ααδδ-tetra-*p*-anisylbutane, which in turn yields 88% of βγ-dichloro-ααδδ-tetra-*p*-anisyl-Δ^{β}-butene, m. p. 182°, and ααα-trichloro-ββ-di-*p*-phenetylethane gives *ββγγ-tetrachloro-ααδδ-tetra*-p-*phenetylbutane*, m. p. 130°, and, on prolonged treatment, *βγ-dichloro-ααδδ-tetra*-p-*phenetyl*-Δ^{β}-*butene* (II), m. p. 146—147°. Reduction of the tetrachlorotetra-arylbutanes by the above method or by zinc dust and glacial acetic acid affords mixtures of the corresponding stereoisomeric dichlorotetra-aryl-Δ^{β}-butenes. On hydrogenation with a nickel catalyst in alcoholic pyridine, ααα-trichloro-ββ-diphenylethane gives, according to the conditions, principally tetrachlorotetraphenylbutane or dichlorotetraphenylbutenes, besides αα-dichloro-ββ-diphenylethane and acetaldehyde. *ααδδ-Tetra*-p-*phenetyl*-$\Delta^{\alpha\beta\gamma}$-*butatriene*, yellow or orange, m. p. 226°, formed together with a product (III, see below) when (II) is boiled with sodium amoxide in amyl alcohol, is converted by direct sunlight into a *dimeride*, $(C_{36}H_{36}O_4)_2$, greenish-yellow, m. p. 237—238°. It is oxidised by chromic acid to di-*p*-phenetyl ketone and carbon dioxide, and reduced by sodium and amyl alcohol to *ααδδ-tetra*-p-*phenetylbutane*, m. p. 88°, and by zinc dust and glacial acetic acid to a *substance*, $C_{36}H_{38}O_4$, m. p. 134°. Magnesium *p*-phenetyl bromide and ethyl succinate give by the usual procedure a *compound*, m. p. 262°, which is hydrolysed to *ααδδ-tetra*-p-*phenetyl*-$\Delta^{\alpha\gamma}$-*butadiene*, m. p. 201—202°. This is isomeric but not identical with the compound, m. p. 134°, which is probably an indene derivative. The red *powder* (III), $C_{36}H_{36}O_4$, m. p. 75—85°, is not identical with 5-ethoxy-1-*p*-phenetyl-3-di-*p*-phenetylmethyleneindene, m. p. 123°, and may be a transformation product of the latter. 5-Methoxyindan-1-one (Ingold and Piggott, J.C.S., 1923, **121**, 1469) and benzaldehyde form *5-methoxy-2-benzylideneindan-1-one*, m. p. 176°. When this is treated with magnesium *p*-anisyl bromide, and the product decomposed with water, a substance, b. p. 230—270° in a high vacuum, is obtained. Attempts to condense the latter with di-*p*-anisyl ketone giving 5-methoxy-1-*p*-anisyl-3-di-*p*-anisylmethyleneindene (cf. A., 1924, i, 720) were unsuccessful.

H. E. F. Notton.

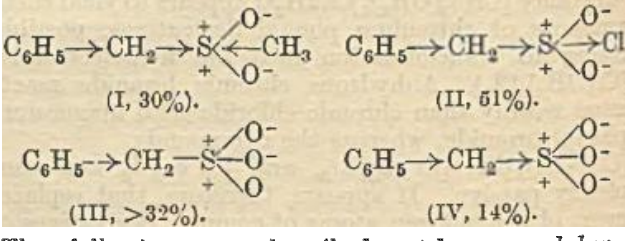
Reaction between nitrosobenzene and magnesium phenyl bromide. H. Gilman and R. McCracken (J. Amer. Chem. Soc., 1927, **49**, 1052—1061).—Nitrosobenzene with 3 mols. of magnesium phenyl bromide (cf. Wieland and Roseeu, A., 1915, i, 797) yields mainly diphenyl and diphenylamine. Phenol is not found except in amounts corresponding with those usually formed during the preparation of magnesium phenyl bromide. The formation of small amounts of azobenzene was confirmed, whilst *p*-diphenylbenzene was also identified. The presence of azobenzene suggests that the diphenyl may be derived in part by reaction between it and the Grignard reagent (cf. Gilman and Pickens, A., 1925, i, 1336). The main reaction apparently proceeds according to the schemes $PhNO+PhMgBr \longrightarrow NPh_2{\cdot}OMgBr$; $NPh_2{\cdot}OMgBr+2PhMgBr \longrightarrow NPh_2MgBr+Ph{\cdot}Ph+(MgBr)_2O$. *p*-Nitrosodimethylaniline also reacts with 3 mols. of magnesium phenyl bromide (cf. Wieland and Kogl, A., 1922, i, 726), giving diphenyl and, presumably, *p*-dimethylaminodiphenylamine.

F. G. Willson.

Nature of the alternating effect in carbon chains. XVII. Directive action of the groups $\cdot CH_2{\cdot}CH_2{\cdot}NO_2$, $\cdot CH{:}CH{\cdot}NO_2$, and $\cdot C(NO_2){:}CHR$ in aromatic substitution. J. W. Baker and I. S. Wilson (J.C.S., 1927, 842—848).—*α-Nitro-β-phenylethane*, b. p. 125—135°/1 mm., prepared by treatment of α-bromo-β-phenylethane with silver nitrite, yields on nitration, 13% of *m*-derivative, whilst with ω-nitrostyrene only 2% of *m*-isomeride is obtained. These results indicate that, in these cases, contrary to the general assumption, the propagation of the effect due to the positive charge on the nitro-group occurs less readily in a conjugated side-chain than in a saturated chain of equal length. It is suggested that this is probably due to the neutralisation of the effect in passing through the field of the double linking, and not to the predominating *op*-orienting influence of the latter, since p-*nitrobenzylidenephenylnitromethane* (ω-4′-*dinitrostilbene*), m. p. 155°, yields 20% of the *m*-derivative on nitration.

M. Clark.

Nature of the alternating effect in carbon chains. XIV. Directive action of groups of the form $-CH_2{\cdot}SO_2{\cdot}R$ in aromatic substitution. C. K. Ingold, E. H. Ingold, and F. R. Shaw (J.C.S., 1927, 813—832).—The proportion of *m*-isomeride formed on nitration of $CH_2Ph{\cdot}SO_2{\cdot}R$ by nitric acid at −10° to −5° is as follows: R=Me, 30; NH_2, 31; NHMe, 29; NHEt, 28; NMe_2, 28; NEt_2, 25; *OH*, 14; OMe, 32; Cl, 51%. These results show (i) that the fractional charges set up by the varying electron-affinities of different neutral atoms are small in comparison with the integral charge on the sulphur atom except in the case of Cl, the electron-attraction of which is very great (I, II); (ii) that the end of a dipolar group more distant from the nucleus has a definite influence on substitution, since the variation of its charge in the ratio of 2 : 3 causes the *meta*-proportion to vary from above 30% to 14% (III, IV); (iii) that a sulphonium sulphur atom is a less effective *m*-directing agent than an ammonium nitrogen atom similarly situated.



The following are described: *toluene-ω-sulphonmethylamide*, m. p. 65—66°; *-diethylamide*, m. p. 29°; *methyl toluene-ω-sulphonate*, m. p. 61—62°; o-, m-, and p-*nitrobenzylmethylsulphones*, m. p. 85—87°, 105—106°, and 167—167°, respectively; m- and p-*nitrotoluene-ω-sulphonmethylamides*, m. p. 106—107 and 143—145°; m- and p-*nitrotoluene-ω-sulphonethylamides*, m. p. 90—91° and 110—111°; m- and p-*nitrotoluene-ω-sulphondimethylamides*, m. p. 116—119 and 167°; *methyl* p-*nitrotoluene-ω-sulphonate*, m. p. 113°; and p-*nitrotoluene-ω-sulphonyl chloride*, m. p. 90°.

M. Clark.

Aromatic and hydroaromatic compounds of lignite tar. J. HERZENBERG and S. RUHEMANN [with F. WICHTERICH] (Ber., 1927, 60, [*B*], 889—902).—The neutral oil is distilled under diminished pressure and the successive fractions (range 110—180°/12 mm.) are distilled with steam. The distillates are treated with hydroferrocyanic acid, whereby oxygenated compounds are largely removed and subsequently distilled over sodium; by this means the sulphur content is greatly reduced, silica gel being less effective for this purpose. The oils thus obtained are all slightly dextrorotatory; they have d^{15} 0·91—0·93, n_D^{15} 1·51—1·52. Dehydrogenation of the fractions is effected by flowers of sulphur. The portion of b. p. 110—116°/10 mm. affords 1-methylnaphthalene, isolated as the picrate and identified further by oxidation to phthalonic acid, 5-*methyl-α-naphthaquinone*, m. p. 102—103°, and hemimellitic acid. From the fraction of b. p. 120—126°/10 mm. a *picrate*, $C_{14}H_{16},C_6H_2(NO_2)_3{\cdot}OH$, m. p. 112°, is derived which yields a *hydrocarbon*, $C_{14}H_{16}$, b. p. 124—126°/10 mm., 248—250°/atm. pressure, d^{15} 1·01997, 1·6130. This latter substance is oxidised by permanganate to phthalonic acid and by chromic and acetic acids to a *quinone*, $C_{14}H_{14}O_2$, m. p. 68°. Oxidation of the quinone with permanganate affords mellophanic acid. Treatment of the hydrocarbon with boiling, dilute nitric acid appears to yield a *methylnaphthoic acid*; it is therefore probable that the hydrocarbon is a methyl*iso*propylnaphthalene. Analogously, from the fraction of b. p. 132—138°/10 mm. a *picrate*, $C_{13}H_{14},C_6H_2(NO_2)_3{\cdot}OH$, m. p. 123—124°, is isolated which yields a *hydrocarbon*, $C_{13}H_{14}$, b. p. 132—134°/10 mm., d_4^{15} 0·90075, 1·5775. The conversion of the hydrocarbon into phthalonic acid and an *α-naphthaquinone*, $C_{13}H_{12}O_2$, m. p. 98°, which is oxidised to hemimellitic acid, indicates that it is probably 1-*iso*propylnaphthalene. The product obtained by dehydrogenation of the fraction, b. p. 160—170°/10 mm., does not yield a homogeneous picrate. Distillation of the hydrocarbons isolated from the mixed picrates permits the isolation of a solid compound, $C_{14}H_{16}$, m. p. 115° (picrate, m. p. 152°), apparently identical with the substance, erroneously formulated $C_{16}H_{18}$ by Oehler; it gives a *mononitro*-derivative, m. p. 102—103°. The filtrate from the solid hydrocarbon yields a *picrate*, $C_{14}H_{16},C_6H_2(NO_2)_3{\cdot}OH$, m. p. 138°, from which the *hydrocarbon*, $C_{14}H_{16}$, b. p. 148—150°/10 mm., d_4^{15} 1·00140, n_D^{15} 1·5991, is obtained. It is oxidised by permanganate to phthalonic acid and by chromic acid to two *quinones*, m. p. 45° and 186° (decomp.), respectively. H. WREN.

Action of chlorosulphonic acid on naphthalene. A. CORBELLINI (Giorn. Chim. Ind. Appl., 1927, 9, 118—120).—Chlorosulphonic acid behaves towards naphthalene, not only as a sulphonating agent (cf. Armstrong, 1871, 24, 173; P., 1886, 231; 1887, 42; 1889, 10), but also, as is the case with benzene, as a chlorosulphonating agent. When solid naphthalene (1 mol.) is treated at 15—45° with chlorosulphonic acid (2 mols.), naphthalene-1 : 5-disulphonic acid is formed, together with varying proportions of the corresponding disulphonyl chloride. When carbon tetrachloride is used as a diluent and the naphthalene (1 mol.) is treated with either 2 or 4 mols. of the acid, sulphonyl chlorides are always formed in addition to the mono- and di-sulphonic acids. In all cases, the naphthalene is attacked only in the 1- and 5-positions. It is probable that the first phase of the reaction consists of the formation of the sulphonic acid, which then passes to the sulphonyl chloride, $C_{10}H_7{\cdot}SO_3H+OH{\cdot}SO_2Cl \longrightarrow C_{10}H_7{\cdot}SO_2Cl+H_2SO_4$, these changes being accompanied by the secondary reactions, $C_{10}H_8+H_2SO_4 \longrightarrow C_{10}H_7{\cdot}SO_3H+H_2O$ and $OH{\cdot}SO_2Cl+H_2O \longrightarrow H_2SO_4+HCl$. The final yields of the various products evidently depend on the velocities of these different reactions, these being governed by the conditions employed. The sulphochlorinating action is favoured by low temperatures. T. H. POPE.

Fluorene derivatives. A. KORCZYNSKI, G. KARLOWSKA, and L. KIERZIK (Bull. Acad. Polonaise, 1926, **A**, 373—386, and Rocz. Chem., 1927, **7**, 124—135).—See this vol., 347.

Modified combustion method for the determination of bromine in organic compounds. F. L. SMITH (Philippine J. Sci., 1927, 32, 315—322).—The bromine content of aromatic as well as aliphatic substances may be determined with fair accuracy by a modification of the combustion method. The substance is heated in a current of oxygen, the resulting gases are passed through a heated tube containing a platinum contact, a layer of asbestos, and a second platinum contact. The gases are then passed into a solution of sodium carbonate containing a small quantity of sodium sulphite. When the substance is completely decomposed and the gases are swept through, the solution is heated with a little hydrogen peroxide to oxidise the sulphite, acidified with nitric acid, and the bromine determined volumetrically (Volhard's method). W. J. POWELL.

Possibility of a direct determination of the saturation capacity for halogen of the alkali salts of fatty and resin acids. B. M. MARGOSCHES and K. FUCHS (Ber., 1927, 60, [*B*], 990—992).—Experiments with the sodium and potassium salts of oleic, ricinoleic, erucic, and linoleic acids show that the iodine value can be determined accurately and directly by Margosches' method (A., 1924, i, 828) using 96% or 50% alcohol as solvent. The method may be extended to potassium abietate. H. WREN.

Spectrophotometric determination of glycuronic acid. G. SCHEFF (Biochem. Z., 1927, **183**, 341—349).—Tables are given whereby the concentration of glycuronic acid (or its menthol derivative) may be obtained from a determination of the extinction coefficient of the band of maximum absorption (617·7 μμ) shown in amyl alcohol solution by the pigment formed when these substances are treated with Bial's orcinol reagent (cf. A., 1924, i, 942, ii, 632). P. W. CLUTTERBUCK.

Determination of formaldehyde. J. BICSKEI (Z. anorg. Chem., 1927, **161**, 309—310).—Alkaline hypochlorite oxidises formaldehyde quantitatively to formic acid. For the analysis of commercial

solutions of the aldehyde, 10 c.c. are diluted to 1 litre and 10 c.c. of this solution are shaken with 40—50 c.c. of 0·1*N*-sodium hypochlorite solution, 1—2 g. of solid potassium iodide are added, followed by an excess of hydrochloric acid, and the liberated iodine is titrated with thiosulphate. A. R. POWELL.

Iodine as a reagent for differentiating between ammonium salts, amines, and amides. J. A. SANCHEZ (Anal. Asoc. Quím. Argentina, 1926, **14**, 366—368).—On adding to a solution of an ammonium salt a 10% solution of potassium iodide and then excess of sodium hypochlorite solution, a black precipitate of nitrogen tri-iodide is obtained. With amides, no precipitate but a yellow coloration is obtained. With amines, a yellow, red, or grey precipitate is obtained. G. W. ROBINSON.

Catalytic reduction of di- and tri-phenylamines with hydrogen and platinum oxide platinum-black. G. S. HIERS and R. ADAMS (J. Amer. Chem. Soc., 1927, **49**, 1099—1103; cf. A., 1926, 402).—Di*cyclo*hexylamine, b. p. 136—138°/26 mm. (*hydrobromide*, subl. 310—320°), is obtained in 80—90% yield by reduction of diphenylamine hydrochloride (0·1 mol.) in absolute alcohol (150 c.c.) at 50° in presence of platinum-black prepared by reduction of platinum oxide (0·25 g.) in absolute alcohol (50 c.c.). Tri*cyclohexylamine*, b. p. 170—171°/4 mm., d_4^{20} 0·9993, n_D^{18} 1·5468 (*picrate*, m. p. 179—180°; *hydrobromide*, m. p. 225—226°), is obtained similarly from triphenylamine and hydrochloric acid, together with small proportions of *cyclo*hexane and di*cyclo*hexylamine. *cyclo*Hexylaniline, b. p. 134—135°/6 mm. (*hydrobromide*, m. p. 177—178°; *picrate*, m. p. 164—165°), is obtained by boiling *cyclo*hexyl bromide and aniline in alcohol. Analogous condensation of *cyclo*hexyl bromide with *cyclo*hexylaniline and di*cyclo*hexylamine could not be effected, *cyclo*hexene being produced. Tri*cyclo*hexylamine forms a mixture of constant b. p., 192—193°/10 mm., with triphenylamine, containing 10—12% of the latter.

F. G. WILLSON.

Aniline–calcium hypochlorite reaction. L. ROSENTHALER (Arch. Pharm., 1927, **265**, 109—110; cf. Hantzsch and Freese, A., 1894, i, 572).—Four samples of benzene free from thiophen (three samples prepared from natural gums and one sample purified by boiling with aluminium chloride) were converted into aniline, and in each case the latter showed the calcium hypochlorite reaction, thus proving that the colour is not produced by impurities, as stated by Hantzsch and Freese. S. COFFEY.

Reduction of aromatic nitro-compounds to amines with hydrogen and platinum oxide platinum-black as catalysts. XIV. R. ADAMS, F. L. COHEN, and O. W. REES (J. Amer. Chem. Soc., 1927, **49**, 1093—1099; cf. A., 1926, 500).—Nitrobenzene (0·1 mol.) in absolute alcohol (150 c.c.) is reduced quantitatively to aniline in 10—11 min. by hydrogen at 2—3 atm. pressure in presence of 0·2 g. of platinum-black prepared by reduction of platinum oxide. Replacement of a portion of the alcohol by water decreases the rate of reduction. The rate of reduction in methyl and *n*-propyl alcohols is the same as that in ethyl alcohol, but is progressively less in *n*-butyl and *iso*amyl alcohols. Ethyl acetate and acetone are as satisfactory solvents as is 95% alcohol, but the reduction is much slower in dry ether and still slower in glacial acetic acid. All the nitrotoluenes and nitrobenzoic acids, *o*- and *p*-chloronitrobenzenes, *p*-nitroanisole, and *p*-nitrophenetole are reduced under the above conditions at approximately the same rate as nitrobenzene, whilst the methyl nitrobenzoates and 1-nitronaphthalene are reduced more rapidly. Exhaustive reduction of the above chloronitrobenzenes under these conditions yielded some *cyclo*hexylamine hydrochloride. Addition of hydrochloric and acetic acids decreases the rate of reduction, whilst this is completely inhibited by the addition of 0·025 mol. of sodium hydroxide in saturated aqueous solution, or by 0·0005 mol. of zinc acetate. Under the above conditions, *m*-nitrostyryl methyl ketone, phenyl *m*-nitrostyryl ketone, and ethyl *m*-nitrocinnamate undergo reduction only at the nitro-group. Addition of acetic acid retards the reaction, but this proceeds until the ethylene linking is also reduced. In the case of a mixture of nitrobenzene and safrole, the former is reduced first, and no reduction takes place in presence of sodium hydroxide. Addition of the latter does not, however, inhibit reduction of safrole alone, indicating the probable formation of a non-reducible compound between the nitrobenzene and the sodium hydroxide. The inhibition of the reduction of nitrobenzene by zinc acetate is partly prevented if safrole is also present. *Phenyl* β-m-*aminophenylethyl ketone*, yellow, m. p. 64—65°, is described. F. G. WILLSON.

Reaction between dichloroacetic acid and aromatic amines. A. S. WHEELER and E. DE W. JENNINGS (J. Amer. Chem. Soc., 1927, **49**, 1091—1093; cf. A., 1923, i, 994).—The transformation of dichloroacetic acid into trichloroacetic acid by the action of amines, previously reported (*loc. cit.*), cannot be confirmed with samples of dichloroacetic acid of known purity. The following salts of dichloroacetic acid (*a*) and trichloroacetic acid (*b*) are described: *methylaniline* (*a*), m. p. 96°, (*b*), m. p. 97°; *o-chloroaniline* (*a*), m. p. 69—70°, (*b*), m. p. 120°; *2 : 4-dichloroaniline* (*a*), m. p. 132—138°, (*b*), m. p. 123—124°; *o-anisidine* (*a*), m. p. 96°, (*b*), m. p. 141°; *benzidine* (*a*), m. p. 203°, (*b*), m. p. 166°; and *p-aminophenol* (*a*), m. p. 148°, (*b*), m. p. 166°. When mixed with pure aniline, pure dichloroacetic acid gives a pure white salt. Impure commercial samples gave, in addition, a deep yellow *product* sparingly soluble in hot benzene. F. G. WILLSON.

Nitration. II. Simultaneous diazotisation and nitration of aromatic amino-compounds. P. S. VARMA and P. V. KRISHNAMURTHY (J. Indian Chem. Soc., 1926, **3**, 323—327).—By the action of nitrous gases (obtained by the action of concentrated nitric acid on arsenious oxide) on eighteen aromatic amines, nitrophenol derivatives have been obtained, simultaneous nitration and diazotisation occurring; *e.g.*, *p*-nitroaniline gave dinitrophenol; *o*-toluidine gave 4-nitro-*o*-cresol. *m*-Nitroaniline yields a *compound*, yellow plates, very explosive, whilst benzidine yields a mononitrophenolic *compound*, m. p. 104°.

J. W. BAKER.

Reaction of nitrogen trichloride with various types of olefine hydrocarbons. G. H. COLEMAN, A. W. CAMPBELL, and G. M. MULLINS (Proc. Iowa Acad. Sci., 1925, 32, 326).—Styrene and nitrogen trichloride afford α-chloro-β-dichloroamino-β-phenylethane, which on treatment in carbon tetrachloride solution with dry hydrogen chloride yields α-chloro-β-amino-β-phenylethane and chlorine. Propylene behaves similarly. β-Methylpropylene gives only ammonium chloride, nitrogen, and chlorinated hydrocarbons. CHEMICAL ABSTRACTS.

Nature of the alternating effect in carbon chains. XIII. Nitration of some γ-phenylpropylamine derivatives. C. K. INGOLD and I. S. WILSON (J.C.S., 1927, 810—813; cf. this vol., 236).—γ-Phenylpropylammonium nitrate and *γ-phenylpropyltrimethylammonium picrate*, m. p. 121°, on nitration in nitric acid (*d* 1·49) at −15°, yield 3% and 5±2% of *m*-isomeride, respectively. In each case, the *p*-derivative is the main product. The following salts have been isolated: γ-p-*nitrophenylpropylammonium nitrate*, m. p. 200° (*chloride*, m. p. 165°); γ-p-*nitrophenylpropyltrimethylammonium picrate*, m. p. 138°; γ-p-*acetamidophenylpropyltrimethylammonium picrate*, m. p. 153°; γ-m-*nitro*-p-*acetamidophenylpropyltrimethylammonium picrate*, m. p. 140°; γ-m-*nitrophenylpropyltrimethylammonium picrate*, m. p. 156°. M. CLARK.

Benzylation of the higher alkylanilines. J. REILLY and P. J. DRUMM (J.S.C.I., 1927, **46**, 84T, 99T).—*Benzyl*-n-*butylaniline*, b. p. 193—195°/17 mm., $d^{16\cdot5}$ 1·005, n_D 1·5804, was obtained in 60% yield from *n*-butylaniline by heating equal molecular proportions of *n*-butylaniline and benzyl chloride with 0·5 mol. of sodium carbonate (aqueous solution) for 6—8 hrs. at 118—120° under pressure. Sulphonation with 100% sulphuric acid at 115—120° gave *benzyl*-n-*butylanilinesulphonic acid*, m. p. 260—262° (*barium* salt, $+1H_2O$). Fusion of the potassium salt with potassium hydroxide gave p-*hydroxybenzyl*-n-*butylaniline*, m. p. 196—198°, faintly green. The position of the sulpho-group in the benzyl radical is inferred, since the phenol obtained does not give a rhodamine with phthalic anhydride and the sulphonic acid forms a nitroso-compound, showing that the *p*-position in the anilino-group is free.

***cyclo*Hexylaniline.** M. BUSCH and F. GEBELEIN (J. pr. Chem., 1927, [ii], **115**, 107—125).—*cyclo*Hexylaniline [hydrochloride, m. p. 210°; *oxalate*, p. 186° (decomp.); *chloroplatinate*, m. p. 190—-23° (decomp.)] is conveniently prepared by heating a mixture of bromo*cyclo*hexane and aniline. The hydrochloride yields the following compounds: *benzenesulphon*cyclo*hexylanilide*, m. p. 147°; with nitric acid, 2 : 4-*dinitrophenyl*cyclo*hexylamine*, m. p. , with nitrous acid and subsequent reduction nitroso-compound with zinc, *α-phenyl*-α-cyclo*hexylhydrazine* (m-*nitrobenzaldehyde*-α-*phenyl*-α-cyclo*hexylhydrazone*, m. p. 78°); with benzenediazonium p-cyclo*hexylaminoazobenzene*, orange-yellow needles, m. p. 112° (*hydrochlorides*, yellow, m. p. 201°, and reddish-violet, m. p. 190—192°); p-*nitro*-p′-cyclo*hexylaminoazobenzene*, reddish-brown plates, (*hydrochloride*, m. p. 197°); with β-naphthalenediazonium chloride, cyclo*hexylaminobenzeneazo*-β-*naphthalene*, orange needles, m. p. 115° (*hydrochloride*, m. p. 223°).

cyclo*Hexyl*-p-*toluidine*, m. p. 41—42°, b. p. 180°/30 mm. (*hydrochloride*, m. p. 222°; *acetyl* derivative, m. p. 67°; *benzoyl* derivative, m. p. 106°; *dinitro*-derivative, m. p. 78°; *trinitro*-derivative, m. p. 121°), cyclo*hexyl*-m-*toluidine*, b. p. 200°/30 mm. (*hydrochloride*, m. p. 178°; *nitrate*, m. p. 125°; *oxalate*, m. p. 157°; *benzoyl* derivative, m. p. 87°; *dinitro*-derivative, m. p. 137°), cyclo*hexyl*-o-*toluidine*, b. p. 230°/50 mm. (*hydrochloride*, m. p. 208°; *perchlorate*, m. p. 184°; *benzoyl* derivative, m. p. 110°; *dinitro*-derivative, m. p. 90°; *trinitro*-derivative, m. p. 125°), and cyclo*hexylmethylaniline* [*hydrochloride*, m. p. 196°; p-cyclo*hexylmethylaminoazobenzene*, m. p. 114° (*hydrochloride*, violet needles); p-cyclo*hexylmethylaminoazobenzene*-p′-*sulphonic acid*, violet plates, m. p. 224—260° (*potassium* salt, orange plates)], are obtained similarly to *cyclo*hexylaniline. R. W. WEST.

New molecular transformation in the naphthylaminesulphonic acid series. A. WAHL and G. VERMEYLEN (Bull. Soc. chim., 1927, [iv], **41**, 514—523).—When heated with concentrated sulphuric acid (93·5%) at 90°, α-naphthylamine-8-sulphonic acid isomerises to α-naphthylamine-4-sulphonic acid (naphthionic acid). Since the rate of hydrolysis of the 1 : 8-acid is greater than that of the 1 : 4-acid, Erdmann's explanation of the isomeric change of the 1 : 4-acid into the 1 : 5- and 1 : 6-acids by successive hydrolysis and sulphonation (A., 1893, i, 653) can be applied to this case also. R. BRIGHTMAN.

Relationships between aromatic nitro-derivatives and azoxy-compounds. D. BIGIAVI (Atti R. Accad. Lincei, 1927, [vi], **5**, 444—450).—The oxygen atom of azoxy-compounds protects from the substituting action of reagents such as halogens or nitric acid the aromatic residue directly united to the nitrogen atom combined with the oxygen, but this protective action is attenuated or annulled by the presence of certain other groupings in the aromatic nucleus. Moreover, in general, nitro-groups present in the aromatic ring of an azo-derivative in the *para*- or *ortho*-position to the azo-group render difficult the addition of oxygen to the azo-group, that is, the passage to the azoxy-compound, by the action of peracetic acid. There exists, indeed, a mutual relation between substituents in the aromatic ring and the quinquevalent nitrogen of the azoxy-group, and a number of instances are cited in which aromatic nitro-derivatives exhibit behaviour similar to that of the azoxy-compounds derivable from them by substitution of :NPh for :O. T. H. POPE.

s-Dibenzeneazoethylenes. D. VORLANDER, W. ZEH, and H. ENDERLEIN (Ber., 1927, **60**, [*B*], 849—857).—The observation that *para*-substituted *s*-dibenzeneazoethylenes have pronounced liquid-crystalline properties favours the linear azo-structure for the osotetrazines in contrast with the cyclic formula (cf. Bucherer, A., 1925, i, 1138; Stollé, A., 1926, 1158). The following substances are described: *glyoxalanisylosazone*, m. p. 219° (slight decomp.); *glyoxalphenetylosazone*, m. p. 181° (slight decomp.);

methylglyoxalanisylosazone, m. p. 171° (decomp.); *methylglyoxalphenetylosazone*, m. p. 159° (decomp.); *dimethylglyoxalmonoanisylhydrazone*, m. p. 118°; *dimethylglyoxalanisylosazone*, m. p. 219°; *dimethylglyoxalmonophenetylhydrazone*, m. p. 116°; *dimethylglyoxalphenetylosazone*, m. p. 210—211° (slight decomp.). Oxidation of the osazones with potassium dichromate in dilute acetic acid solution yields the following substances: *di*-p-*anisoleazoethylene*, m. p. I, 220° (decomp.), II, 158° (decomp.); *di*-p-*phenetoleazoethylene*, m. p. I, about 220° (decomp.), II, 167° (decomp.); *di*-p-*anisoleazomethylethylene*, m. p. I, about 200°, II, 123—124° (decomp.); *di*-p-*phenetoleazomethylethylene*, m. p. I, about 210°, II, 115° (decomp.); *di*-p-*anisoleazodimethylethylene*, m. p. I, about 188°, II, 171° (decomp.); *di*-p-*phenetoleazodimethylethylene*, m. p. I, about 187°, II, 170° (decomp.). With the requisite amines, glyoxal and its homologues give the following derivatives: *glyoxylidenedianisidine*, m. p. I, 142°, II, 158°; *glyoxylidenediphenetidine*, m. p. I, 165°, II, 150°; *methylglyoxylidenedianisidine*, m. p. 107°; *methylglyoxylidenediphenetidine*, m. p. I, 113·5°, II, 110°; *dimethylglyoxylidenedianisidine*, m. p. 186°; *dimethylglyoxylidenediphenetidine*, m. p. 181°.

The presence of a double linking in dibenzeneazoethylene cannot readily be established by means of halogen hydride, hydrogen peroxide, ozone, or permanganate. Bromine yields a *compound*, m. p. about 176°. Ethyl sodiomalonate condenses with dibenzeneazoethylene, yielding the *compound* (?) PhN<N———H C(OH):C(CO$_2$Et)>C:N·NHPh, m. p. 154° (decomp.), converted by acetic anhydride and sodium acetate into the *diacetate*, m. p. 223—225° (decomp.). Methyl sodiomalonate affords the corresponding *methyl* ester, m. p. 164—165° (decomp.), and m. p. about 275° after resolidification. Hydrolysis of the esters yields the *acid*, N:CH——C=N NPh·C(OH):C·CO >NPh, m. p. about 283° (decomp.). Ethyl sodioacetoacetate and dibenzeneazoethylene give a *substance*, m. p. about 209° (decomp.). H. WREN.

Preparation of phenylhydrazine. N. PUTOCHIN (Trans. Inst. Pure Chem. Reagents, Moscow, 1927, 70—72).—The preparation of phenylhydrazine from sodium benzenediazosulphonate, either in the laboratory or on an industrial scale, may be simplified if the reduction is effected by means of sulphur dioxide instead of by zinc dust and acetic acid. Details of the procedure are given. T. H. POPE.

Preparation of optically active hydrazines. III. Active-amyl' phenylhydrazines. J. W. E. GLATTFELD and C. N. CAMERON (J. Amer. Chem. Soc., 1927, **49**, 1043—1048; cf. A., 1922, i, 385).—α-Phenyl-β-methyl-*n*-butane, b. p. 192°/710—720 mm. (cf. Dumesnil, A., 1917, i, 653), was prepared by reduction of benzylmethylethylcarbinol, b. p. 133—134°/30 mm. (cf. Davies and Kipping, J.C.S., 1911, **99**, 298), with hydriodic acid, phosphorus, and iodine, by similar reduction of *sec.*-butylphenylcarbinol (cf. Dumesnil, *loc. cit.*), from benzyl chloride, *sec.*-butyl bromide, and sodium, from magnesium benzyl chloride and *sec.*-butyl bromide, and from benzyl chloride and magnesium *sec.*-butyl bromide. Treatment with cold nitric and sulphuric acids yields the p-*nitro*-derivative, b. p. 141°/14 mm., which, on reduction with tin and hydrochloric acid, affords the corresponding *amine*, b. p. 133—140°/15 mm. (*benzoyl* derivative, m. p. 118°). Condensation of the amine with *d*-hydroxymethylenecamphor yields two isomeric crystalline derivatives, "α," m. p. 173°, $[\alpha]_D$ +269° in chloroform, and "β," m. p. 122°, $[\alpha]_D$ +251·0° in chloroform, together with a liquid derivative. Both solid derivatives afford, on hydrolysis, the same d-α-p-*aminophenyl*-β-*methyl*-n-*butane*, b. p. 136°/15 mm., b. p. 142—143°/27 mm., $[\alpha]_D$ +6·0°, whilst the liquid isomeride yields similarly l-α-p-*aminophenyl*-β-*methyl*-n-*butane*, b. p. 140—141°/26 mm., $[\alpha]_D^{20}$ −6·0°. The corresponding dl-*phenylhydrazine*, b. p. 136—137°/8 mm., and the *d*- and *l*-isomerides, b. p. 139—140°/9 mm., $[\alpha]_D$ +6·86° and −6·42°, respectively, in light petroleum, are obtained by Fischer's method from the respective amines. F. G. WILLSON.

Action of bromo*cyclo*hexane on arylhydrazines. M. BUSCH and G. HAASE (J. pr. Chem., 1927, [ii], **115**, 186—200).—When phenylhydrazine or its sodium derivative is treated with bromo*cyclo*hexane, it yields α-phenyl-α-*cyclo*hexylhydrazine, m. p. 33·5° (*hydrochloride*, m. p. 196°; *nitrate*, m. p. 167°; *sulphate*, m. p. 83°; *acetyl* derivative, m. p. 91°; *benzoyl* derivative, m. p. 212°), which reacts with phenyl cyanate to give αδ-*diphenyl*-α-cyclo*hexylsemicarbazide*, m. p. 156°, with phenyl thiocyanate to give αδ-*diphenyl*-α-cyclo*hexylthiosemicarbazide*, m. p. 156°, and is readily oxidised by mercuric oxide, yielding *diphenyldi*cyclo*hexyltetrazene*, m. p. 101° (decomp.). The *phenyl*cyclo*hexylhydrazones* of the following aldehydes and ketones are described: benzaldehyde, m. p. 58°; *p*-nitrobenzaldehyde, m. p. 88°; *p*-dimethylaminobenzaldehyde, m. p. 69°; salicylaldehyde, m. p. 59°, which probably has the quinonoid structure; cinnamaldehyde, m. p. 62°; acetophenone, m. p. 85°.

The following compounds are obtained by similar reactions to those described: α-o-*tolyl*-α-cyclo*hexylhydrazine* (*dihydrochloride*, m. p. 207°; *sulphate*, m. p. 212°; *dibenzoyl* derivative, m. p. 141°; *diacetyl* derivative, m. p. 110·5°) yields the o-*tolyl*cyclo*hexylhydrazones* of *o*-nitrobenzaldehyde, m. p. 76°, *m*-nitrobenzaldehyde, m. p. 79°, *p*-nitrobenzaldehyde, m. p. 94°, and *p*-dimethylaminobenzaldehyde, m. p. 106—107°; α-m-*tolyl*-α-cyclo*hexylhydrazine* (*hydrochloride*, m. p. 203°; *benzoyl* derivative, m. p. 119°); α-p-*tolyl*-α-cyclo*hexylhydrazine*, m. p. 55° (*hydrochloride*, m. p. 208°; *nitrate*, m. p. 149°; *benzoyl* derivative, m. p. 201°), which yields *di*-p-*tolyldi*cyclo*hexyltetrazene*, m. p. 151—152° (decomp.), and p-*nitrobenzaldehyde*-p-*tolyl*cyclo*hexylhydrazone*, m. p. 119°. R. W. WEST.

Chloro- and bromo-derivatives of *o*- and *m*-cresol. E. BURES (Chem. Listy, 1927, **21**, 108—114, 148—162).—The following substances have been prepared: 3 : ɔ-*dichloro*-o-*tolyl ethyl ether*, m. p. 27·5°, b. p. 137°; 3 : 5-*dichloro*-o-*tolyl acetate*, m. p. 28·5°, b. p. 254°; phenyl 3 : 5-dichloro-o-tolyl ether, m. p. 114°, b. p. 240°; *tri*-3 : ɔ-*dichloro*-o-*tolyl phosphate*, m. p. 248° (decomp.), and 3 : ɔ-*dibromo*-o-*cresol*, m. p. 57°. R. TRUSZKOWSKI.

3-Nitro-2-aminophenol. E. FOURNEAU and J. and (MME.) J. TRÉFOUEL (Bull. Soc. chim., 1927, [iv], **41**, 448—450).—Benzoxazolone-5-arsinic acid (B., 1926, 28) on nitration with sulphuric and nitric acids at 10° affords *3-nitrobenzoxazolone-5-arsinic acid*, which on hydrolysis with sulphuric acid yields *3-nitro-2-aminophenol*, m. p. 212° (sublimes about 190°), converted into 2 : 3-diaminophenol with iron and acetic acid. R. BRIGHTMAN.

Phenylalanine derivatives. VIII. Hexahydrotyramine. E. WASER and H. FAUSER (Helv. Chim. Acta, 1927, **10**, 262—267).—Dry distillation of hexahydrotyrosine (Waser and Brauchli, A., 1924, i, 1068; cf. also Waser, A., 1926, 65) at 310—340° under 12—21 mm. and fractionation of the distillate yields *hexahydrotyramine* [β-*4-hydroxy*cyclo*hexylethylamine*], m. p. 44—52°, b. p. 141—143°/10 mm. (corr.), in a yield which may be as great as 80%. The following derivatives were prepared: *hydrochloride*, m. p. 160° (decomp.); *oxalate*, m. p. 211°; *chloroplatinate*, m. p. 204—205° (decomp.); *picrate*, *picrolonate*, and *styphnate* (all oily); ON-*diacetyl* derivative; ON-*di*-p-*nitrobenzoyl* derivative, m. p. 181—182°. J. W. BAKER.

New synthesis of thymol. G. AUSTERWEIL and L. LEMAY (Bull. Soc. chim., 1927, [iv], **41**, 454—457).—2-Nitro-*p*-cymene, d^{15} 1·075, b. p. 130°/9 mm., obtained by Andrews' method (A., 1918, i, 339), on reduction with aluminium amalgam in light petroleum in the cold, affords cymyl-2-hydroxylamine, the hydrochloride or sulphate of which isomerises to the corresponding salt of *p*-aminothymol (2-amino-5-hydroxy-*p*-cymene) when heated at 60—80°. By diazotising the aminothymol at 0° to −5° in presence of zinc sulphate and pouring the diazo-solution into stannous chloride in hydrochloric acid solution, thymol is obtained in 70% of the theoretical yield. At higher temperatures, cymylhydroxylamine tends to undergo transformation to azoxycymene, cymidine, or nitrosocymene (cf. Bert and Dorier, A., 1926, 164). R. BRIGHTMAN.

Direct introduction of substituents in aromatic mercaptans. T. VAN HOVE (Bull. Acad. roy. Belg., 1926, [v], **12**, 929—943).—Bromination of phenyl methyl sulphide in carbon disulphide affords *p*-bromophenyl methyl sulphide, m. p. 37·3°, b. p. 148·6—149°/40 mm. (cf. Taboury, A., 1904, i, 493), 5—6% of the *o*-bromo-isomeride being also formed. On oxidation with potassium permanganate, *p*-bromophenyl methyl sulphide affords p-*bromophenylmethylsulphone*, m. p. 102—102·5°, which, like the original sulphide, is converted by nitric acid (*d* 1·2) at 160° into *p*-dinitrobenzene; but at 100° the same acid oxidises the sulphide to p-*bromophenylmethylsulphoxide*, m. p. 83°. Sulphonation of phenyl methyl sulphide with chlorosulphonic acid affords about 90% of *thioanisole*-p-*sulphonic acid* (*barium* salt; *amide*, m. p. 163°) and 10% of the o-*sulphonic acid* (*barium* salt, *amide*, m. p. 211°), the *p*-isomeride affording the less soluble barium salt. The constitution of these [illegible]s is established by their conversion by dilute [illegible]ric acid at 175° into the corresponding dinitro[illegible]ration phenyl methyl sulphide, with [illegible] sulphuric acid, afforded no nitro-deriv[illegible], the sulphide linking being attacked, with production of a yellow liquid, b. p. 236·5—264°, probably the sulphoxide. o-*Bromophenyl methyl sulphide*, b. p. 152—153°/35 mm., 253·5°/760 mm., congealed at −24·5°, was obtained by methylation of o-*bromophenylmercaptan*, b. p. 128—130°/25 mm., prepared by treating diazotised *o*-bromoaniline with potassium ethyl xanthate and hydrolysing the product with alcoholic potassium hydroxide. R. BRIGHTMAN.

Thiophenols. XI. Refractometry of methoxy- and methylmercapto-compounds. K. BRAND and K. W. KRANZ (J. pr. Chem., 1927, [ii], **115**, 143—162; cf. A., 1925, i, 397).—The effect on the physical properties of benzene and toluene produced by the introduction of the groups ·SMe, ·OMe, and ·NMe_2 is discussed. The following general effects are noticed: density and refractive index, ·SMe>·OMe>·NMe_2; dispersion and molecular refraction, ·NMe_2>·SMe>·OMe. The relative increases caused by the substitution of Br, NH_2, and NO_2 groups in the *o*- and *p*-positions in these compounds is *p*->*o*- for dispersion and molecular refraction, and, in general, *o*->*p*- for density and refractive index. The constants for these series of compounds are tabulated. R. W. WEST.

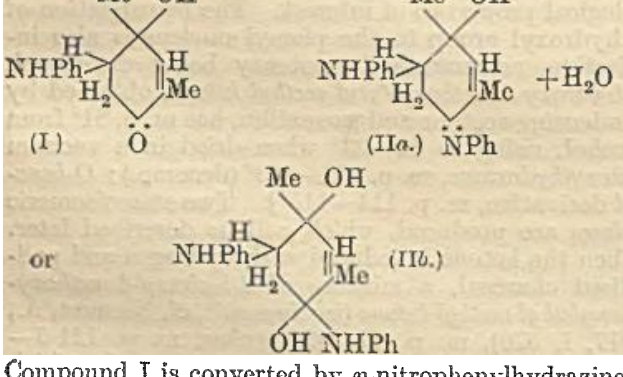
Homoeugenol (2-methoxy-4-Δ^{β}-butenylphenol). C. MANNICH and K. W. MERZ (Arch. Pharm., 1927, **265**, 104—106; cf. following abstract).—Treatment of 2-methoxy-4-γ-hydroxy-*n*-butylphenol with boiling 60% sulphuric acid furnishes 2-methoxy-4-Δ^{β}-butenylphenol, designated *homoeugenol*, a weakly fluorescent oil, b. p. 144—146°/12 mm., with an odour more reminiscent of cresol than of eugenol. The *benzoyl* derivative, m. p. 75—76°, when hydrogenated with the aid of palladised charcoal, is converted into *2-methoxy-4-n-butylphenyl benzoate*, m. p. 84—85°. Homoeugenol with methyl sulphate gives a *methyl ether* (90% yield), b. p. 142—144°/11 mm., which on treatment with ozone furnishes homoveratraldehyde, identified as its oxime. S. COFFEY.

Phenolic bases derived from γ-phenyl*iso*butylamine. C. MANNICH and K. W. MERZ (Arch. Pharm., 1927, **265**, 15—26).—None of the following substituted γ-phenylalkylamines possesses pharmacological properties of interest. The benzoylation of a hydroxyl group in the phenyl nucleus is also ineffective, no anæsthetic potency being developed. *3-Hydroxy-4-methoxystyryl methyl ketone*, obtained by condensing acetone and *iso*vanillin, has m. p. 81° from alcohol, rising to 92—93° when dried in a vacuum [*phenylhydrazone*, m. p. 138—139° (decomp.); *O-benzoyl* derivative, m. p. 114—115°]. Two stereoisomeric *oximes* are produced, which will be described later. When the ketone is reduced with hydrogen and palladised charcoal, a mixture of *3-hydroxy-4-methoxyphenylethyl methyl ketone* (iso*zingerone*, cf. Nomura, A., 1917, i, 570), m. p. 41—42° (*oxime*, m. p. 121·5—122·5°; *benzoyl* derivative, m. p. 55·5—56·5°), which is separated as its hydrogen sulphite compound, and *γ-3-hydroxy-4-methoxyphenyliso*butyl *alcohol*, m. p. 59°, b. p. 190—192°/17 mm., is produced. The oxime of the ketone is reduced by sodium amalgam in warm glacial acetic acid to *γ-3-hydroxy-4-methoxyphenyliso*butylamine, m. p. 114—115° (*hydrochloride*, m. p. 163—164°; this with potassium cyanate yields a *ureide*, m. p. 162—163°). When benzoylated by the

Schotten–Baumann procedure, the amine yields the ON-*dibenzoyl* derivative, m. p. 146—148°, whereas when its hydrochloride is heated at 140—145° with benzoyl chloride, a mixture of the dibenzoyl and O-*monobenzoyl* derivatives is produced; the latter is an oil (*hydrobromide*, m. p. 166—168°). When γ-3-hydroxy-4-methoxyphenyl*iso*butyl alcohol is treated with thionyl chloride and pyridine, an impure chloro-compound is obtained, which interacts with piperidine at 120—130° to give δ-3-*hydroxy*-4-*methoxyphenyl*-β-*piperidinobutane*, m. p. 78—79°, b. p. 205—210°/13 mm. (*benzoate*, m. p. 188—189°). *p*-Hydroxybenzaldehyde and acetone yield p-*hydroxystyryl methyl ketone*, m. p. 112° (*oxime*, m. p. 141—143°; *phenylhydrazone*, m. p. 130—131°; *benzoyl* derivative, m. p. 130—131°). This ketone is readily reduced to γ-p-*hydroxyphenyl*iso*butyl alcohol*, m. p. 69—70°, and β-p-*hydroxyphenylethyl methyl ketone*, m. p. 83·5—84·5° (*oxime*, m. p. 97—98°; *benzoyl* derivative, m. p. 72·5—73·5°), the oxime of which is reduced by sodium amalgam and acetic acid to γ-p-*hydroxyphenyl*iso*butylamine*, m. p. 110° (*ureide* with potassium cyanate, m. p. 160—161°; ON-*dibenzoyl* derivative, m. p. 149°; O-*benzoyl* derivative, m. p. 117—119°, yielding a *hydrochloride*, m. p. 176—178°). 4-Hydroxy-3-methoxystyryl methyl ketone (*oxime hydrochloride*, m. p. 128—129°; *phenylhydrazone*, m. p. 127—128°; *benzoyl* derivative, m. p. 121—122°), prepared as described by Nomura (*loc. cit.*), is readily reduced to zingerone and the corresponding alcohol. Sodium amalgam and acetic acid reduce the oxime of zingerone to γ-4-*hydroxy*-3-*methoxyphenyl*iso*butylamine*, m. p. 103—104° (*hydrochloride*, m. p. 189—190°; ON-*dibenzoyl* derivative, m. p. 107—108°; O-*benzoyl* derivative *hydrobromide*, m. p. 207—208°).

W. A. SILVESTER.

Additive product from 2 : 4-dimethylquinol and aniline. E. BAMBERGER (Ber., 1927, **60**, [*B*], 977—982).—The action of aniline on 2 : 4-dimethylquinol gives *compounds* I and II, m. p. 136—137° and 211·5—212° after softening, to which the following structures are tentatively assigned:



Compound I is converted by *p*-nitrophenylhydrazine into the corresponding p-*nitrophenylhydrazone*, m. p. 202—203°. Compounds I and II appear convertible into nitrosoamines.

H. WREN.

Sulphuric acid esters of hydroxyalkyl compounds of the aromatic series [sulphatoalkyl ethers of phenols]. I. G. FARBENIND. A.-G.—See B., 1927, 324.

Manufacture of new aromatic compounds and dyes therefrom [thiol derivatives of aminodiarylamines]. L. CASSELLA & CO., G.M.B.H.—See B., 1927, 325.

Catalytic formation of mixed cholesteryl ethers. C. E. BILLS and F. G. MCDONALD (J. Biol. Chem., 1927, **72**, 1—11).—Ethers of cholesterol, in general, may be prepared by heating cholesterol or cholesteryl acetate with excess of the appropriate alcohol in solution in benzene, toluene, or xylene in presence of activated fuller's earth or of certain other catalysts. This observation leads to the conclusion that the compound previously obtained (A., 1926, 981) by heating cholesterol alone under these conditions was dicholesteryl ether; in concordance with this, the mol. wt. is now found to be 725—775. *Cholesteryl methyl ether* has m. p. 82°, $[\alpha]_D$ —40·5°; *cholesteryl ethyl ether*, m. p. 89°, $[\alpha]_D^{20}$ —33·0°; *cholesteryl* n-*propyl ether*, m. p. 100°, $[\alpha]_D^{20}$ —31·0°; *cholesteryl* iso*propyl ether*, m. p. 132°, $[\alpha]_D^{20}$ —31·1°; *cholesteryl* n-*butyl ether*, m. p. 86° (turbid at 79°), $[\alpha]^{20}$ —28·8°; *cholesteryl* iso*butyl ether*, m. p. 113°, $[\alpha]_D$ —28·7°; *cholesteryl* iso*amyl ether*, m. p. 98° (turbid at 94°), $[\alpha]^{20}$ —28·4°; *cholesteryl* n-*hexyl ether*, m. p. 79° (turbid at 68°), $[\alpha]_D^{20}$ —26·0°; *cholesteryl* n-*heptyl ether*, m. p. 96°, $[\alpha]_D^{20}$ —25·6°; *cholesteryl* sec.-*octyl ether*, m. p. 89°, $[\alpha]_D^{20}$ —24·8°; *cholesteryl allyl ether*, m. p. 78°, $[\alpha]_D$ —32·7°; *cholesteryl phenyl ether*, m. p. 155°, $[\alpha]_D^{20}$ —28·6°; *cholesteryl* d-*bornyl ether*, m. p. 177°, $[\alpha]_D^{20}$ —17·0°.

C. R. HARINGTON.

Cholesterol. II. E. MONTIGNIE (Bull. Soc. chim., 1927, [iv], **41**, 524—527).—Dehydrogenation of cholesterol with sulphur at 200° or with 1 mol. of iodine at 170° affords no retene, as would be expected if the relationship of cholesterol to the rosin acids suggested by Aschan (A., 1921, i, 512), from a comparison of colour reactions, is valid. In the former case, hydrogen sulphide and methyl mercaptan are evolved, but the residue is a black, uncrystallisable mass, partly soluble in ether, which combines with bromine. The reaction product with iodine on treatment with chlorine in chloroform affords a *substance*, $C_{26}H_{44}O_2Cl_5$, m. p. 75°, yielding with nitric acid a *nitro*-derivative, m. p. 53°. With potassium hydrogen sulphate at 145°, cholesterol affords β-cholesterylene, m. p. 188—193° (tetrabromide, m. p. 164—166°). When heated with glacial acetic and phosphoric acids, cholesterol yields α-cholesterylene, m. p. 79—80°, and an *acetate*, m. p. 112°, hydrolysed by 0·1*N*-potassium hydroxide solution to iso*cholesterol*, m. p. 94·5° (*bromide*, m. p. 91—92°; *benzoate*, 108—109°). With alcoholic potassium hydroxide both *iso*cholesterol and its acetate afford cholesterol.

R. BRIGHTMAN.

Alleged action of *X*-rays on cholesterol. J. HIEGER (Biochem. J., 1927, **21**, 407—411).—Cholesterol in chlorine-containing solvents such as chloroform or carbon tetrachloride is attacked by the chlorine liberated by the action of *X*-rays. In benzene, no change is produced, whilst in chlorobenzene the change is very slight. Radiations from radium have the same action as *X*-rays on cholesterol in chlorine-containing solvents.

S. S. ZILVA.

Transformations of cholesterol. A. WINDAUS (Annalen, 1927, 453, 101—112).—When cholesterol hydrochloride is boiled with anhydrous sodium acetate in absolute alcohol (cf. Mauthner, A., 1906, i, 579), allo*cholesterol*, m. p. 117°, is obtained. The new isomeride is reconverted into cholesterol at the ordinary temperature in ethereal solution in presence of platinum or when its xylene solution is boiled. With bromine, it gives cholesterol dibromide, and with acetic anhydride, cholesteryl acetate. The mother-liquors from the acetylation yield on hydrolysis a little β-cholesterol. Catalytic hydrogenation of *allo*cholesterol in amyl ether affords principally coprosterol with a little dihydrocholesterol. This indicates that in *allo*cholesterol the double linking is probably attached to the 1-carbon atom (for notation, cf. A., 1926, 723), which thereby loses its asymmetry, and suggests a possible mechanism for the transformation of cholesterol into coprosterol in the organism. When cholesterol is heated with finely-divided nickel (cf. A., 1916, i, 813) at 180°, the double linking is hydrogenated at the expense of the alcoholic group and the configuration of the 1-carbon atom is partly changed, cholestanone, coprostanone, and a little of a *substance*, m. p. 82°, being formed. The formation of these ketones, in which *allo*cholesterol is probably an intermediate stage, explains the hydrogenation of cholesterol to γ-cholestanol (*loc cit.*) under similar conditions. The latter is also obtained by heating cholesterol at 180° with alcoholic sodium ethoxide. The reduction of a double linking under these conditions is abnormal and may again be due to intermediate formation of cholestanone and coprostanone. β-Cholesterol (Diels and Linn, A., 1908, i, 164) is catalytically hydrogenated in ether–glacial acetic acid to dihydrocholesterol. If it differed from cholesterol in the configuration of the hydroxyl group, ε-cholestanol should be formed, so that probably only the position of the double linking is different. H. E. F. NOTTON.

Optically active diphenylhydroxyethylamines and isohydrobenzoins. I. J. READ and (MISS) C. C. STEELE (J.C.S., 1927, 910—918).—*dl*-Diphenylhydroxyethylamine is resolved into its optically active components by means of *d*-hydroxymethylenecamphor or *d*-camphorsulphonic acid. The isomerides show strong mutarotation in acetone. The externally compensated base, on treatment with nitrous acid, gives a mixture containing hydrobenzoin, *dl-iso*hydrobenzoin, and probably deoxybenzoin, whilst the products from *l*- and *d-iso*diphenylhydroxyethylamine yield, on purification, *l*- and *d-iso*hydrobenzoin, respectively. The nitrous acid reaction cannot be used to determine the configuration of these substances, but Erlenmeyer's conclusions (A., 1897, i, 480; 1899, i, 882) are confirmed on other grounds. Mixed crystals of *d*- and *l-iso*hydrobenzoin, exhibiting hemihedral facets, separate from ethereal solutions of *dl-iso*hydrobenzoin. Complete optical resolution cannot, therefore, be effected by mechanical separation (cf. Erlenmeyer, *loc. cit.*). Formyl-*dl-neo*menthylamine also separates from solution in mixed possessing hemihedral facets (A., 1926, i, 1147). The following are described: d-*diphenylhydroxyethylamino*-d-*methylenecamphor*, m. p. 146°, $[\alpha]_D$ +235° in alcohol; d- and l-*diphenylhydroxyethylamine hydrobromide*, m. p. 192°, $[\alpha]_D$ ±59·0° in water; d-*diphenylhydroxyethylamine*, m. p. 143°, $[\alpha]_D$ +10° in alcohol, +15·1° in acetone, mutarotating to −120·8° in 6 hrs. (*hydrochloride*, $[\alpha]_D$ +69·3° in water); *benzylidene*-d-*diphenylhydroxyethylamine*, m. p. 109°, $[\alpha]_D$ −81·4° in alcohol; dl-*diphenylhydroxyethylamine hydrobromide*, m. p. 184°; *benzylidene*-dl-*diphenylhydroxyethylamine*, m. p. 120·5°; dl-*diphenylhydroxyethylamine* d-*bromocamphorsulphonate*, m. p. 210° (decomp.), $[\alpha]_D$ +52·1° in water; d-*diphenylhydroxyethylamine* d-*camphorsulphonate*, m. p. 193°, $[\alpha]_D$ +51·5° in water; *l-iso*diphenylhydroxyethylamine, m. p. 115°, $[\alpha]_D$ −125° in alcohol, −102·2° in acetone, mutarotating to −90·3° in 3 hrs. (*hydrochloride*, $[\alpha]_D$ −81·7° in water)—Erlenmeyer gives m. p. 113—114°, $[\alpha]_D$ −109·6° for the base; l-iso*hydrobenzoin*, m. p. 146°, $[\alpha]_D$ −89·7° in alcohol; d-iso*diphenylhydroxyethylamine hydrogen l-tartrate*, m. p. 177°, $[\alpha]_D$ +43·4° in water; d-iso*diphenylhydroxyethylamine*, $[\alpha]_D$ +125·5° in alcohol; d-iso*hydrobenzoin*, m. p. 146°, $[\alpha]_D$ +90·5° in alcohol.

M. CLARK.

o-Cresolbenzein and some of its derivatives. W. R. ORNDORFF and S. A. MCNULTY (J. Amer. Chem. Soc., 1927, 49, 992—997).—*o*-Cresolbenzein (cf. Schroeter, A., 1890, 898) is obtained, together with phenyl 4-hydroxy-*m*-tolyl ketone, by adding benzotrichloride (1 mol.) to *o*-cresol (2·1 mols.) at 80° over a period of several hours. The stable form, m. p. 260—262° (decomp.), is reddish-orange and has therefore the quinonoid structure. It is converted into the colourless carbinol form by dissolution in aqueous sodium hydroxide, followed by addition of ammonium chloride solution in presence of ether. The carbinol is reconverted into the quinonoid form by loss of 1 mol. of water, in a current of dry air. The *hydrochloride*, red, m. p. 222—223°, *sulphate*, red, m. p. 231—232°, *diacetate*, m. p. 104—105°, and *dibenzoate*, m. p. 128—129°, are described. Treatment of *o*-cresolbenzein with fuming nitric acid in glacial acetic acid affords a *dinitro*-derivative, m. p. 127°, whilst bromination in the same solvent affords *dibromo-o-cresolbenzein hydrobromide*, m. p. 230°, which is converted into *dibromo-o-cresolbenzein*, $(+0{\cdot}5C_7H_8)$, red, m. p. 238°, when boiled in toluene. The latter absorbs 1 mol. of dry ammonia, forming a deep blue *salt*, whilst dry hydrogen chloride yields the *dihydrochloride*. The colourless carbinol form of the dibromo-derivative is obtained by dissolving the above quinonoid form in aqueous sodium hydroxide and reprecipitating with ammonium chloride in presence of a mixture of ether and light petroleum. Reduction of *o*-cresolbenzein with zinc dust and glacial acetic acid affords *phenyl*-4 : 4′-*dihydroxydi-m-tolylmethane*, m. p. 107—109° (*diacetate*, m. p. 109—110°; *dibenzoate*, m. p. 145°; *dimethyl ether*, m. p. 100°), which, on treatment with bromine in glacial acetic acid, yields the above hydrobromide of dibromo-*o*-cresolbenzein. The same product is obtained by condensing *o*-cresol with benzaldehyde in presence of zinc chloride. When heated with 5% aqueous potassium hydroxide, *o*-cresolbenzein yields phenyl 4-hydroxy-*m*-tolyl ketone, m. p. 170—171°

(cf. Bartolotti, A., 1901, i, 36), of which the *acetate*, m. p. 66·5°, and *benzoate*, m. p. 96°, are described.

F. G. Willson.

Synthesis and indicator properties of some new sulphonephthaleins. B. Cohen (U.S. Pub. Health Rep., 1926, **41**, 3051—3074).—*m*-Cresolsulphonephthalein (*m*-cresol-purple) is a brilliant and stable indicator of acidity in the region p_H 1·2—2·8; 1·51. absorption maximum 533, colour change red to yellow. The second colour change is from yellow to purple in the region p_H 7·4—9·0; p 8·32, corresponding with the dissociation of the phenolic hydrogen ion, absorption maximum 580. In this zone, the disadvantage of dichromatism interferes with the accurate matching of colours. The tetrabromo-derivative (bromocresol-green), m. p. 217—218°, is more stable in solution than methyl-red; absorption maximum 617, p_{Ka} 4·67, useful p_H range 3·8—5·4, colour change yellow to blue. The tetrachloro-derivative (chlorocresol-green), m. p. 200—201°, has absorption maximum 612, p_{Ka} 4·8, useful p_H range 4·0—5·6, colour change yellow to blue.

Dibromophenolsulphonephthalein (bromophenol-red), m. p. 230°, absorption maximum 574, p_{Ka} 6·16, has useful p_H range 5·2—6·8, colour change yellow to red. The dichloro-derivative (chlorophenol-red) has m. p. 261—262°, absorption maximum 573, p_{Ka} 5·98, useful p_H range 4·8—6·4, colour change yellow to red. The dichlorodibromo-derivative (bromochlorophenol-blue) has m. p. 250—251°, absorption maximum 596, useful p_H range 3·0—4·6, 3·98, colour change yellow to blue. 2 : 6-Xylenolsulphonephthalein has m. p. 253—254°, p_{Ka} 8·6.

Chemical Abstracts.

Organic acids and bases in non-aqueous solution. III. Aliphatic dicarboxylic and aromatic acids. F. Holzl (Monatsh., 1926, **47**, 755—783).—The behaviour of (*a*) oxalic, (*b*) malonic, (*c*) benzoic, (*d*) salicylic, and (*e*) phthalic acids towards bases in absolute alcoholic solution has been examined by conductivity measurements at 25° (cf. A., 1926, 1206). Under these conditions, the nature of the compound formed depends more on the dissociation coefficients of the components than on the number of acidic or basic groups they contain. Fairly strong acids and bases form salts of normal type, but if either the acidic or basic component is weak, the compound is usually of the type AB (A=1 mol. of acid, B—1 mol. of base). The results frequently differ from those obtained from thermal diagrams (cf. Kremann, A., 1926, 393). All the acids examined give compounds of the type AB with trimethylamine, aniline, methylaniline, dimethylaniline, *p*-toluidine, and *o*-, *m*-, and *p*-phenylenediamines, but no compound with diphenylamine. Further results may be summarised as follows, stating (1) the base, (2) the acid, and (3) the type of compound obtained: ammonia: with (*a*), (*b*), and (*e*), AB and AB_2; with (*c*) and (*d*), AB; diethylamine: with (*a*), (*b*), (*d*), and (*e*), AB and AB_2; with (*c*), AB; ethylenediamine: with (*b*), A_2B, AB, and AB_3; with (*c*), AB; with (*d*), A_2B and AB; with (*e*), AB and AB_2; benzylamine: with (*a*) and (*b*), AB and AB_2; with (*c*) and (*d*), AB; α-naphthylamine: with (*a*), (*b*), (*d*), and (*e*), AB; with (*c*), A_2B and AB_2; β-naphthylamine: with (*a*), (*b*), (*d*), and (*e*), AB; with (*c*), A_2B and AB_2; carbamide: with (*a*), (*b*), and (*e*), AB_2; with (*c*) and (*d*), AB. H. E. F. Notton.

Nature of the alternating effect in carbon chains. XVI. Directive action of some groups of the form –COR in aromatic substitution. K. E. Cooper and C. K. Ingold (J.C.S., 1927, 836—841).—Progressively increasing *m*-directive power is shown by the groups –Me, $-NH_2$, –OH, and –Cl in association with a carbonyl group attached to the benzene nucleus. Thus acetophenone, benzamide, benzoic acid, and benzoyl chloride give, on nitration, 55, 69, 82, and 90% of *m*-nitro-derivative, respectively. This corresponds with the conception of direction by a permanent dipole as opposed to competition between conjugative electron displacements.

M. Clark.

Derivatives of diphenylamine-2-carboxylic acid. II. H. Goldstein and M. Piolino (Helv. Chim. Acta, 1927, **10**, 332—334).—Reduction of 2 : 4-dinitrodiphenylamine-6-carboxylic acid (Ullmann and Engi, A., 1909, i, 473) with stannous chloride yields the *double tin* salt of the diamino-acid, of which the dihydrochloride is obtained on treatment with hydrogen sulphide. This on esterification with methyl alcohol and hydrogen chloride yields the *dihydrochloride* of *methyl* 2 : 4-*diaminodiphenylamine*-6-*carboxylate*, the free *base*, m. p. 133°, being obtained by the action of ammonia (*diacetyl* derivative, m. p. 226—227°). 4'-Dimethylaminodiphenylamine-6-carboxylic acid similarly yields a *methyl* ester, m. p. 99—100°, whilst reduction of 4-nitro-4'-dimethylaminodiphenylamine-6-carboxylic acid (*potassium* salt) with stannous chloride yields 4-*amino*-4'-*dimethylaminodiphenylamine*-6-*carboxylic acid*, m. p. 208° (decomp.) (*dihydrochloride*; *diacetyl* derivative, m. p. 219°; *methyl* ester, m. p. 111°; *dihydrochloride* of methyl ester). J. W. Baker.

Mechanism of the reaction between a carboxylic ester and a Grignard reagent. D. R. Boyd and H. H. Hatt (J.C.S., 1927, 898—910).—The reaction between a carboxylic ester and a Grignard reagent in presence of metallic magnesium results in pinacone as well as tertiary alcohol formation. Intermediate production of a ketone is therefore postulated and the mechanism of its formation is discussed. The hypothesis of Stadnikov (A., 1914, i, 954) is criticised, and his experimental evidence for formation of the ketone R·CO·R′ as an intermediate product is shown to be incorrect. The product supposed to be triphenylethylene is shown to be diphenyl.

Certain pinacones may be advantageously prepared by this method. Thus with ethyl *o*-toluate and magnesium phenyl bromide, the yields of pinacone and tertiary alcohol are 38% and 23% respectively. The following are described: *tetra*-o-*tolylpinacol*, m. p. 158°; *di*-o-*tolylcarbinol*, m. p. 119—119·5°.

M. Clark.

Nature of the alternating effect in carbon chains. XV. Directive action of some groups of the form –CR′R″·COR in aromatic substitution. J. W. Baker and C. K. Ingold (J.C.S., 1927, 832—836).—Ethyl phenylacetate and ethyl phenyl-

malonate on nitration in nitric acid (*d* 1·5) at or below 0° give, respectively, 9% and 20% of the *m*-derivative. These results are taken to indicate the occurrence of a permanent fractional dipole in the carbonyl group similar to, but weaker than, the permanent integral dipole present in semi-polar double linkings. M. CLARK.

Isomerism of anilino-*m*-nitrophenylacetonitrile. II. G. HELLER and E. SCHÜTZE (Ber., 1927, **60**, [*B*], 909—912; cf. A., 1925, i, 814).—The yellow form of anilino-*m*-nitrophenylacetonitrile invariably separates from acidic solvents, whereas an equilibrium between the yellow and colourless varieties is slowly established in neutral media, from which, when rapidly cooled, the two forms are deposited. There is no evidence of polymerisation. The yellow variety is transformed by cold, concentrated sulphuric acid into yellow *anilino*-m-*nitrophenylacetamide*, m. p. 150° [*sulphate*, m. p. about 203° (decomp.) after darkening at 180°; *hydrochloride*]; crystallisation of the yellow amide from alcohol under certain conditions affords the colourless *amide*. The persistence of isomerism in the amides renders the cyclic structure, $NO_2{\cdot}C_6H_4{\cdot}CH<^{NPh}_{CH}>N$, for the yellow nitrile (*loc. cit.*) untenable. *m*-Nitromandelonitrile and *p*-chloroaniline afford p'-*chloroanilino*-m-*nitrophenylacetonitrile*, yellow crystals, m. p. 98—99°, with some *m*-nitrobenzylidene-*p'*-chloroaniline, m. p. 86°, whereas *m*-nitromandelonitrile and *m*-chloroaniline give solely *m*-nitrobenzylidene-*m'*-chloroaniline, m. p. 103·5°. *o*-Toluidine gives colourless and yellow o-*toluidino*-m'-*nitrophenylacetonitriles*, m. p. 135°, which are less sharply differentiated than the anilino-derivatives. *m*-Toluidine yields solely colourless m-*toluidino*-m'-*nitrophenylacetonitrile*, m. p. 104°, whereas p-*toluidino*-m'-*nitrophenylacetonitrile*, m. p. 75—76°, could be obtained only in the yellow form. H. WREN.

Syntheses of amino-acids. A. SKITA and C. WULFF (Annalen, 1927, **453**, 190—210).—The condensation product, m. p. 144° (this vol., 157), of benzylidene*cyclo*hexylamine and pyruvic acid is hydrogenated, in presence of colloidal platinum, to a cyclo*hexylaminophenylpropanecarboxylic acid*, $C_{16}H_{23}O_2N$, m. p. 250° (*methyl* ester, b. p. 150—152°/0·03 mm., and its *hydrochloride*, m. p. 148°, and *nitroso*-derivative, m. p. 63°). Similarly, iso*butylidene*cyclo*hexylamine*, b. p. 207—209°, gives with pyruvic acid an unstable compound, which is hydrogenated to a cyclo*hexylaminoheptanecarboxylic acid* (*ethyl* ester, b. p. 145—148°/12 mm., and its *hydrochloride*, m. p. 215°). Ethylidene*cyclo*hexylamine and pyruvic acid, however, in dry ethereal solution yield acetaldehyde and the extremely unstable, yellow, amorphous α-cyclo*hexyliminopropionic acid*, which is readily hydrogenated to α-cyclo*hexylaminopropionic acid*, m. p. 230° (*ethyl* ester, b. p. 110—112°/12 mm., and its *hydrochloride*, m. p. 173°, and *picrolonate*, m. p. 164°). A second, less unstable, condensation product, α-cyclo*hexylamino*-α-*hydroxypropionic acid*, m. p. 67°, prepared from *cyclo*hexylamine or α-*propylidene*cyclo*hexylamine*, b. p. 59—61°/15 mm., and pyruvic acid in ethereal solution, yields the same *cyclo*hexylalanine on reduction. The constitution of the latter is confirmed by synthesis from *cyclo*hexylamine and α-bromopropionic acid, and also by conversion into *cyclo*hexylethylamine.

Contrary to the statements of Knoop and Oesterlin (A., 1925, i, 1493), faintly acid aqueous-alcoholic solutions containing ethylamine and pyruvic or glyoxylic acid are hydrogenated, in presence of colloidal platinum, to α-*ethylaminopropionic acid*, m. p. 211—215° (*methyl* ester, b. p. 44°/11 mm.; *ethyl* ester, b. p. 53°/10 mm., and its *hydrochloride*, m. p. 129°), and ethylaminoacetic acid (*ethyl* ester, b. p. 58°/16 mm., and its *hydrochloride*, m. p. 135°), respectively. In this reaction, the ethylamine may be replaced by aldehyde-ammonia, which is reduced to ethylamine under these conditions, or by ethylidene-ethylamine. Under analogous conditions, alanine (30%) is obtained from a solution containing ammonia and pyruvic acid. A new synthesis of β-amino-acids is afforded by the observation that, unlike the parent substance, the acetyl and *N*-alkyl derivatives of ethyl β-iminobutyrate are readily hydrogenated. Accordingly, the following derivatives of ethyl butyrate: β-acetimido-; β-cyclo*hexylimino*-, b. p. 156—157°/12 mm.; β-*ethylimino*-, b. p. 103—104°/8 mm.; β-iso*amylimino*-, b. p. 148—149°/12 mm., and β-phenylimino-, were reduced to the *ethyl* esters, b. p. 158°/12 mm.; b. p. 130°/17 mm. (*hydrochloride*, m. p. 156—157°); b. p. 82—85°/19 mm. (*hydrochloride*, m. p. 123—124°); b. p. 108—110°/17 mm. (*hydrochloride*, m. p. 115—116°; *nitrobenzoyl* derivative, m. p. 74—75°), and b. p. 149—152°/17 mm. (hydrochloride, m. p. 174—175°), respectively, of β-*acetamido*-; β-cyclo*hexylamino*-, m. p. 150—155° (*hydrochloride*, m. p. 177°); β-*ethylamino*-, m. p. 159—160° (*hydrochloride*, m. p. 70°); β-iso*amylamino*-, m. p. 170°, and β-anilino- (Stormer and Robert, A., 1922, i, 519) butyric acids. H. E. F. NOTTON.

Preparation and resolution of α-*p*-nitrophenylbutyric acid. E. FOURNEAU and G. SANDULESCO (Bull. Soc. chim., 1927, [iv], **41**, 450—454).—α-Phenylbutyronitrile (Bodroux and Taboury, A., 1910, i, 257) is hydrolysed only on heating with hydrochloric acid in a sealed tube; on nitration with nitric and sulphuric acids at 0—5°, it affords α-p-*nitrophenylbutyronitrile*, which is readily hydrolysed by dilute sulphuric acid to α-p-*nitrophenylbutyric acid*, m. p. 122—123° (*amide*, m. p. 139—140°). Attempts to resolve the acid with cinchonine, cinchonidine, quinine, quinidine, strychnine, and brucine were unsuccessful. The *d*-acid, m. p. 108—109°, $[\alpha]_D$ +53·33° (in alcohol), has been obtained by crystallisation of the *morphine* salt. The *l*-acid has not been obtained pure. α-p-*Aminophenylbutyric acid*, m. p. 142—143° (*acetyl* derivative, m. p. 208—209°), is described. R. BRIGHTMAN.

Preparation of *dl*-*p*-αβ-dimethyl-*n*-propylbenzoyl chloride and resolution of αβ-dimethyl-*n*-propylaniline. J. W. E. GLATTFELD, H. H. HOPKINS, and F. H. THURBER (J. Amer. Chem. Soc., 1927, **49**, 1039—1042; cf. A., 1921, i, 63).—p-αβ-Dimethyl-*n*-propylaniline was converted by the Sandmeyer reaction into the corresponding *nitrile*, b. p. 125—126°/8 mm. (decomp.), from which, by alkaline hydrolysis, p-αβ-*dimethyl*-n-*propylbenzoic acid*, m. p.

77—78°, was obtained. Treatment with phosphorus pentachloride yielded the acid *chloride*, b. p. 118—120°/2 mm. By the use of *d*-camphorsulphonic acid, *d*- and *l*-*p*-αβ-dimethylpropylanilines have been obtained, having $[\alpha]_D$ +3·85° and −3·5°, respectively. F. G. WILLSON.

Phenylstearic acid from oleic acid. B. H. NICOLET and C. M. DEMILT (J. Amer. Chem. Soc., 1927, **49**, 1103—1106).—*Phenylstearic acid*, b. p. 250°/4 mm., m. p. not above −15°, n^{20} 1·4905, is obtained by the action of aluminium chloride on oleic acid in benzene solution, in 35% yield. The *silver* salt, *lead* salt, m. p. about 86°, *methyl* ester, b. p. 228°/4 mm., n^{20} 1·4840, *amide*, liquid, *anilide*, b. p. 282°/4 mm., and a *dinitro*-derivative, red, viscous, are described. Oleic acid appears to react analogously with toluene and naphthalene. F. G. WILLSON.

Oxidation of cinnamic acid. L. ROSENTHALER (Arch. Pharm., 1927, **265**, 110—111).—Oxidation of cinnamic acid with cold alkaline permanganate or warm dilute nitric acid produces benzaldehyde, benzoic acid, and oxalic acid. S. COFFEY.

Superheating of uniform organic compounds. III. Aryl esters of unsaturated acids. S. SKRAUP and E. BENG (Ber., 1927, **60**, [*B*], 942—950; cf. A., 1924, i, 1185).—The type of thermal decomposition observed with esters of saturated acids and acrylic acid is not generally shared by esters of unsaturated acids, which behave individually. Phenyl cinnamate at 290—300° in a sealed tube or under atmospheric pressure gives stilbene and carbon dioxide with a little phenol. *Phenyl* p-*chlorocinnamate*, m. p. 100°, and p-*chlorophenyl cinnamate*, m. p. 105°, similarly yield *p*-chlorostilbene and carbon dioxide. *Phenyl* α-*bromo*-β-*methylbutyrate*, b. p. 149—150°/16 mm., obtained by heating phenol with α-bromo*iso*valeryl bromide, is converted by pyridine bases into *phenyl* ββ-*dimethylacrylate*, b. p. 127°/11 mm., which passes at 220—230° into o-ββ-*dimethylacrylylphenol*, m. p. 88° (*phenylhydrazone*, m. p. 118°), which is also obtained from the ester and zinc chloride at 140—160°. The phenol is hydrolysed by alcoholic potassium hydroxide to *o*-hydroxyacetophenone. p-*Chlorophenyl* α-*bromo*-β-*methylbutyrate*, b. p. 170—171°/15 mm., is transformed by pyridine into p-*chlorophenyl dimethylacrylate*, b. p. 155—156°/15 mm., which is similarly converted into *p*-chloro-*o*-ββ-dimethylacrylylphenol, identified by its hydrolysis to 5-chloro-2-hydroxyacetophenone. Thermal decomposition of the acrylic esters is greatly facilitated if they are not completely free from the parent bromo-compounds. Thermal decomposition of *phenyl oleate*, b. p. 256—257°/12 mm., and *phenyl elaidate*, b. p. 256—257°/12 mm., m. p. 22°, yields phenol, and appears to be accompanied by partial isomerisation of the esters. Analogous results are recorded with (non-homogeneous) phenyl erucate, b. p. 285°/12 mm., m. p. 18°, and *phenyl brassidate*, b. p. 285°/12 mm., m. p. 44°. H. WREN.

Transformation of *allo*cinnamylideneacetic acid into the normal form with iodine as photocatalyst in methyl alcohol solution. II. J. C. GHOSH and M. N. MITRA (J. Indian Chem. Soc., 1926, **3**, 273—290).—The transformation of *allo*cinnamylideneacetic acid into the normal form with iodine as a photocatalyst has been investigated in methyl alcohol solution by a method analogous to that previously employed in chloroform solution (Ghosh and Gupta, A., 1926, 400). Equilibrium is attained when 90% conversion has been effected, this value being independent of the concentration of the iodine and the intensity of the light, and almost independent of temperature. The velocity constants k' and k'' for a homogeneous, unimolecular reversible reaction for freshly-prepared solutions are constant when the concentration of the iodine is greater than $0{\cdot}024N$, but below this the value of k' increases continually, denoting a period of induction. With increasing concentration of iodine, the value of k' passes through a maximum and then diminishes. When old solutions are used, the values of k' and k'' are smaller, but are constant throughout the reaction. The values of the constants decrease with increasing initial concentration of the *allo*-acid and are proportional to the intensity of the light (λ=500 $\mu\mu$). The temperature coefficient of the reaction is very small. It is calculated that each quantum of light transforms $4{\cdot}23\times10^2$ mols., but Einstein's law of photochemical equivalence does not seem to be applicable to the reaction. The results are discussed and the maximum in the velocity constant–iodine concentration curve is explained on the basis of Perrin's assumptions (A., 1924, ii, 713; cf. Rule, A., 1926, 361). J. W. BAKER.

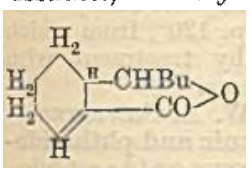
Isomeric phenylserines. M. O. FORSTER *and* K. A. N. RAO (J. Indian Inst. Sci., 1927, 9A, 193—201).—See A., 1926, 1037.

Hydrophthalides. II. Action of sodium amalgam on monoalkylidenephthalides. S. BERLINGOZZI and L. CIONE (Gazzetta, 1927, **57**, 243—248; cf. A., 1926, 835).—By reducing the corresponding alkylidenephthalides, obtained by the action of phthalic anhydride on an aliphatic anhydride, with sodium amalgam in the cold, ethylphthalide, m. p. 12° (cf. Gottlieb, A., 1899, i, 511), propylphthalide, b. p. 154°/10 mm. (cf. Gucci, A., 1898, i, 665), and iso*butylphthalide*, b. p. 159°/10 mm. (from *iso*butylidenephthalide, m. p. 97°), were obtained. Reduction of these in boiling alkaline solution by pure sodium amalgam gave ethyl-, propyl-, and iso*butyl*- (b. p. 161°/10 mm.) Δ^6-tetrahydrophthalides. E. W. WIGNALL.

Hydrophthalides. III. Derivatives of $\Delta^{2,6}$-dihydrophthalide. S. BERLINGOZZI [with C. MENNONNA and A. PALMIA] (Gazzetta, 1927, **57**, 248—254; cf. preceding abstract).—By the action of magnesium alkyl iodides on $\Delta^{2:6}$-dihydrophthalic anhydride, the following $\Delta^{2:6}$-dihydrophthalides are prepared: *methyl*-, b. p. 148°/14 mm.; *ethyl*-, b. p. 143°/6 mm., 151°/10 mm.; n-*propyl*-, b. p. 160°/9 mm.; iso*butyl*-, b. p. 164°/10 mm.; the last three derivatives are also obtained by careful reduction of the corresponding alkylphthalides by sodium amalgam. The ethyldihydrophthalide is hydrolysed by sodium hydroxide solution to 2-α-*hydroxypropyl*-$\Delta^{2\cdot6}$-*dihydrobenzoic acid*, isolated as the *silver* salt, oxidised by alkaline permanganate to succinic and oxalic acids, decomposed by alkali fusion to propionic acid and other

substances, reduced by sodium amalgam, in the cold to ethyl-Δ^6-tetrahydrophthalide, and in alcohol in the hot probably to *ethylhexahydrophthalide*, which is hydrolysed to 2-α-*hydroxypropylhexahydrobenzoic acid*, isolated as the *silver* salt. These reactions indicate its $\Delta^{2,6}$-structure. E. W. WIGNALL.

Hydrophthalides. IV. *n*-Butyl derivative of Δ^6-tetrahydrophthalide. S. BERLINGOZZI and G. LUPO (Gazzetta, 1927, **47**, 255—264; cf. preceding abstracts).—n-*Butyl*-Δ^6-*tetrahydrophthalide* (annexed formula), b. p. 187—188°/17 mm., $[R_L]_\alpha$ 55·30, $[R_L]_\beta$ 56·70, is obtained from magnesium iodide and Δ^2-tetrahydrophthalic anhydride, and also from phthalic anhydride and sodium *n*-valerate. These condense to give n-*butylidenephthalide*, m. p. 82—83°, somewhat unstable, which is reduced to *n*-butylphthalide, which on hydrolysis gives *o*-α-hydroxyamylbenzoic acid (cf. Ciamician and Silber, A., 1897, i, 483, 484). Reduction of hot *n*-butylphthalide by sodium amalgam gives *n*-butyl-Δ^6-tetrahydrophthalide. This substance, which has an odour resembling celery oil and may be named *iso*sedanolide (cf. Ciamician, *loc. cit.*), hydrolyses to syrupy 2-α-*hydroxyamyl*-Δ^6-*tetrahydrobenzoic acid* (*silver* salt), which is oxidised by alkaline permanganate to α-hydroxyamylbenzoic acid, and is reduced by sodium in alcohol to α-hydroxyamylhexahydrobenzoic acid. Fusion with alkali yields tetrahydrobenzoic acid. E. W. WIGNALL.



Hydrophthalides. V. Relation between constitution and odour. S. BERLINGOZZI (Gazzetta, 1927, **57**, 264—268; cf. preceding abstracts).—Unsubstituted phthalide has an odour resembling that of bitter almonds, and $\Delta^{2:6}$-dihydro-, Δ^6-tetrahydro-, and hexahydrophthalides have terpene-like odours. Dialkylphthalides have, however, a slight odour resembling celery, which becomes stronger with alkylidenephthalides, and strongest with monoalkyl derivatives, especially those of tetrahydro- and hexahydro-phthalides. This odour is increased with increased size of the substituent group, but arylphthalides have no such odour.

Phenyl-$\Delta^{2:6}$-*dihydrophthalide*, m. p. above 5°, b. p. 197—198°/14 mm., obtained from $\Delta^{2,6}$-dihydrophthalic anhydride and magnesium phenyl bromide, is oxidised by alkaline permanganate to benzoic, succinic, and oxalic acids. Phenyl-Δ^6-tetrahydrophthalide, b. p. 192—193°/14 mm., which oxidises to benzoic and Δ^1-tetrahydrobenzoic acids, is obtained similarly, and also by reduction by zinc and acetic acid of 2-*benzoyl*-Δ^6-*tetrahydrobenzoic acid* obtained by condensation of Δ^2-tetrahydrophthalic anhydride with benzene (*silver* salt prepared). E. W. WIGNALL.

2-Methoxydiphenyl-2′-carboxylic acid and its demethylation with thionyl chloride. H. G. RULE and E. BRETSCHER (J.C.S., 1927, 925—928).—Methylon the lactone of 2-hydroxydiphenyl-2′-carboxylic acid gives 2-*methoxydiphenyl*-2′-*carboxylic acid*, p. 152—153° (corr.) (*methyl* ester, b. p. 181—182°/ mm.). When warmed with thionyl chloride, this unstance is demethylated, regenerating the lactone. M. CLARK.

Esters of hexahydrophenylglycine-*o*-carboxylic acid. D. VORLANDER and W. FACHMANN (Ber., 1927, **60**, [*B*], 844).—In amplification of previous work (A., 1926, 1139), the following constants are recorded: dimethyl ester, b. p. 163—170°/23—25 mm., 140—152°/10—12 mm., 148—152°/12 mm.; diethyl ester, b. p. 170—173°/15—16 mm., 165—166°/12 mm. The hydrochlorides of the dimethyl and diethyl esters have m. p. 159° (decomp.) and about 80° (decomp.), respectively. H. WREN.

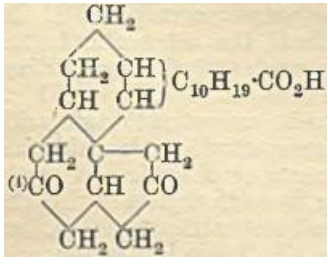
Ethyl benzoylpyruvate. H. GAULT and A. FUNKE (Bull. Soc. chim., 1927, [iv], **41**, 473—499). Ethyl benzoylpyruvate condenses with formaldehyde in presence of diethylamine with or without alcohol as solvent, affording in 80—90% yield *ethyl methylenebisbenzoylpyruvate* (*ethyl* βδ-*dibenzoyl*-αε-*diketopimelate*), $CH_2[CH(COPh)\cdot CO\cdot CO_2Et]_2$ (I) (*monohydrate*, m. p. about 95°; *diphenylhydrazone*, m. p. 100°; *oxime*, oily). Acetaldehyde and its homologues do not condense under these conditions, but in presence of hydrochloric acid afford furan derivatives. Hydrolysis of (I) with cold dilute alkali or with boiling hydrochloric or 20% sulphuric acid affords oxalic acid and αε-diphenylpentane-αε-dione. Dehydration with cold sulphuric acid affords (yield 2%, 26% in presence of alcohol) *ethyl methylenebis*-3-*indone*-1-*carboxylate*, $\left[C_6H_4<\begin{matrix}CO\\C(CO_2Et)\end{matrix}>C-\right]_2CH_2$ (II), yellow, m. p. 104° (*diphenylhydrazone*, m. p. 150°). On hydrolysis with dilute alkali, the ester affords the *acid*, red, m. p. 170° (*monophenylhydrazone*, *sodium* salt). Methylenebis-3-indone-1-carboxylic acid is stable towards mineral acids, except sulphuric acid, but is decomposed by strong alkalis. On oxidation with potassium permanganate or chromic and acetic acids, it affords 60% of the theoretical yield of phthalic acid. Hydriodic acid is almost without action, but with sodium amalgam in alkaline solution the acid affords a colourless, amorphous product, $C_{24}H_{16}O_6$, in which the presence of hydroxyl groups could not be established, but which regenerates methylenebis-3-indone-1-carboxylic acid on oxidation with dilute nitric acid. Thionyl chloride affords a *substance*, m. p. 129°, containing only 5—6% of chlorine.

Acetaldehyde and ethyl benzoylpyruvate in ethereal solution in presence of hydrogen chloride afford 3-*benzoyl*-4 : 5-*diketo*-2-*methylfuran*, m. p. 129° [*copper* salt (+$2H_2O$)], affording an *anilide*, m. p. 220—225° (decomp.), and on hydrolysis with dilute alkali, acetaldehyde, acetophenone, and oxalic acid. Heptaldehyde and ethyl benzoylpyruvate condense directly, affording 3-*benzoyl*-4 : 5-*diketo*-2-n-*hexylfuran* (hexylketoparacophenone), m. p. 136° (*copper* salt, +$2H_2O$; *anilide*, m. p. 140°), affording on alkaline hydrolysis acetophenone, heptaldehyde, and oxalic acid. R. BRIGHTMAN.

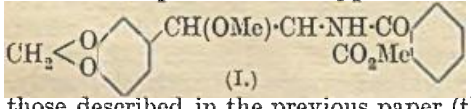
Some reactions of δ-ketonic nitriles. II. C. F. H. ALLEN (J. Amer. Chem. Soc., 1927, **49**, 1112—1115; cf. A., 1925, i, 963).—Knoevenagel's condensation of benzoyl cyanide with *p*-methoxyphenyl styryl ketone in presence of sodium ethoxide (A., 1895, i, 48) has been modified, and a solid product, αβ-*diphenyl*-γ-p-*methoxybenzoylbutyronitrile* (I), m. p. 116°, obtained in 93—94% yield. β-*Phenyl*-α-p-*nitro*-

phenyl-γ-p-methoxybenzoylbutyronitrile, m. p. 151°, was obtained similarly from *p*-nitrobenzoyl cyanide. Hydrolysis of (I) with hydrochloric acid at 130—140° yields *αβ-diphenyl-γ-p-methoxybenzoylbutyric acid*, m. p. 200—201° (*methyl* ester, m. p. 169°). Treatment of (I) with hydrogen bromide in glacial acetic acid yields first *αβ-diphenyl-γ-p-methoxybenzoylbutyramide*, m. p. 248—250°, and then *2-keto-3 : 4-diphenyl-6-p-methoxyphenyltetrahydropyridine*, m. p. 199°, which, on treatment with butyl nitrite in glacial acetic acid, yields *2-hydroxy-3 : 4-diphenyl-6-p-methoxyphenylpyridine*, m. p. 249°. Bromination of (I) in chloroform affords *2-bromo-6-hydroxy-3 : 4-diphenyl-6-p-methoxyphenyl-5 : 6-dihydropyridine*, m. p. 119°, and *2-bromo-3 : 4-diphenyl-6-p-methoxyphenylpyridine*, m. p. 152°, the latter being also obtainable from the former product by treatment with acetyl chloride. F. G. Willson.

Bile acids. XV. Electro-reduction of dehydrodeoxycholic acid to hydroxyketocholanic acid. Conversion of the product into 7-ketocholanic acid. M. Schenck and H. Kirchhof (Z. physiol. Chem., 1927, **163**, 120—133; cf. Wieland and Boersch, A., 1919, i, 572; Borsche and Hallwass, A., 1922, i, 1158, 1159).—Electro-reduction of dehydrodeoxycholic acid (α-diketocholanic acid, annexed formula), m. p. 188—189°, in 10% aqueous-alcoholic sodium hydroxide at 35—40° yields hydroxyketocholanic acid (·CH·OH in position 4), isolated as ethyl ester, m. p. 132—134° (ester *oxime*, m. p. 168—170°); the free acid contains $1H_2O$ (sinters at 105—107°), and after drying at 125° has m. p. 155—160°. Dehydration of the ethyl ester gives *ethyl ketocholenate*, m. p. 105—108°, which is reduced by hydrogen and palladium to 7-ketocholanic acid (·CH_2· in position 4), m. p. 185° (oxime, m. p. 245°), unobtainable by direct reduction of hydroxyketocholanic acid. C. Hollins.



Derivatives of phthalamic acid and phthalimide. C. Mannich and O. Walther (Arch. Pharm., 1927, **265**, 11—15).—It was to be expected that the compounds of the type,



analogous to those described in the previous paper (this vol., 579), would condense to form *iso*quinoline derivatives, and even further to give fused ring compounds of benzanthrone type. Actually only phthalimide derivatives are produced when these compounds are treated with phosphorus oxychloride in hot xylene.

Methyl β-methoxy-β-3 : 4-methylenedioxyphenylethylphthalamate (I), m. p. 141—142°, is converted in this way into 3 : 4 *ethylenedioxystyrylphthalimide*, $CH_2O_2{:}C_6H_3{\cdot}CH{:}CH{\cdot}N{<}\begin{matrix}CO\\CO\end{matrix}{>}C_6H_4$, m. p. 181—182°, which is hydrolysed by alcoholic potassium hydroxide to 3 : 4-*methylenedioxystyrylphthalamic acid*, m. p. 185° (decomp.). When β-methoxy-β-phenylethylamine is treated with *o*-carbomethoxybenzoyl chloride by the Schotten–Baumann method, *methyl β-methoxy-β-phenylethylphthalamate*, m. p. 119—120°, is produced normally, together with the free *acid*, m. p. 140°, as a by-product. When treated with phosphorus oxychloride, the ester yields *styrylphthalimide*, m. p. 184—185°, which is hydrolysed by alcoholic potassium hydroxide to *styrylphthalamic acid*, m. p. 170° (decomp.). β-Methoxy-β-phenylethylphthalamic acid is converted by phosphorus oxychloride in hot xylene into *β-methoxy-β-phenylethylphthalimide*, m. p. 120°, from which styrylphthalimide is obtained by treatment with phosphorus pentoxide in hot xylene.

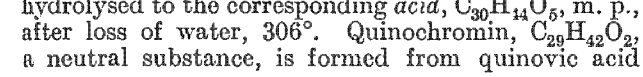
W. A. Silvester.

Tautomerism in the phthalonic and phthalidecarboxylic acids. I. M. A. Cornillot (Ann. Chim., 1927, [x], **7**, 227—273).—An introductory, theoretical paper in which various philosophical aspects of tautomerism are considered together with the logical methods of investigation involved in each view. The problem of the real structure of a tautomeric substance is studied (also means of its representation), and the relative value of physical and chemical tests of its homogeneity are considered. On the basis of Laar's original hypothesis, the author attempts to develop an atomistic theory of tautomerism. The displacement of any atom within a molecule from its mean position by thermal agitation is resisted by the potentials involved in its displacement, but in certain cases it may come within the field of another *atom*, thus causing a deformation of the potential–displacement curve, passing, at the threshold of the two fields, through an active state, and leading, respectively, to isomerism, pseudomerism, desmotropy, tautomerism, and allotropy, the conditions for which are elaborated. Pseudomerism, which the author prefers to the term "mesomerism," is regarded as due to different affinity relationships, desmotropy to a duality of the mean structure, and tautomerism to a duality of the active phases of the molecule.

J. W. Baker.

Quinovic acid. I. H. Wieland and M. Erlenbach (Annalen, 1927, **453**, 83—100).—Analyses of quinovic acid and its derivatives (cf. Liebermann and Giesel, A., 1884, 1191; Kremp, Diss., Freiburg, 1924) indicate that it has the formula $C_{30}H_{46}O_5$, and contains one hydroxyl group and two carboxyl groups. The tribenzoyl derivative must therefore contain two mixed anhydride groups; these are hydrolysed by boiling with moist pyridine, giving a *monobenzoyl* derivative, m. p. 284° (decomp.). Similarly, the triacetyl derivative affords with boiling methyl alcohol a *monoacetyl* derivative, m. p. 284°. Pyroquinovic acid, $C_{28}H_{43}(OH){\cdot}CO_2H$ (*methyl* ester, m. p. 116°), gives a *diacetyl* derivative, m. p. 157°, and a *monoacetyl* derivative, m. p. 240°. Novic acid, $C_{29}H_{43}O_2{\cdot}CO_2H$, obtained by Liebermann and Giesel by treatmg quinovic acid with sulphuric acid, is conveniently prepared by reducing this substance in acetic acid solution with amalgamated zinc. Although it is probably the γ-lactone of quinovic acid, it is extremely difficult to hydrolyse, and gives with alcoholic potassium hydroxide in a sealed tube the isomeric *anhydroquinovic acid*, $C_{28}H_{42}(CO_2H)_2$, m. p.

225°, decomposing above this temperature into *pyroanhydroquinovic acid*, $C_{28}H_{42}{\cdot}CO_2H$, m. p. 188°, and carbon dioxide. Novic acid is oxidised by chromic acid to a yellow *substance*, $C_{20}H_{40}O_4$, m. p. 231°. The neutral products of the action of sulphuric acid on quinovic acid are quinochromin and a little *dehydroquinovic anhydride*, $C_{30}H_{12}O_4$, m. p. 306°, which is hydrolysed to the corresponding *acid*, $C_{30}H_{14}O_5$, m. p., after loss of water, 306°. Quinochromin, $C_{29}H_{42}O_2$, a neutral substance, is formed from quinovic acid



(I) by loss of $CO+2H_2O$. The latter must therefore be an α-hydroxycarboxylic acid. Since quinochromin (II) is not a lactone, the second carboxyl group has apparently undergone ring closure, giving a cyclic ketone. No derivatives of the ketonic function have yet been obtained. The above partial formulæ express the probable relationship of the two substances. H. E. F. NOTTON.

Constituents of the kawa root. III. Catalytic hydrogenation of methysticin. W. BORSCHE (Ber., 1927, **60**, [*B*], 982—984; cf. A., 1915, i, 438; 1921, i, 862).—The failure of Goebel (A., 1922, i, 657) to add more than 1 mol. of hydrogen to methysticin by catalytic hydrogenation is explained, since the cyclic structure,

$CH_2O_2{:}C_6H_3{\cdot}CH{:}CH{\cdot}CH{<}\begin{matrix}CH_2{-}CO\\O{\cdot}C(OMe)\end{matrix}{>}CH$, must be

assigned to it, owing to the observation of Murayama and Shinozaki (Chem. Zentr., 1925, II, 2062) that it exists in optically active forms and hence contains an asymmetric carbon atom. *iso*Methysticin, $CH_2O_2{:}C_6H_3{\cdot}[CH{:}CH]_2{\cdot}CO{\cdot}CH_2{\cdot}CO_2Me$, and methysticic (? *iso*methysticic) acid, derived from it, readily add 2 mols. of hydrogen. Dihydromethysticin, m. p. 114°, and tetrahydromethysticole, $CH_2O_2{:}C_6H_3{\cdot}[CH_2]_4{\cdot}COMe$, b. p. 183—184°/11 mm., m. p. 28° (*semicarbazone*), are described. The latter substance is converted by condensation with benzaldehyde in alkaline solution, followed by catalytic reduction of the product of the reaction, into *α-phenyl-η-methylenedioxyphenylheptan-γ-one*, m. p. 40—41°. H. WREN.

Compounds of aromatic aldehydes with dimethylhydroresorcinol (dimethyl*cyclo*hexanedione). II. A. BERNARDI (Annali Chim. Appl., 1927, **17**, 163—166).—*Compounds* analogous to those formed with vanillin and piperonal (*ibid.*, 1926, **16**, 132) are formed by dimethyl*cyclo*hexanedione with: salicylaldehyde, $C_{23}H_{28}O_5$, m. p. 208—209°; anisaldehyde, m. p. 142—143°; acetylvanillin, $C_{26}H_{32}O_7$, m. p. 167—168°; citronellal, $C_{26}H_{40}O_4$, m. p. 70—71°; citral, $C_{26}H_{38}O_4$, liquid. These compounds give characteristic colour reactions with concentrated sulphuric acid, nitrous acid, nitric acid, and alcoholic ferric chloride solution. T. H. POPE.

Agnotobenzaldehyde. G. HELLER and H. HERRMANN (Ber., 1927, **60**, [*B*], 912—913; cf. Heller and Tourlis, A., 1908, i, 208).—Confirmation of the view that agnotobenzaldehyde (Bamberger and Remmert, A., 1907, i, 163) obtained by cautious reduction of *o*-nitrobenzaldehyde is a molecular compound of *o*-nitro- and *o*-hydroxylamino-benzaldehyde is afforded by the observation that it is converted by *p*-toluidine into *o*-nitrobenzylidene-*p*-toluidine, m. p. 74°. Further, it is transformed by aniline and *p*-toluidine in presence of potassium cyanide into 3-cyano-2-phenylindazole-*N*-oxide and 3-cyano-2-*p*-tolylindazole-*N*-oxide, respectively. In all cases, the residual *o*-hydroxylaminobenzaldehyde is isolated as anthranil. H. WREN.

Isomerism of the oximes. XXIX. Isomeric *p*-nitrobenzyl and methyl ethers of some aldoximes. O. L. BRADY and L. KLEIN (J.C.S., 1927, 874—894).—The evidence for the existence of two *O*-methyl ethers of *m*-nitrobenzaldoxime has been extended and may be summarised as follows. Both of the supposed *O*-ethers give quantitative yields of methyl iodide when heated with hydriodic acid; both have normal mol. wt.; *O*-methylhydroxylamine and *m*-nitrobenzaldehyde give a mixture of the α- and β-*O*-ethers, the former greatly preponderating; the α- is partly converted into β- by ultra-violet light, and the β- is completely converted into α-ether by the action of hydrogen chloride at the ordinary temperature.

In addition, pairs of *p*-nitrobenzyl *O*-ethers have been prepared from ten aldoximes, thus removing all doubt of the existence of these isomerides. Only one *N*-ether was obtained from each oxime. The following are described: O-p-*nitrobenzylhydroxylamine*, m. p. 56° [*hydrochloride*, m. p. 217° (decomp.)], prepared by hydrolysis of *O*-*p*-nitrobenzylbenzhydroxamic acid and converted, by treatment with potassium cyanate, into p-*nitrobenzyloxycarbamide*, m. p. 206° (decomp.); β-O-p-*nitrobenzylbenzaldoxime*, m. p. 54°; α-O-, β-O-, and N-p-*nitrobenzylcinnamaldoximes*, m. p. 83°, 86°, and 135°; α-O-, β-O-, and N-p-*nitrobenzyl*-o-*nitrobenzaldoximes*, m. p. 112°, 116°, and 203° (decomp.); α-O-, β-O-, and N-p-*nitrobenzyl*-m-*nitrobenzaldoximes*, m. p. 87—88°, 118°, and 223° (decomp.); α-O- and β-O-p-*nitrobenzyl*-p-*nitrobenzaldoximes*, m. p. 179° and 184°; *N*-*p*-nitrobenzyl-*p*-nitrobenzaldoxime, m. p. 234—235° (decomp.)—literature, 227—228°; α-O-, β-O-, and N-p-*nitrobenzylpiperonaldoximes*, m. p. 110°, 125°, and 144°; α-O- and N-p-*nitrobenzyl*-o-*methoxybenzaldoximes*, m. p. 88° and 141°; α-O-, β-O-, and N-p-*nitrobenzylanisaldoximes*, m. p. 122°, 74°, and 150°; α-O-p-*nitrobenzyl*-3-*nitroanisaldoxime*, dimorphous, m. p. 117° and 105°; β-O- and N-p-*nitrobenzyl*-3-*nitroanisaldoximes*, m. p. 152° and 232° (decomp.); α-O-, β-O-, and N-p-*nitrobenzyl*-5-*nitro*-2-*methoxybenzaldoximes*, m. p. 149°, 153°, and 237° (decomp.); and β-O-*methyl*-6-*nitropiperonaldoxime*, m. p. 122°. M. CLARK.

Isomerism of the oximes. XXX. Preparation of *o*-methoxybenzaldoxime from bisnitrosyl-*o*-methoxybenzyl. O. L. BRADY and C. L. BENNETT (J.C.S., 1927, 894—898).—*o*-Methoxybenzyl chloride condenses with β-anisaldoxime to form N-o-*methoxybenzylanisaldoxime*, m. p. 123°, hydrolysed by 20% hydrochloric acid to N-o-*methoxybenzylhydroxylamine hydrochloride*, m. p. 136°. This compound is converted by treatment with aqueous sodium nitrite into *nitroso*-N-o-*methoxybenzylhydroxyl*-

amine, m. p. 73—74°, which, with a trace of nitric acid, yields *bisnitrosyl-o-methoxybenzyl*, m. p. 125°. The last-named compound, on treatment with alkali, gives *o*-methoxybenzaldoxime, and, although it was not possible to isolate the β-oxime with certainty, evidence was obtained that it does accompany the α-oxime in this reaction. In a single case, a *product*, m. p. 101—102°, changing after a few days to the α-oxime, m. p. 92°, was obtained. M. CLARK.

Hydroxymethylene-aldehydes. I. Hydroxymethylenephenylacetaldehyde. H. RUPE and E. KNUP (Helv. Chim. Acta, 1927, **10**, 299—309).—Hydroxymethylenephenylacetonitrile, CPh(CN):CH·OH (Wislicenus, A., 1896, 552), in aqueous-alcoholic solution is reduced by hydrogen in presence of a nickel catalyst at the ordinary temperature and pressure to yield *hydroxymethylenephenylacetaldimine*, m. p. 110°, which on hydrolysis with an aqueous solution of oxalic acid yields *hydroxymethylenephenylacetaldehyde*, m. p. 95°, b. p. 85°/15 mm. (*benzoyl* derivative, m. p. 115°), which is purified through its *copper* salt. It does not react as phenylmalondialdehyde, but the aldehyde and hydroxymethylene groups each exhibit their own characteristic reactions. Thus as an aldehyde it yields an *aldehyde-ammonia*, m. p. 123°; *semicarbazone*, m. p. 160° (which reacts with ethyl aminoacetate to yield a condensation *product*, NH_2·CO·NH·N:CH·CPh:CH·NH·CH_2·CO_2Et, the free aldehyde itself not reacting); a condensation *product*, CPh(:CH·OH)·CH:C$<^{NH}_{CO\ NH}>$CO, m. p. 234°, with hydantoin (*copper* salt), which is readily hydrolysed by barium hydroxide at 100°; and a condensation *product*, CPh(:CH·OH)·CH:N·CO·NH_2, m. p. 183°, with carbamide in alcoholic solution at 60°. The free aldehyde does not form an anil, but with hydroxylamine in the cold it yields *hydroxyaminomethylenephenylacetaldehyde*, m. p. 125° (*semicarbazone*, m. p. 216°), which condenses with aniline to yield an *anil*, m. p. 179°. The free aldehyde reacts with aniline to yield *anilinomethylenephenylacetaldehyde*, m. p. 132°; with phenylhydrazine either in alcohol or acetic acid solution to yield 1 : 4-diphenylpyrazole, m. p. 97°, and with hydroxylamine on warming in alcoholic solution to yield 4-*phenylisoxazole*, m. p. 46°. Equimolecular quantities of the aldehyde and carbamide when heated together for 4 hrs. at 120° yield 2-*hydroxy-5-phenylpyrimidine*, m. p. 237° (*hydrochloride*), the *silver* salt of which with methyl iodide yields 2-*hydroxy-5-phenyl-3-methylpyrimidine*, m. p. 170° [*hydrochloride*, m. p. 300° (decomp.)]. J. W. BAKER.

New monobromo-derivatives of vanillin. L. C. RAIFORD and W. C. STOESSER (J. Amer. Chem. Soc., 1927, **49**, 1077—1080).—2-*Bromovanillin*, m. p. 154—155° (p-*bromophenylhydrazone*, m. p. 157°; *semicarbazone*, m. p. 216—217°), can be obtained by the Sandmeyer reaction from 2-aminovanillin (p-*bromophenylhydrazone*, m. p. 168°). 6-*Bromovanillin*, m. p. 178° (p-*bromophenylhydrazone*, m. p. 176°; *semicarbazone*, m. p. 231—232°; *oxime*, m. p. 158—159°), is obtained by the action of bromine in acetic acid at 45°, in presence of sodium acetate and a trace of iodine, on acetylvanillin, with subsequent hydrolysis of the resulting *acetyl* derivative. *Di-2-bromovanillylidene-*, m. p. 221—222°, and *di-6-bromovanillylidenebenzidine*, m. p. 268—269°, are described. Bromination of vanillin in acetic acid at the ordinary temperature yields 5-bromovanillin, irrespective of the proportion of bromine applied. Bromination of acetylvanillin under similar conditions yields 5- and 6-bromovanillins, together with 5 : 6-*dibromovanillin*, m. p. 218°, which is obtained by further bromination of the 5- or 6-bromo-derivatives. The formation of 5-bromovanillin appears to be due to bromination of the vanillin formed by hydrolysis of the acetyl derivative by the liberated hydrogen bromide, this action being prevented by sodium acetate.

F. G. WILLSON.

Constitution of isomeric monomethyl ethers of phloroglucinolaldehyde and of cotoin. P. KARRER and A. BLOCH (Helv. Chim. Acta, 1927, **10**, 374—380).—Partial methylation of 2 : 4 : 6-trihydroxybenzaldehyde with diazomethane in absolute ether at −15° yields a mixture of 2 : 6-dihydroxy-4-methoxybenzaldehyde, m. p. 203° (decomp.), obtained by Herzig and Wenzel (A., 1904, i, 251; cf. also Karrer, Rüdlinger, Glattfelder, and Waitz, A., 1921, i, 800; Pratt and Robinson, A., 1924, i, 305), sparingly soluble in water, and a more readily soluble isomeric *dihydroxymethoxybenzaldehyde*, m. p. 139—140°, which are also obtained together by the method of the earlier authors (*loc. cit.*). The isomerides may also be separated by crystallisation from benzene, the *iso*-compound being the more soluble. By the action of nitrous acid on the isomeride of m. p. 203°, only a *mono*iso*nitroso*-derivative, m. p. 166° (decomp.), is obtained; but the other isomeride, m. p. 139—140°, yielded no definite product, so that Pollak's rule (A., 1902, i, 165) cannot be applied to the determination of its constitution. On the other hand, *iso*cotoin (phenyl dihydroxymethoxyphenyl ketone, Pollak, *loc. cit.*) prepared in an analogous manner to the dihydroxymethoxybenzaldehyde, m. p. 203°, by the action of benzonitrile and hydrogen chloride on phloroglucinol monomethyl ether, yields no definite *iso*nitroso-derivative, whilst the isomeric cotoin is known to yield a definite, crystalline, mono-*iso*nitroso-derivative (Pollak, *loc. cit.*). Phloro*iso*hexophenone (Karrer and Rosenfeld, A., 1921, i, 793) yields a crystalline *di*iso*nitroso*-derivative, m. p. 202° (decomp.). The constitution of these compounds cannot, therefore, be decided by this method. J. W. BAKER.

Action of diazomethane on aromatic acyl chlorides. IV. Reaction products from the three nitrobenzoyl chlorides. R. T. DALE and M. NIERENSTEIN (Ber., 1927, **60**, [*B*], 1026—1027; cf. A., 1925, i, 34).—*m*-Nitrobenzoyl chloride is converted by diazomethane into ω-*chloro-3-nitroacetophenone*, m. p. 97°, converted by sodium acetate in alcoholic solution into 3-*nitro-ω-acetoxyacetophenone*, m. p. 110°. ω-*Chloro-4-nitroacetophenone*, m. p. 107°, and 4-*nitro-ω-acetoxyacetophenone*, m. p. 132°, are similarly obtained. *o*-Nitrobenzoyl chloride appears to yield a *chloronitraldin*, m. p. 67° (cf. Arndt and Partale, this vol., 360). H. WREN.

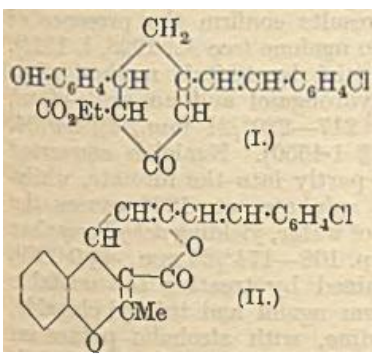
Bromination of *p*-acetamidophenyl methyl ketone. L. C. RAIFORD and H. L. DAVIS (Proc.

Iowa Acad. Sci., 1925, 32, 324).—With *p*-acetamidophenyl methyl ketone, the highest yield of nuclear bromo-derivative is obtained by allowing 1·84 mols. of bromine in 19·8 vols. of glacial acetic acid to drop during 20 min. into 1 mol. of the ketone in 20 parts of 50% acetic acid, with shaking, at 20—21°, and keeping for 3·75 hrs. In absence of water, substitution usually takes place in the side-chain (cf. Baeyer and Bloem, A., 1884, 1026). CHEMICAL ABSTRACTS.

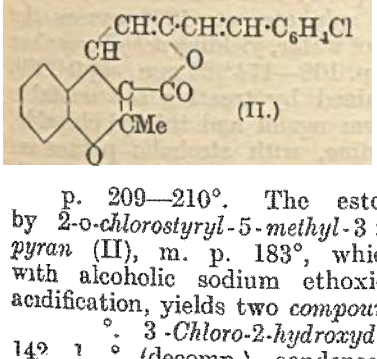
Action of anhydrous aluminium chloride on tolyl benzoates. E. H. Cox (J. Amer. Chem. Soc., 1927, 49, 1028—1030).—Anhydrous aluminium chloride (40 g.) is added in small portions to *o*-tolyl benzoate (50 g.) and the mixture heated at 160° for 45 min. Decomposition of the product with warm dilute hydrochloric acid affords *p*-benzoyl-*o*-cresol (phenyl 4-hydroxy-*m*-tolyl ketone), b. p. 240—260°/12—15 mm. Treatment of *m*-tolyl benzoate in carbon disulphide with aluminium chloride, followed by removal of the solvent and heating at 90°, affords phenyl 4-hydroxy-*o*-tolyl ketone, m. p. 63°, b. p. 195—215°/14 mm., together with phenyl 2-hydroxy-*p*-tolyl ketone, m. p. 129°, b. p. 220—240°/13 mm. In absence of solvent, the action of aluminium chloride on *m*-tolyl benzoate at 130° affords the former product in practically quantitative yield. Phenyl 6-hydroxy-*m*-tolyl ketone, m. p. 87°, is obtained by treating *p*-tolyl benzoate with aluminium chloride at 140—200°. The constitution of the above ketones is established by their conversion into the corresponding substituted toluic acids on fusion with potassium hydroxide.

F. G. WILLSON.

Interaction of ethyl acetoacetate with distyryl ketones. III. Chloro-o-hydroxydistyryl ketones. I. M. HEILBRON and R. HILL (J.C.S., 1927, 918—924; cf. A., 1925, i, 1284).—*2′-Chloro-2-hydroxydistyryl ketone*, m. p. 153° (decomp.), prepared by the interaction of 2-hydroxystyryl methyl ketone and *o*-chlorobenzaldehyde, condenses with ethyl acetoacetate, giving *ethyl* 3-*o*-*hydroxyphenyl*-5-*o*-*chlorostyryl*-Δ^5-cyclo*hexen*-1-*one*-2-*carboxylate* (I), m. p. 177—178°. On oxidation with potassium permanganate, it yields *o*-chlorobenzoic acid,



(I.)



(II.)

entered at the ethenoid linking adjacent to the *o*-hydroxyl group (cf. A., 1924, i, 1323). Hydrolysis of the ester with 20% sulphuric acid gives 3-*o*-*hydroxyphenyl*-5-*o*-*chlorostyryl*-Δ^5-cyclo*hexen*-1-*one*, p. 209—210°. The ester is accompanied by 2-*o*-*chlorostyryl*-5-*methyl*-3 : 4-*coumalo*-6-*benzopyran* (II), m. p. 183°, which, after treatment with alcoholic sodium ethoxide and subsequent acidification, yields two *compounds*, m. p. 121—122° and 142—143° (decomp.), condenses similarly to give *ethyl* 3-*o*-*hydroxyphenyl*-5-*m*-*chlorostyryl*-Δ^5-cyclo*hexen*-1-*one*-2-*carboxylate*, m. p. 169° (3-*o*-*hydroxyphenyl*-5-*m*-*chlorostyryl*-Δ^5-cyclo*hexen*-1-*one*, m. p. 221°), and 2-*m*-*chlorostyryl*-5-*methyl*-3 : 4-*coumalo*-6-*benzopyran*, m. p. 170°. *4′-Chloro-2-hydroxydistyryl ketone*, m. p. 152° (decomp.), gives *ethyl* 3-*o*-*hydroxyphenyl*-5-*p*-*chlorostyryl*-Δ^5-cyclo*hexen*-1-*one*-2-*carboxylate*, m. p. 199—200° (3-*o*-*hydroxyphenyl*-5-*p*-*chlorostyryl*-Δ^5-cyclo*hexen*-1-*one*, m. p. 176°), and 2-*p*-*chlorostyryl*-5-*methyl*-3 : 4-*coumalo*-6-*benzopyran*, m. p. 261—262°. *4′-Chloro-2-methoxydistyryl ketone*, m. p. 74—75°, gives *ethyl* 3-*o*-*methoxyphenyl*-5-*p*-*chlorostyryl*-Δ^5-cyclo*hexen*-1-*one*-2-*carboxylate*, m. p. 160°. The action of sodium ethoxide on an alcoholic solution of 2′-chloro-2-hydroxydistyryl ketone and ethyl benzoylacetate gives *ethyl* 4-*o*-*chlorostyracyl*-2-*phenyl*-1 : 4-*benzopyran*-3-*carboxylate*, m. p. 195° (+0·5Et·OH, m. p. 144—145°). Similarly, phenyl 2-hydroxystyryl ketone and ethyl acetoacetate give 2-*phenyl*-5-*methyl*-3 : 4-*coumalo*-6-*benzopyran*, m. p. 214°, together with 4-*phenacyl*-2-*methyl*-1 : 4-*benzopyran*, m. p. 171°. The latter is also obtained by the action of acetylacetone on phenyl 2-hydroxystyryl ketone.

M. CLARK.

Unsaturated 1 : 4-diketones. III. Mode of addition of halogen to dibenzoylethylene. R. E. LUTZ (J. Amer. Chem. Soc., 1927, 49, 1106—1111; cf. this vol., 61).—Addition of bromine to *cis*- and *trans*-dibenzoylethylene in chloroform at −12° affords, respectively, the α-, m. p. 108°, and β-dibenzoylethylene dibromide, m. p. 178°. dl-*Dichlorosuccinyl chloride* (I), m. p. 39°, b. p. 78·5°/7 mm., and dl-*dibromosuccinyl chloride* (II), b. p. 85°/4 mm., were obtained by the action of phosphorus pentachloride on the corresponding acids. Addition of (I) and (II) in benzene solution to benzene suspensions of aluminium chloride yields the α- (lower-melting) isomerides of the dibenzoylethylene dichloride and dibromide, respectively, whilst *meso*-dichloro- and -dibromo-succinyl chlorides afford similarly the β-dihalides. It is concluded that the configurations of the dihalogenosuccinyl chlorides are unchanged in the above condensations, so that the α-derivatives are *dl*, and the β-derivatives *meso*, whilst addition of halogens to the dibenzoylethylenes must be *trans*. When aluminium chloride is added to *meso*dichlorosuccinyl chloride in benzene, there is obtained, in addition to the above product, *αβ-dichloro-γγ-diphenylbutyrolactone*, $\begin{matrix}\mathrm{CHCl{\cdot}CPh}\\ \mathrm{CHCl{-}CO}\end{matrix}\!>\!\mathrm{O}$, m. p. 141—142°.

F. G. WILLSON.

Acetovanillone, *iso*acetovanillone, and *o*-acetovanillone. (Wandering of an acetyl group to the *meta* position.) T. REICHSTEIN (Helv. Chim. Acta, 1927, 10, 392—397).—The action of anhydrous zinc chloride on a mixture of guaiacol and acetic anhydride (or on guaiacol acetate) yields a mixture of 4-hydroxy-3-methoxyacetophenone (acetovanillone), 3-hydroxy-4-methoxyacetophenone (*iso*acetovanillone), and, in small quantity, 2-*hydroxy*-3-*methoxyacetophenone* (*o*-acetovanillone), m. p. 53—54°, the acetyl group wandering to the positions *o*-, *m*-, and *p*- to the hydroxyl group. Separation of the isomerides is effected by a method depending on the slight solubility of acetovanillone in benzene, and this product therefore

crystallises out. When the benzene mother-liquor is shaken with water, the *iso*acetovanillone separates as a less soluble form ($+1H_2O$). For the separation of the *o*-acetovanillone from the other two isomerides, advantage is taken of its being a much weaker acid and not extracted by aqueous sodium carbonate from ether. Acetovanillone yields a semicarbazone, m. p. 173·5—174·5° (corr.) (Finnemore, J.C.S., 1908, **93**, 1520, gives 166—167°). *iso*Acetovanillone yields an *ethyl ether*, m. p. 70—71°, which on complete oxidation yields 4-methoxy-3-ethoxybenzoic acid. *o*-Acetovanillone is also obtained by the demethylation of 2 : 3-dimethoxyacetophenone by aluminium chloride in toluene solution, only the methoxy-group *ortho* to the carbonyl group being attacked. Ethylation and complete oxidation yields the same benzoic acid as is obtained from *o*-vanillin. J. W. Baker.

Synthesis of a new gallacetophenone. F. Mauthner (J. pr. Chem., 1927, [ii], **115**, 137—142).—When 3 : 4 : 5-trimethoxyacetophenone is treated with aluminium chloride in chlorobenzene solution, it yields 3 : 4 : 5-*trihydroxyacetophenone*, m. p. 187—188° (*p-nitrophenylhydrazone*, decomp. 260°; *semicarbazone*, m. p. 216—217°; *triacetate*, m. p. 111—112°). R. W. West.

Condensation of phenolic aldehydes and their ethers with methyl ethyl ketone. K. Iwamoto (Bull. Chem. Soc. Japan., 1927, **2**, 51—57; cf. Ryan and Cahill, A., 1925, i, 558).—In presence of hydrochloric acid, methyl ethyl ketone condenses with veratraldehyde, protocatechualdehyde, *m*-methoxybenzaldehyde, and *m*-hydroxybenzaldehyde, forming, respectively, 3 : 4 : 3′ : 4′-*tetramethoxy-α-methyldistyryl ketone*, 3 : 4 : 3′ : 4′-*tetrahydroxy-α-methyldistyryl ketone*, 3 : 3′-*dimethoxy-α-methyldistyryl ketone*, and 3 : 3′-*dihydroxy-α-methyldistyryl ketone*. Methoxy- or hydroxy-groups in the *m*-position to the aldehyde group appear to favour the formation of diarylidene compounds, since the corresponding condensation product with *p*-hydroxybenzaldehyde is p-*hydroxy-α-methylstyryl methyl ketone*, m. p. 108·5—109·5° (*oxime*, m. p. 147—148°; *benzoyl* derivative, m. p. 124—125°), and with piperonal is piperonylidene ethyl ketone [*oxime*, m. p. 173° (decomp.); *dibromide*, m. p. 93·5—94°]. Similarly, anisaldehyde forms p-*methoxy-α-methylstyryl methyl ketone*, m. p. 27·5—28° (*oxime*, m. p. 126·5—128°; *dibromide*, m. p. 70·5—71°), or, in presence of sodium hydroxide, *p*-methoxystyryl ethyl ketone, m. p. 58·5—59° (*oxime*, m. p. 138—139°; dibromide, decomp. 87·5°). B. W. Anderson.

Addition of acetylene and carbon monoxide: synthesis of benzoquinone. J. F. Durand and M. Banos (Compt. rend., 1927, **184**, 972—973).—When acetylene and carbon monoxide are passed into pyridine in the presence of cuprous chloride, and the black product (containing cuprous acetylide) obtained after evaporation of the pyridine is extracted with ether, *p*-benzoquinone is obtained. The synthesis cannot be effected in absence of the copper salt as a catalyst, nor in hydrochloric acid, ammonia, quinoline, diethylamine, or acetone as solvents. J. W. Baker.

Anthraquinonesulphonic acids. J. P. Wibaut (Helv. Chim. Acta, 1927, **10**, 380).—In his re-investigation of the sulphonation of anthraquinone in presence of mercury salts, Fierz-David (this vol., 463) overlooked the earlier results of Coppens (A., 1925, i, 1432), in which a more detailed investigation of the effect of mercury salts is described. J. W. Baker.

New synthesis of alizarin. (Condensation of phthalic anhydride with *o*-chlorophenol.) M. Tanaka (Proc. Imp. Acad. Tokyo, 1927, **3**, 82—85).—Condensation by means of a mixture of concentrated sulphuric acid and boric acid at 195° yields 3-chloro-2-hydroxyanthraquinone (*acetyl* derivative, m. p. 197—200°), whilst at 225° the product is 2-*chloro*-1-*hydroxyanthraquinone*, m. p. 215° (*acetyl* derivative, m. p. 176—179°). Fusion with potassium hydroxide converts these substances into alizarin, which is produced directly in 75% yield when the above condensation takes place at 255°. J. M. Gulland.

Alanines of the anthraquinone series and derivatives thereof. I. G. Farbenind. A.-G.—See B., 1927, 326.

Vat colours of the anthraquinone series [acylated aminoanthraquinones]. Badische Anilin- & Soda-Fabr.—See B., 1927, 326.

Vat dyes [dialkoxy*iso*dibenzanthrones]. Badische Anilin- & Soda-Fabr.—See B., 1927, 326.

Constituents of *Myoporum lætum*, Forst. (the "ngaio"). II. Hydrogenation of ngaione and ngaiol and dehydration of ngaiol. F. H. McDowall (J.C.S., 1927, 731—740).—Complete hydrogenation of ngaione and ngaiol in presence of colloidal palladium gives *tetrahydrongaione*, b. p. 196—198°/29 mm., 0·9977, $[\alpha]_D$ −5·41°, 1·4652 (*p-nitrophenylhydrazone*; *oxime*; *semicarbazone*), and *tetrahydrongaiol*, b. p. 202—206°/29 mm., d_{20}^{20} 0·9917, $[\alpha]_D$ +2·96°, n_D^{20} 1·4674 (*acetate*, b. p. 205°/29 mm., d_{20}^{20} 1·0096, n_D 1·4615). *Dihydrongaiol* has b. p. 199—202°/28 mm., 1·0009, $[\alpha]_D$ −11·73°, 1·4702 (*acetate*, b. p. 192°/29 mm., d_{20}^{20} 1·0152, n_D^{20} 1·4631). Reduction of tetrahydrongaioneoxime with sodium and alcohol yields *tetrahydrongaiylamine*, b. p. 198—200°/29 mm., 0·968, n_D^{20} 1·4718 (*picrolonate*, m. p. 184—185°). These results confirm the presence of two double linkings in ngaione (see A., 1925, i, 1521). Hydrogenation of ngaiol by Skita's method gives a mixture of tetrahydrongaiol and an *oxido-glycol*, $C_{15}H_{28}O(OH)_2$, b. p. 217—220°/21 mm., d_{20}^{20} 0·9734, n_D^{20} 1·4668 (*acetate*, n_D^{20} 1·4550). Ngaiol is converted by 90% formic acid partly into the formate, whilst potassium hydrogen sulphate at 190° causes the alcohol to lose 1 mol. of water, yielding *dehydrongaiene dioxide*, $C_{15}H_{22}O_2$, b. p. 168—174°/29 mm., d_{20}^{20} 0·9689, n^{20} 1·4914, also obtained by treating the unstable chloride prepared from ngaiol and thionyl chloride, in presence of pyridine, with alcoholic potassium hydroxide (b. p. 170—175°/28 mm., d_{20}^{20} 0·9751, $[\alpha]_D$ −10·84°, n_D^{20} 1·4854). The dioxide rapidly absorbs oxygen from the air, and when hydrogenated in presence of palladium forms *tetrahydrongaiene dioxide*, $C_{15}H_{28}O_2$, b. p. 170—180°/29 mm., 0·9379, n_D^{20} 1·4631. These results indicate the presence of two oxide rings in ngaione. Thionyl chloride converts ngaiol in presence of quinoline into iso*dehydrongaiene dioxide*, b. p. 168—174°/29 mm., d_{20}^{20} 0·9654, 1·4801,

whilst boiling 33% sulphuric acid produces a small amount of a *substance*, b. p. 182—189°/29 mm., d_{20}^{20} 1·0008, n_D^{20} 1·4802, together with resin. Ngaione oxime is reduced by sodium and alcohol to *ngaiylamine*, b. p. 184—186°/29 mm., d^{20} 0·9940, $[\alpha]_D$ −18·63°, n_D^{20} 1·4822 (*chloroplatinate*, decomp. 170—180°; *hydrobromide*, m. p. 190—191°; *benzenesulphonyl* derivative, m. p. 107—108°; *picrolonate*, m. p. 162—163°). Distillation of the amine phosphate yielded no recognisable product. *Tetrahydrongaionehydrazone*, b. p. 210—220°/13 mm., 1·4921, and ngaionehydrazone decompose, with loss of carbon from the molecule, when heated with sodium ethoxide. H. BURTON.

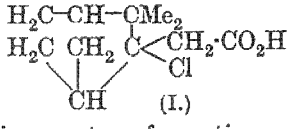
Enolic forms of ketones. V. GRIGNARD and J. SAVARD (Bull. Soc. chim. Belg., 1927, **36**, 97—107; cf. A., 1925, i, 111; 1926, 72, 408; Bredt-Savelsberg, A., 1924, i, 530).—The enolisation of pulegone by magnesyl compounds varies according to the nature of the organic radical and the halogen used, and the temperature; the relative proportions and concentration of the reagents and the duration of the reaction have no appreciable influence. Enolisation increases with increasing mol. wt. in homologous series of radicals, and diminishes with increasing at. wt. of the halogen. Secondary and tertiary magnesyl bromides produce complete enolisation at 40°. The enolic form of pulegone, produced in the form of its bromomagnesium derivative, −CH:C(O·MgBr)−, by the action of magnesium methyl or *iso*propyl bromide on ordinary pulegone (containing 15—18% of *iso*pulegone), gives a *benzoate*, m. p. 230°, stable to the usual hydrolysing agents, but converted by alcoholic potassium hydroxide into ketonic pulegone. The *acetate* and *propionate*, on the other hand, are hydrolysed at once by water and give *enolic pulegone*, b. p. 79—81°/3 mm. (cf. ketonic pulegone, b. p. 74—76°/3 mm.), d_4^{16} 0·9087, n_D^{16} 1·47690. Although stable in the dark for a year or more, it is ketonised completely by mineral acids, alkalis, magnesia, or traces of bromine. The enol is obtained directly from the magnesium complex by treatment with cold concentrated ammonium chloride solution, the ammonia produced being neutralised by gradual addition of acetic acid. Pure (β-)pulegone, b. p. 84°/6 mm., d_4^{15} 0·9346, n_D 1·48940, $[\alpha]_D$ +21°, yields by this method pure enolic (β-)pulegone, b. p. 85°/6 mm., d_4^{13} 0·916, 1·48312, $[\alpha]_D$ +24·6°, whilst from pure *iso*(α)-pulegone, b. p. 78°/5 mm., d_4^{14} 0·9097, n_D^{14} 1·46332, $[\alpha]_D$ +34·3°, there is obtained the pure enolic *iso*(α-)pulegone, b. p. 79—81°/6 mm., d_4^{14} 0·8965, 1·46732, $[\alpha]_D$ −4·3°. Enolic menthone, b. p. 75—77°/2 mm., d_4^{11} 0·893, n_D 1·45987 (acetate, b. p. 210—222°), is rapidly ketonised on keeping even in the dark.

Butyrone (di-*n*-propyl ketone) is only partly enolised by magnesyl compounds. The enol, prepared by hydrolysis of its butyrate, has b. p. 152°/753 mm., d_4^{11} 0·8107, n_D^{11} 1·42071, and is completely ketonised after 30 min. C. HOLLINS.

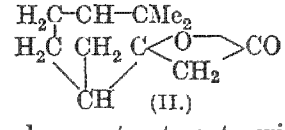
Catalytic hydrogenation of some cyclic ketones. VAVON and A. COUDERC (Bull. Soc. chim. Belg., 1927, **36**, 57—63).—The relative ease of reduction of cyclic ketones with hydrogen and platinum-black is determined by reduction of equimolecular mixtures of an optically inactive ketone and menthone with only one molecular proportion of hydrogen, the partition of the hydrogen between the two ketones being followed by measurements of optical activity. The results show that a substituent in position 2 diminishes the ease of hydrogenation, the effect being more marked for *iso*propyl than for *n*-propyl groups. The order of reactivity is: *cyclo*hexanone, 4-methyl-, 2-methyl-, 2-propyl-, 2-*iso*propyl-, 2-*cyclo*hexyl-*cyclo*hexanones, menthone, *cyclo*pentanone, 2-*iso*propyl*cyclo*pentanone, camphor, fenchone. C. HOLLINS.

Verbenol. A. BLUMANN and H. SCHMIDT (Annalen, 1927, **453**, 48—52).—*d*-Verbenol (A., 1913, i, 495) is conveniently prepared by heating *d*-verbenone with *iso*propyl alcohol and aluminium *iso*propoxide (Ponndorf, A., 1926, 520). The product, after purification through the benzoate, had m. p. 8°, $[\alpha]_D^{100}$ +124°, whilst a similar product purified through the orthoborate remained liquid on cooling, $[\alpha]_D$ +66·4°. Both specimens were reoxidised to pure *d*-verbenone. In order to ascertain if these differences in rotation are due to the presence in different proportions of the two possible stereoisomeric *d*-verbenols, the first sample is boiled with acetic anhydride and sodium acetate. The product is principally *d*-verbenene, which is obtained pure after removal of the verbenyl acetate by hydrolysis and heating with boric acid. The verbenol, $[\alpha]_D$ +54·2°, recovered from the borate does not solidify on cooling. The presence in the starting material of both stereoisomerides, which are unequally stable towards dehydration, is thus indicated. H. E. F. NOTTON.

Stabilisation of the camphene ring by carboxylic substitution. G. LANGLOIS (Bull. Soc. chim., 1927, [iv], **41**, 384—390).—Camphenylideneacetic acid in glacial acetic acid combines with halogen hydrides, affording products which possess the camphene type of structure (I), but, unlike Meerwein and van Emster's camphene hydrochloride, m. p. 125—127° (A., 1920, i, 855), do not undergo the



(I.)

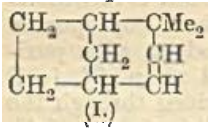


(II.)

pinene transformation, and on treatment with 1—2% sodium hydroxide yield camphene, sodium halide, and sodium carbonate. It is suggested that the presence of the carboxyl group increases the affinity of the tertiary carbon atom and thereby the stability of the camphene ring. Further support for this view is afforded by the following facts: (1) Camphenylideneacetic acid when heated above its m. p., or boiled at atmospheric pressure, or with 20% sulphuric acid, loses carbon dioxide, giving camphene. (2) On treatment with 87% formic acid (cf. Semmler, A., 1907, i, 1062), camphenylideneacetic acid affords a *lactone*, $C_{11}H_{16}O_2$, m. p. 198°, together with some *iso*bornyl formate. The lactone itself contains the camphene ring, its structure, (II), being deduced from (*a*) its oxidation with alkaline potassium permanganate to camphenilone (semicarbazone, m. p. 226°), (*b*) its conversion into camphene by heating at 270°, (*c*) the formation

with hydrogen chloride in acetic acid of the same *hydrochloride*, m. p. 155—156°, as is obtained direct from camphenylideneacetic acid. Hydrogen bromide does not behave thus. The *hydrogen bromide* compound of camphenylideneacetic acid has m. p. 144—145°; the *hydrogen iodide* compound decomposes at 50—60°. Attempts to obtain the hydroxy-acid from the lactone failed. R. BRIGHTMAN.

"Endocamphene," and its significance for the constitution of camphene. P. LIPP, A. GOTZEN, and F. REINARTZ (Annalen, 1927, **453**, 1—15).—Further evidence in favour of the Wagner formula for camphene is furnished by the preparation of



(I.)

"endocamphene" (I), which has the constitution proposed by Aschan (A., 1910, i, 709) for camphene. Unlike the latter, it has a normal mol. refractive power, $[R]_D^{12\cdot4}$ 43·52 (calculated for one double linking, 43·51). It readily absorbs bromine in chloroform with evolution of hydrogen bromide, decolorises permanganate in the cold, and is oxidised by warm nitric acid, forming oily products in each case. When heated at 90—100° with glacial acetic and sulphuric acids, it forms only a trace of ester, b. p. about 95°/12 mm., being mainly recovered unchanged. It is hydrogenated in presence of platinum-black to *dihydroendocamphene*, b. p. 171·5—173°, $d_4^{17\cdot4}$ 0·8770, $n_l^{17\cdot4}$ 1·46847, which also has a normal mol. refraction and does not react with bromine in chloroform.

The ketone of the C_{10}-series (A., 1923, i, 1105) obtained by chromic acid oxidation of dicamphenyl ether is identical, except in optical activity, with homocamphenilone. The following specimens are described, the two first being obtained from alkaline fusions of ω-bromocamphene: (*a*) $[\alpha]_D^{20}$ −12·69° (semicarbazone, m. p. 210—211°; *oxime*, m. p. 99—99·5°; *monobromo*-derivative, m. p. 112—113°, b. p. 106—115°/0·6 mm.), which is reduced by sodium and absolute alcohol to homocamphenilol (*phenylurethane*, m. p. 119—120°; *acetate*, b. p. 100—104°/10 mm.); (*b*) inactive (semicarbazone, m. p. 213—214°) from *dl*-camphene; (*c*) m. p. 39°, $[\alpha]_D^{20}$ −8·44° (semicarbazone, m. p. 201—202°; oxime, m. p. 103—103·5°, b. p. 104—105°/0·5 mm.), from the oxidation of dicamphenyl ether. The presence of a ·CH_2·CO· grouping in homocamphenilone is confirmed by the formation of a *hydroxymethylene* derivative, b. p. 75—76°/0·5 mm., which oxidises in the air to camphenecamphoric and formic acids, and an *isonitroso*-derivative, m. p. 144—145°, sintering at 140°. This is hydrolysed in presence of formaldehyde to a (?) *diketone*, m. p. 138—139°, which affords camphenecamphoric acid on oxidation. Of the alternative formulæ proposed (*loc. cit.*) for homocamphenilone, that with the ·CH_2· group adjacent to the *iso*propyl residue is the more probable, since it does not undergo ring-fission when boiled with sodamide in benzene solution. *Homocamphenilol*, m. p. 73—76°, b. p. 107—110°/10 mm., from sample (*c*) is dehydrated by zinc chloride at 100° to *endocamphene*, b. p. 170·6—171·6°/744·5 mm. (corr.), $d_4^{12\cdot4}$ 0·8957, $n_D^{12\cdot4}$ 1·48442, and a little of a *substance*, b. p. 120—130°/0·15 mm., possibly dihomocamphenilyl ether. H. E. F. NOTTON.

Intramolecular displacements of atoms in the camphor series. H. MEERWEIN [with O. HAMMEL, A. SERINI, and J. VORSTER] (Annalen, 1927, **453**, 16—47).—The tendency of bornyl chloride, *iso*bornyl chloride, and camphene hydrochloride to pass into equilibrium mixtures containing all three substances (cf. A., 1922, ii, 751; 1924, i, 186—192) is shown in varying degree by the corresponding esters of other acids. The order of ease of transformation of camphene hydrate esters into *iso*bornyl esters under comparable conditions is: 2-chlorocymene-5-sulphonate > bromide > chloride > trichloroacetate > *m*-nitrobenzoate, the first-named being so unstable that it cannot be isolated, whilst the last is transformed only in presence of catalysts. This is also the order of decreasing strength of the corresponding acids. The order of activity of solvents in accelerating the reaction is the same in all cases, the activity increasing with the dielectric constant. All substances capable of combining with the acid present in the ester to give a stronger complex acid catalyse the transformation, so that the efficiency of a catalyst may vary with different esters of the same alcohol. These facts are in complete agreement with the theory that isomeric change takes place only in the free positive ions. *Camphene hydrobromide* is prepared from dry hydrogen bromide and excess of camphene dissolved in light petroleum. The crystalline product contains *iso*bornyl bromide (20—25%) and camphene (5—15%). It is rapidly converted in presence of acids or moisture into *isobornyl bromide*, m. p. 133° (identical with Semmler's "camphene hydrobromide," A., 1900, i, 90). The same change has been followed in nitrobenzene, anisole, toluene, ether, and light petroleum solutions at 20°, and also in the solid material preserved in a vacuum over potassium hydroxide, by means of analytical methods similar to those previously used for the chloride. In solution, the equilibrium mixture contains about 5% of camphene hydrobromide. Pure anhydrous 2-chlorocymene-5-sulphonic acid is not hygroscopic. With pinene, it gives *bornyl 2-chlorocymene-5-sulphonate*, m. p. 127—129° (decomp.), which is rapidly decomposed by boiling alcohol into camphene and free acid. On hydrolysis with 20% aqueous sodium hydroxide, it is converted into (?) *iso*borneol (10%), camphene hydrate (77%), and camphene (13%). Camphene and chlorocymenesulphonic acid in ether at 0° do not give the expected camphene hydrate derivative, but only *isobornyl 2-chlorocymene-5-sulphonate* and a small amount (2%) of the bornyl ester. The latter increases in amount with rising temperature, becoming the main product at 100°. The *iso*bornyl ester decomposes on keeping or treatment with solvents, and is hydrolysed by aqueous sodium hydroxide to *iso*borneol (12%), camphene (15%), and camphene hydrate (72%), whilst with methyl alcohol and potassium carbonate the methyl ethers of camphene hydrate (75%) and *iso*borneol (25%) are formed. Both these esters, therefore, react like a labile mixture of all three possible isomerides. Liquid *camphene hydrate trichloroacetate*, containing free acid (20%) and *iso*bornyl ester (10%) is obtained from camphene and trichloroacetic acid in benzene at 15°. In chemical properties, it closely resembles cam-

phene hydrochloride; it is converted by methyl alcohol in absence of free acid into almost pure camphene hydrate methyl ether. iso*Bornyl trichloroacetate*, m. p. 30—31°, from camphene and trichloroacetic acid at 80°, is hydrolysed by alcoholic potassium hydroxide to pure *iso*borneol. In presence of water, phenol, and magnesium hydroxide at 130°, however, a mixture of camphene (60%), *iso*borneol (16%), and camphene hydrate (42%) is formed, indicating the intermediate formation of an equilibrium mixture of esters. *Camphene hydrate* m-*nitrobenzoate*, m. p. 86—86·5°, from the potassium derivative of camphene hydrate and *m*-nitrobenzoyl chloride, is scarcely transformed into iso*bornyl* m-*nitrobenzoate*, m. p. 78—78·5°, even at 180°, but in presence of stannic chloride the change takes place rapidly at the ordinary temperature. The following method of analysis of mixtures containing camphene hydrate, camphene, and *iso*borneol gives results accurate within 3—4%: the camphene is determined by direct titration with perbenzoic acid and the *iso*borneol by determination of the ester content of the product obtained on acetylation with acetic anhydride and sodium acetate, camphene and camphene hydrate being esterified to the extent of only 1 or 2% under these conditions.

H. E. F. Notton.

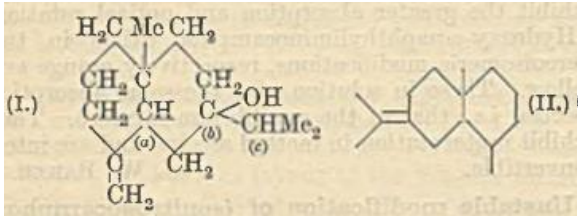
Separation of *d*-neobornylamine from *d*-bornylamine. J. A. Goodson (J.C.S., 1927, 930—931; cf. Forster, *ibid.*, 1898, **73**, 390; Forster and Hart-Smith, *ibid.*, 1900, **77**, 1152).—The mixture of *d*-bornylamine and *d*-neobornylamine hydrochlorides obtained by reducing *d*-camphoroxime is crystallised from water. The crystalline material is basified and an ethereal solution extracted with successive quantities of approximately 0·6*N*-hydrochloric acid. The bases obtained from the crystallisation liquors are treated similarly. Evaporation to dryness of five of such extracts gave hydrochlorides with $[\alpha]_D$ varying from +19·1° to −22·6°. Crystallisation of the dextrorotatory fractions from water yielded pure *d*-bornylamine hydrochloride, $[\alpha]_D^{20}$ (alcohol) +23·3° (Forster, *loc. cit.*, gives +22·7°), whilst from the lævorotatory fractions, *d*-neobornylamine hydrochloride was obtained with $[\alpha]_D^{20}$ (alcohol) −49·4° (Forster and Hart-Smith, *loc. cit.*, give −44·2°). H. Burton.

Dependence of optical activity on chemical constitution. VII. Stereoisomeric aryl derivatives of imino- and bisimino-camphor and their absorption spectra. B. K. Singh and R. Rai (J. Indian Chem. Soc., 1926, **3**, 389—396).—In an attempt to determine the configurations of the two orms of *pp'*-diphenylene- and *oo'*-ditolylene-bisiminocamphor (Singh, Singh, and Lal, J.C.S., 1921, **119**, 1) by the application of Stewart's rule (*ibid.*, , **91**, 199) that the *trans*- or *anti*-form exhibits ıe greater absorption and greater optical rotation, ıe absorption curves of the compounds have been p otted. Whilst the yellow variety of the *oo'*-di- o ylene compound exhibits greater absorption and greater rotation than the green isomeride, and may ıerefore be regarded as the *anti*-form, in the case *pp* -diphenylene derivative, the green form, wl i ı ex its greater optical rotation, has the smaller absorption. The absorption spectra of chloroform solutions of *m*- and *p*-phenylene-, and 1 : 4-naphthylene-bisiminocamphor, phenyl-, α-naphthyl-, and 4-hydroxy-α-naphthyl-iminocamphor are plotted, and in every case the compounds which possess the greater number of unsaturated, conjugated linkings exhibit the greater absorption and optical rotation. 4-Hydroxy-α-naphthyliminocamphor exists in two stereoisomeric modifications, respectively orange and yellow. These in solution give the same absorption spectra, *i.e.*, that of the equilibrium mixture. They exhibit mutarotation in methyl alcohol and are interconvertible. J. W. Baker.

Unstable modification of *iso*nitrosocamphor. M. O. Forster and K. A. N. Rao (J. Indian Inst. Sci., 1927, **9A**, 202—206).—See A., 1926, 1251.

Higher terpene compounds. XXX. Constitution of eudesmol. L. Ruzicka and E. Capato (Annalen, 1927, **453**, 62—82).—The carbon framework attributed to eudesmol on account of its dehydration to eudalene, and by analogy with other sesquiterpene derivatives (A., 1922, i, 560; 1923, i, 119, 1216), has now been confirmed and the position of the hydroxyl group and double linking ascertained. When eudesmol is boiled with 10% alcoholic sulphuric acid, a *hydrocarbon** (an asterisk indicates that the substance may be a mixture of isomerides with different positions of the double linking), b. p. 128—132°/12 mm., d_4^{20} 0·9214, n_D^{20} 1·5125, $[\alpha]_D$ +106·5°, isomeric with eudesmene, is formed. Since this is dehydrogenated to eudalene, and its hydrochloride is identical with eudesmene dihydrochloride, is must be formed from eudesmene by the displacement of a hemicyclic double linking into the ring. In order to determine the position of this linking, a light petroleum solution of eudesmol is ozonised at 0°, the ozonide decomposed with water, and boiled with sodium hydroxide to remove peroxides. The neutral fraction of the product gives, on distillation, a *ketone*, b. p. 95—110°/0·2 mm. (*semicarbazone*, m. p. 225°), and 3-*hydroxy*-9-*methyl*-3-iso*propyldecahydronaphthalen*-5-*one*, b. p. 141—142°/0·2 mm. [*semicarbazone*, m. p. 185° (decomp.)], the constitution of which follows from its composition and its ultimate conversion into 2-*iso*propylnaphthalene. The methylene group which has thus been removed from eudesmol was therefore in the 5-position. The hydroxyketone is dehydrated by 90% formic acid to 3-iso*propylidene*-9-*methyldecahydronaphthalen*-5-*one*,* b. p. 142—143°/12 mm., d_4^{20} 0·9782, n_D^{20} 1·5051 (*semicarbazone*, m. p. 215°, apparently identical with that of m. p. 225°, above). This is not reduced by zinc and sodium hydroxide, but sodium in absolute alcohol converts it into 3-iso*propylidene*-9-*methyldecahydronaphthalen*-5-*ol** which, after purification through the *hydrogen phthalate*, is a solid, b. p. 145—146°/12 mm. It is dehydrated on heating with potassium hydrogen sulphate to 3-iso*propylidene*-9-*methyl*-1 : 2 : 3 : 4 : 7 : 8 : 9 : 10-*octahydronaphthalene**, b. p. 125—126°/12 mm., and dehydrogenated by sulphur-fusion to 2-*iso*propylnaphthalene (picrate, m. p. 91°; cf. Roux, A., 1888, 1305). For comparison, the latter has been synthesised by treating ethyl 2-naphthoate with magnesium methyl iodide and dehydrating the product, b. p. 120—130°/2 mm., with acetic anhydride to

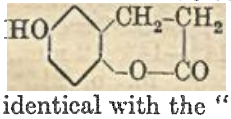
2-iso*propylidenenaphthalene*, b. p. 126—127°/12 mm. This is reduced by sodium and absolute alcohol to 2-iso*propyl*-1 : 4-*dihydronaphthalene*, b. p. 125°/12 mm., which gives 2-*iso*propylnaphthalene, b. p. 125°/12 mm., when heated with sulphur.



Since eudesmol is a tertiary alcohol, the hydroxyl group must be in position (*a*), (*b*), or (*c*) (I). In order to determine which of these is correct, dihydroeudesmol has been dehydrated to dihydroeudesmene (Semmler and Tobias, A., 1913, i, 885) and the latter ozonised in glacial acetic acid solution. After decomposing the ozonide with water and boiling the product with sodium hydroxide, a *ketone*, $C_{12}H_{20}O$, b. p. about 140°/12 mm. (*semicarbazone*, m. p. 218°), may be isolated from the neutral fraction. On account of its composition, this is regarded as 5 : 9-*dimethyldecahydronaphthalen*-3-*one*, and dihydroeudesmene must correspond, in part at least, with the formula (II). The hydroxyl is therefore not in position (*a*), whilst position (*c*) is excluded by the non-identity of eudesmene dihydrochloride and the doubly-unsaturated hydrocarbon regenerated from it with selinene dihydrochloride and selinene, respectively (cf. A., 1913, i, 987). Accordingly, eudesmol is represented by formula (I), and eudesmene dihydrochloride is probably 3 : 5-dichloro-5 : 9-dimethyl-3-*iso*propyldecahydronaphthalene.

H. E. F. Notton.

Electrochemical oxidation of β-phenylpropionic acid. II. F. Fichter and E. Schlager (Helv. Chim. Acta, 1927, **10**, 406—412).—Electrochemical oxidation of β-phenylpropionic acid in 0·5*N*-sulphuric acid with a lead cathode and a lead oxide anode, using a diaphragm, yields *p*-hydroxyphenylpropionic acid, *p*-benzoquinone (and its degradation products, maleic and succinic acids), propionic acid, a diphenolic compound of high mol. wt., and the lactone of 2 : 5-dihydroxy-6-phenylpropionic acid,



(*acetyl* derivative, m. p. 85·5°), identical with the " anhydride " of this acid obtained by Neubauer and Flatow (A., 1907, i, 771). *o*-Hydroxyphenylpropionic acid on electrolytic oxidation, without a diaphragm, also yields this lactone, so that this acid is an intermediate compound in the original electrolytic oxidation, a hydroxyl group entering both the *o*- and *p*-positions (cf. Fichter and Uhl, A., 1920, i, 234). On methylation with sodium methoxide and methyl iodide, the lactone yields 2 : 5-*dimethoxyphenylpropionic acid*, m. p. 65·5°, b. p. 185°/13 mm., which is synthesised from 2 : 5-dimethoxycinnamic acid (Kaufmann and Burr, A., 1907, i, 605) by electrolytic reduction in potassium hydroxide solution with a mercury cathode. Umbelliferone (Pechmann, A., 1884, 1173), on reduction with potassium hydroxide and sodium amalgam, yields the *lactone* of 2 : 4-dihydroxy-β-phenylpropionic acid, m. p. 131°, different from the lactone (above) obtained by the electrolytic oxidation of β-phenylpropionic acid. Similar reduction of 6-hydroxyhydrocoumarin in an attempt to prepare the latter lactone yielded a product, m. p. 157°. No Kolbe synthesis of the hydrocarbon, diphenylbutane, which would result by the decomposition of phenylpropionyl peroxide, could be detected. J. W. Baker.

α-Furfuryl iodide (2-iodomethylfuran). α-Furfuryl ethers. I. J. E. Zanetti (J. Amer. Chem. Soc., 1927, **49**, 1061—1067).—α-Furfuryl iodide is obtained in ethereal solution in 40—45% yield by adding furfuryl alcohol to an ethereal suspension of phosphorus tri-iodide. The simultaneous deposition of a crystalline orange or yellowish-brown precipitate suggests the formation of a phosphorus oxy- or hydroxy-iodide. The furfuryl iodide decomposes violently when its ethereal solution is evaporated, but can be converted into α-furfuryl ethers by treatment, in ethereal solution, with solid potassium hydroxide and alcohols.

α-Furfuryl bromide can be obtained in ethereal solution by a method analogous to that described above for the iodide. Treatment of this solution with solid potassium hydroxide and an alcohol, followed by evaporation of the solvent, affords the corresponding α-furfuryl ether in good yield. The following α-furfuryl ethers are described: n-*butyl*, b. p. 189—190°/765 mm.; iso*butyl*, b. p. 179—180°/755 mm.; n-*heptyl*, b. p. 99—101°/2 mm.; *allyl*, b. p. 172—173°/757 mm.; *benzyl*, b. p. 118—120°/2 mm.; *cinnamyl*, b. p. 138—140°/2 mm., and *α-furfuryl*, b. p. 101—102°/2 mm. These are very hygroscopic and decompose rapidly when moist. They can be kept in sealed vessels under reduced pressure, and are stabilised to air by traces of quinol.

F. G. Willson.

New γ-pyrone [1 : 4-pyrone] synthesis. W. Borsche and W. Peter (Annalen, 1927, **453**, 148—162).—Compounds of the type CHPh:CH·CO·CH:CR·OH (I) cannot be caused to isomerise to dihydropyrone derivatives analogous to the β-form of mesityloxidoxalic acid (Dieckmann, A., 1920, i, 813), but when their dibromides, CHPhBr·CHBr·CO·CH:CR·OH, are warmed at 50° with anhydrous potassium acetate in absolute alcohol, satisfactory yields of 1 : 4-pyrones, $CO<\begin{matrix}CH:CPh\\CH:CR\end{matrix}>O$ are obtained. Ethyl cinnamoylpyruvate [(I), R = CO_2Et; Schiff and Gigli, A., 1898, i, 489] [*copper* derivative, $(C_{14}H_{13}O_4)_2Cu$, m. p. 207—208°] gives a *dibromide*, m. p. 104°, from which *ethyl* 2-*phenyl*-1 : 4-*pyrone*-6-*carboxylate*, m. p. 119·5°, is readily obtained. The latter is hydrolysed by boiling hydrochloric acid to 2-*phenyl*-1 : 4-*pyrone*-6-*carboxylic acid*, m. p. 231°, which decomposes on distillation in a vacuum into 2-*phenyl*-1 : 4-*pyrone*, m. p. 104°. This is converted by catalytic hydrogenation with a palladium colloid into a *tetrahydro*-derivative (*phenylcarbamylhydrazone*, m. p. 195—196°), by ammonia into 2-*phenyl*-4-*pyridone* (+0·5H_2O), m. p. 155°, by aniline acetate into *α-anilino-δ-benzoyl-Δ$^{\alpha}$-buten-γ-one*, m. p. 128°, an

by sodium methoxide into *α-methoxy-δ-benzoyl-Δ^{α}-buten-γ-one*, isolated as the *copper* derivative, $(C_{12}H_{11}O_3)_2Cu$, m. p. 203°. Ethyl cinnamoylpyruvate yields with hydrazine or semicarbazide in alcoholic solution *ethyl 3-styrylpyrazole-5-carboxylate*, m. p. 143—144°, and with 2-nitro-4-cyanophenylhydrazine, *ethyl 1-nitrocyanophenyl-3-styrylpyrazole-5-carboxylate*, m. p. 221—222°. It is catalytically hydrogenated in presence of colloidal palladium to *ethyl β-phenylpropionylpyruvate* (*copper* derivative, m. p. 164—165°), which gives, with 2-nitro-4-cyanophenylhydrazine, *ethyl 1-nitrocyanophenyl-3-β-phenylethylpyrazole-5-carboxylate*, m. p. 152—153°. Cinnamoylacetone (cf. Ryan and Dunlea, A., 1913, i, 1067) and cinnamoylacetophenone [(I), R=Ph] are conveniently prepared by the ketonic fission of ethyl cinnamoylacetoacetate (*copper* derivative, m. p. 164°) and ethyl cinnamoylbenzoylacetate (*copper* derivative, m. p. 202°), respectively, in presence of water at 130—135°. Cinnamoylacetone and bromine in carbon disulphide give a *dibromide*, m. p. 161°, which readily loses hydrogen bromide, giving *bromocinnamoylacetone*, CPhBr:CH·CO·CH$_2$·CO·Me (two crystalline forms), m. p. 97°. 2-Phenyl-6-methyl-1 : 4-pyrone, m. p. 79·5° (Ruhemann, J.C.S., 1908, **93**, 431, gives 87—88°) (*hydrochloride*, m. p. 164°), is obtained from the dibromide and sodium acetate. *Cinnamoylacetophenone dibromide*, m. p. 164° (decomp.), is similarly converted into 2 : 6-diphenyl-1 : 4-pyrone, m. p. 142° (*loc. cit.*). When 1 mol. of cinnamoyl chloride is treated with 2 mols. of ethyl sodioacetoacetate and the product liberated with acid and distilled in a vacuum, a neutral *substance*, m. p. 80°, is produced. It is hydrolysed by dilute acids or alkalis to *γ*-acetyl-β-phenylbutyric acid, and is probably the *lactone* of *δ-hydroxy-γ-carbethoxy-β-phenyl-Δ^{γ}-hexenoic acid*.

H. E. F. Notton.

Formation of hydroxy-derivatives of diphenylene oxide from resorcinol. Y. Tsuzuki (Bull. Chem. Soc. Japan, 1927, **2**, 79—83).—Resorcinol when heated at 500—550° in presence of blue oxide of tungsten yields two substances, one of which was previously described as 2 : 6-dihydroxydiphenyl (Kubota, Fujimura, and Akashi, A., 1925, i, 809), but is now shown to be *4-hydroxydiphenylene oxide*, m. p. 138—138·5° (*methyl ether*, m. p. 93—94°), which affords phenylmalonic acid on oxidation. The other product, probably *4 : 5-dihydroxydiphenylene oxide*, brown prisms containing $0·5H_2O$, m. p. 241—242° (*dimethyl ether*, m. p. 150°; *diacetyl* derivative, m. p.), gives with ferric chloride a green coloration, changing to light brown on addition of sodium carbonate. Both substances yield diphenylene oxide o distillation zinc dust. A dinitro-derivative o^f 4-hydroxydiphenylene oxide, probably 1 : 3-*dinitro-4-hydroxydiphenylene oxide*, m. p. 216—217° ecomp.), is described, and absorption curves of di-hydroxydiphenylene oxide, 2 : 2′- and -dihydroxydiphenyl, and of 2- and 4-hydroxydiphenyl are given.

W. J. Powell.

Plant-colouring matters. III. Colouring matter from saffron. P. Karrer and H. Salomon (Helv. Chim. Acta, 1927, **10**, 397—405).—Three colouring matters have been isolated from *Crocus sativus*, L. The dried saffron, freed from fats and ethereal oils by extraction with ether and alcohol, is treated in aqueous solution with cold 1% potassium hydroxide solution, which precipitates a mixture of γ-crocetin and the potassium salt of β-crocetin. Acidification of the alkaline filtrate precipitates *α-crocetin*, $C_{24}H_{28}O_5$, m. p. 272—273° (0·7%), which is purified by way of its *sodium* salt (*barium* salt). It is soluble in alkalis, but is reprecipitated on passing carbon dioxide into the solution, and is therefore a phenol. It contains no methoxyl group, and may be identical with crocetin obtained by Decker (A., 1914, i, 979), although addition of ammonium carbonate to its solution in alkali precipitates, not the ammonium salt, but the free phenol. It crystallises from pyridine (+1C_5H_5N, which is lost in a vacuum at 100°). *γ-Crocetin*, $C_{24}H_{26}O_3(OMe)_2$, m. p. 202—203° (0·3%), is extracted from the mixture with the potassium salt of the β-compound by means of chloroform, and appears to be a dimethoxy-derivative of α-crocetin. It is not acidic. *β-Crocetin*, $C_{24}H_{27}O_4(OMe)$, m. p. 205—206° (*potassium* salt), appears to be the monomethoxy-derivative of the α-compound.

J. W. Baker.

Action of piperidine on α-bromobenzylideneacetophenone. C. Dufraisse and H. Moureu (Bull. Soc. chim., 1927, [iv], **41**, 457—473).—The red substance, m. p. 99—100°, obtained by Watson (J.C.S., 1904, **85**, 1322) by the action of excess of piperidine on α-bromobenzylideneacetophenone is not, as was supposed, stereoisomeric with Andre's β-piperidinobenzylideneacetophenone (A., 1913, i, 1065), but is an α-piperidino-derivative, affording on hydrolysis phenylbenzylglyoxal. With 1 mol. of piperidine in ether at −10° to −15°, α-bromobenzylideneacetophenone affords (yield 90%) *α-bromo-α-piperidinobenzylacetophenone*, m. p. 164°, decomp. 120° on slow heating, and oxidised in air to benzaldehyde. With dilute hydrobromic acid, this substance affords (yield 86%) a *hydrobromide*, m. p. 192°; on warming with 10% sulphuric acid, benzaldehyde and phenylbenzylglyoxal are formed. With sodium ethoxide, it gives a 90% yield of α-piperidinobenzylideneacetophenone, m. p. 101—102°, together with a little yellow *substance*, m. p. 212°. With cold potassium acetate solution, α-bromo-α-piperidinobenzylacetophenone affords α-piperidinobenzylideneacetophenone and *α-piperidino-α-acetylbenzylacetophenone*, m. p. 165°, converted by sodium ethoxide into phenylbenzylglyoxal. Excess of piperidine in alcoholic solution converts α-bromo-α-piperidinobenzylacetophenone into the mixture of α-piperidinobenzylacetophenone and the pale yellow, saturated dipiperidine derivative, m. p. 174° (Watson, *loc. cit.*). The α-bromo-α-piperidino-derivative must therefore represent the first stage of the reaction between piperidine and α-bromobenzylideneacetophenone, and the addition of the base thus takes place in positions 1 : 2, and not 1 : 4, as with benzylideneacetophenone (A., 1912, i, 787), or in the action of sodium ethoxide (A., 1922, i, 843; Kohler, A., 1905, i, 215). The dipiperidino-derivative is not obtained by addition of piperidine to α- or to β-piperidinobenzylideneacetophenone, but from the reaction of α-bromo-α-piper-

idinobenzylacetophenone with potassium acetate the dipiperidino-derivative is probably αα-dipiperidinobenzylideneacetophenone, $COPh{\cdot}CBr(NC_5H_{10}){\cdot}CH_2Ph \longrightarrow COPh{\cdot}C(NC_5H_{10})_2{\cdot}CH_2Ph$. On hydrolysis with 15% sulphuric acid, however, only small amounts of phenylbenzylglyoxal are obtained, the main product being *ω-piperidinoacetophenone* (*N-phenacylpiperidine*), b. p. 161—163°/12 mm., d_4^{17} 1·0453, $n_{18\cdot7}$ 1·5433, a decomposition which is more easily interpreted on the αβ-dipiperidinobenzylacetophenone structure. ω-Piperidinoacetophenone is also obtained by the action of piperidine on phenacyl chloride. β-Piperidinobenzylideneacetophenone has m. p. 98—99° (cf. André, *loc. cit.*). R. BRIGHTMAN.

Intramolecular alkylation with the bromination of δε-unsaturated ketonic bases. C. MANNICH and T. GOLLASCH (Annalen, 1927, **453**, 177—190).—Unsaturated ketoalkylamines of the general formula $NR_2{\cdot}CH_2{\cdot}CR'(COMe){\cdot}CH_2{\cdot}CH{:}CH_2$ (cf. this vol., 231), like the corresponding amino-acids (A., 1925, i, 1037), yield dibromides which are in most cases immediately transformed into pyrrolidine derivatives, $\begin{matrix}CH_2{-}{-}CH{\cdot}CH_2Br\\ |\qquad\quad >NR_2Br\\ CR'Ac{\cdot}CH_2\end{matrix}$. γ-Dimethylaminomethyl-Δ^ε-hexen-β-one and bromine in chloroform solution give *4-acetyl-1 : 1-dimethyl-2-bromomethylpyrrolidinium bromide*, m. p. 191°. γ-Piperidinomethyl-Δ^ε-hexen-β-one hydrobromide yields, in a similar way, the normal dibromide, *εζ-dibromo-γ-piperidinomethylhexan-β-one hydrobromide*, m. p. 144°. The corresponding oily free *base* soon passes into *4-acetyl-2-bromomethylpyrrolidinium*spiro-1 : 1′-*piperidinium bromide*, m. p. 189°. Free γ-piperidinomethyl-Δ^ε-hexen-β-one reacts differently with bromine, forming principally *α-bromo-γ-piperidinomethyl-Δ^ε-hexen-β-one hydrobromide*, m. p. 160—161°. The free *base* passes rapidly into *3-keto-4-allylpyrrolidinium*spiro-1 : 1′-*piperidinium bromide*, m. p. 217°. *Ethyl γ-dimethylaminomethyl-Δ^ε-hexen-β-one-γ-carboxylate*, b. p. 128—130°/15 mm. (*hydrobromide*, m. p. 134°), from dimethylamine, formaldehyde, and ethyl allylacetoacetate, is converted by bromine into *4-acetyl-4-carbethoxy-1 : 1′-dimethyl-2-bromomethylpyrrolidinium bromide*, m. p. 168° (decomp.), which is hydrolysed by barium hydroxide to *4-carboxy-1 : 1-dimethyl-2-methylenepyrrolidinium bromide*, m. p. 184·5°. This is catalytically hydrogenated in presence of palladium to *4-carboxy-1 : 1 : 2-trimethylpyrrolidinium bromide*, m. p. 197°, and debrominated by silver oxide to neutral *4-carboxy-1 : 1-dimethyl-2-methylenepyrrolidinium betaine*, $\begin{matrix}CH_2{-}{-}C{:}CH_2\\ |\quad\quad\quad\\ CO{\cdot}O{\cdot}NMe_2\\ |\quad\quad\quad\\ CH{-}{-}{-}CH_2\end{matrix}$, m. p. 189—190°. In a similar way, *ethyl γ-piperidinomethyl-Δ^ε-hexen-β-one-γ-carboxylate*, b. p. 162°/12 mm., from piperidine, formaldehyde, and ethyl allylacetoacetate, is successively converted into *4-acetyl-4-carbethoxy-2-bromomethylpyrrolidinium*spiro-1 : 1′-*piperidinium bromide*, m. p. 189°; *4-carboxy-2-methylenepyrrolidinium*spiro-1 : 1-*piperidinium bromide*, m. p. 174°, and *4-carboxy-2-methylenepyrrolidinium*spiro-1 : 1′-*piperidinium betaine* (+2H$_2$O), m. p. 87—88°.

H. E. F. NOTTON.

Preparation of Bz-halogenated derivatives of oxindole-3-acetic acid. CHEM. FABR. AUF AKTIEN. —See B., 1927, 379.

Manufacture of vat dyes and intermediates [isatins and thionaphthens]. SOC. CHEM. IND. IN BASLE.—See B., 1927, 360.

Reactions of nitroso-derivatives with unsaturated compounds. V. Nitronic, isatogenic, and indolic derivatives of *o*-nitroacetylenes. L. ALESSANDRI (Gazzetta, 1927, **57**, 195—223; cf. A., 1926, 287, 1038).—When a solution containing *o*-nitrophenylacetylene and nitrosobenzene is kept in the dark, the products formed vary with the solvent. In ether, the *o*-nitrophenylacetylene condenses to form di-isatogen, and reacts to give a substance regarded as *2-phenyliminoindoxyl N′-oxide*, $C_6H_4<\begin{matrix}CO\\ NH\end{matrix}>C{:}NPh{:}O$, m. p. 195—196°. This substance is quite distinct from isatinphenylhydroxylamine, $C_6H_4<\begin{matrix}CO\\ -N\end{matrix}>C{\cdot}NPh{\cdot}OH$ (Rupe and Stocklin, A., 1924, i, 764; Rupe and Guggenbühl, A., 1925, i, 1100); it is hydrolysed by dilute sulphuric acid to isatin and *p*-aminophenol, is reduced by aluminium amalgam to α-anilinoisatin, and with phenylhydrazine gives isatin-α-phenylhydrazone; it is stable to light. During the reaction in ether, azoxybenzene, formic acid, and a *substance*, $C_{14}H_{10}O_3N_2$, m. p. 150—151°, are obtained. In benzene, the products are di-isatogen, the above oxide, and the last-named "substance." In acetic acid, di-isatogen, azoxybenzene, and *N*-hydroxyisatin are obtained. As it might be supposed that *o*-nitrophenylacetylene first condenses to give *oo′*-dinitrodiphenyldiacetylene, this substance itself was treated with nitrosobenzene in acetic acid, but gave no di-isatogen, and thus is not an intermediate product. In chloroform solution, a little *N*-hydroxyisatin, with traces of di-isatogen, the above oxide, and isatin was obtained. When the oxide is treated with nitrosobenzene in chloroform, azoxybenzene and isatin are formed in small quantity. Speculations are made on the course of the various reactions. *o*-Nitrophenylacetylene, when exposed to sunlight in benzene solution, deposits a red substance.

E. W. WIGNALL.

Stereochemistry of dicyclic ring-systems. IV. Decahydroquinoline. W. HUCKEL and F. STEPF (Annalen, 1927, **453**, 163—176).—Attempts to prepare 2-ketodecahydroquinoline by the catalytic hydrogenation of *o*-nitrocinnamic acid or its *cyclohexyl* ester, m. p. 55—56°, gave principally 2-keto-1 : 2 : 3 : 4-tetrahydroquinoline. Although quinoline had been reduced to the decahydro-derivative in many ways (cf. Sabatier, A., 1914, i, 323; Skita, A., 1913, i. 54), the formation of more than one isomeride had not hitherto been observed. Hydrogenation of quinoline hydrogen oxalate in presence of colloidal platinum affords, however, in addition to (*trans*)-decahydroquinoline, m. p. 48°, b. p. 203°/735 mm., $d_4^{55\cdot5}$ 0·9021, $n_{He}^{55\cdot8}$ 1·47190 (*benzoyl* derivative, m. p. 56°), a liquid (cis-)*isomeride* (10%), f. p. about −40°, b. p. 205°/735 mm., $d_4^{56\cdot0}$ 0·9191, $n_{He}^{55\cdot7}$ 1·47681 (*hydrochloride*, m. p. 226°; *picrate*, m. p. 142—145°; *dithio-*

carbamate, m. p. 143°; *phenylurethane*, m. p. 163—165°). In presence of excess of hydrochloric acid, the product contains 65% of the new isomeride, whilst in neutral solution only 1 : 2 : 3 : 4-tetrahydroquinoline is formed. The following derivatives of the *cis*- and *trans*-forms had been previously obtained, but incorrectly formulated by Bamberger (A., 1890, 1318; 1894, i, 427), their former names and m. p. being given in parentheses: cis-*benzoyldecahydroquinoline*, m. p. 96° (*trans*-, m. p. 96°); cis-β-2-*benzamidocyclohexylpropionic acid*, m. p. 156° (β-2-benzamidocyclohexylacrylic acid, m. p. 153°); trans-β-2-*benzamidocyclohexylpropionic acid*, m. p. 202—203° (identical with Bamberger's *cis*-, m. p. 196°, and *trans*-, m. p. 205°, acids); *cis*-2-ketodecahydroquinoline, m. p. 129° (2-keto-octahydroquinoline, m. p. 127°), and Bamberger's decahydro-α-quinolone (2-ketodecahydroquinoline), m. p. 151°, which is the *trans*-form. It is improbable that Perkin and Sedgwick's octahydroacridines are related as these authors suggest, since, in order to explain the racemisation of the optically active forms without interconversion of A and B, it is necessary to assume that a change of configuration can take place simultaneously in both centres of asymmetry, but not in one at a time.

H. E. F. Notton.

Qualitative organic analysis. III. Isolation of nitrogen-alkylated pyrroles. T. Reichstein (Helv. Chim. Acta, 1927, **10**, 387—392).—1-Alkylpyrroles may be readily isolated from mixtures in which they are present only in small quantity by coupling them with diazonium compounds, the resulting azo-compounds being readily purified by distillation in a high vacuum. The latter form definite crystalline complex compounds with picric acid and trinitrobenzene. Thus 1-*n*-butylpyrrole (10%) was isolated as the *picrate*, m. p. 139—140° (decomp.), of p-*methoxybenzeneazo*-1-n-*butylpyrrole*, b. p. 185°/0·5 mm. (*trinitrobenzene* compound, m. p. 72—73°), when it was mixed with anisole (90%), 80% of the anisole being recovered. Benzeneazo-1-methylpyrrole (Plancher and Soncini, A., 1903, i, 449) yields a trinitrobenzene compound which is decomposed on crystallisation from alcohol. The following compounds are, however, stable: p-*toluene-azo*-1-*methylpyrrole*, m. p. 99·5—100·5° (corr.) [*trinitrobenzene* compound, m. p. 99—100° (corr.)]; *benzeneazo*-1-n-*butylpyrrole*, b. p. 150—155°/0·5 mm. [*picrate*, m. p. 131—133° (decomp.)]; *benzeneazo*-1-*isoamylpyrrole*, b. p. 155—160°/0·5 mm. [*picrate*, m. p. 123° (decomp.)]; p-*methoxybenzeneazo*-1-iso-*amylpyrrole*, m. p. 33—34°, b. p. 195°/0·5 mm. [*picrate*, m. p. 144—145° (decomp.); *trinitrobenzene* compound, m. p. 42·5—44°].

J. W. Baker.

Preparation of iodinated pyridine derivatives. Deutsche Gold- u. Silber-Scheideanstalt, vorm. Roessler.—See B., 1927, 379.

Derivatives of pyridine and piperidine obtained rom hydroxymethylene ketones. E. Benary (Ber 1927, **60**, [*B*], 914—918; cf. A., 1926, 500). he sodium derivative of *n*-propyl β-hydroxyvinyl e one in dry ether is converted by a solution of mmonium acetate in glacial acetic acid into a x ure of 5-n-*butyryl*-2-n-*propylpyridine*, b. p. 152°/13 mm., d^{26} 0·9782 (*oxime*, m. p. 85—86°), and *di*-β-n-*butyrylvinylimine*, b. p. 189—191°/13 mm. The pyridine derivative is oxidised by nitric acid to 2-n-*propylpyridine*-5-*carboxylic acid*, m. p. 124—125° (decomp.) [*nitrate*, m. p. 141°; *copper* salt, m. p. 242° (decomp.)], which, when decarboxylated, affords 2-*n*-propylpyridine. Reduction of the ketone with sodium and alcohol yields 2-n-*propyl*-5-n-*butylpiperidine*, b. p. 115°/13 mm. Analogously, 5-benzoyl-2-phenylpyridine is reduced mainly to 2-*phenyl*-5-*benzylpiperidine*, b. p. 229°/14 mm., 2-phenylpiperidine, b. p. 245°/756 mm. (*monohydrate*, m. p. 60—61°), being obtained in minor amount. The hydroxymethylene compound of mesityl oxide (cf. Couturier, A., 1910, i, 299) gives a dark green copper salt and a *benzeneazo*-derivative, $C_{13}H_{14}O_2N_2$, m. p. 98°. Its sodium derivative is converted by ammonium acetate into 5-β′-*methylcrotonyl*-2-β-*methyl*-Δ$^{\alpha}$-*propenylpyridine*, m. p. 73—74° (*picrate*, m. p. 175—176°; additive *compound* with mercuric chloride, m. p. 135°), oxidised by nitric acid to pyridine-2 : 5-dicarboxylic acid.

H. Wren.

Derivatives of pyridine. A. Pieroni (Atti R. Accad. Lincei, 1927, [vi], **5**, 303—306).—Like *p*-chloronitrobenzene, 2-chloro-5-nitropyridine reacts with aqueous potassium hydroxide, giving 2-hydroxy-5-nitropyridine, and with methyl- or ethyl-alcoholic potassium hydroxide, giving 5-nitro-2-methoxy- or -2-ethoxy-pyridine, m. p. 95° (Tschitschibabin and Bylinkin, A., 1923, i, 595, gave m. p. 72°). 5-*Carbamido*-2-*ethoxypyridine*, m. p. 175°, has a sweet taste; 5-*carbamido*-2-*methoxypyridine* has m. p. 185°, and 5-amino-2-acetamidopyridine, which readily changes, m. p. 154°. The last reacts with yellow mercuric oxide, giving, among other products, the compound $\left[\mathrm{NHAc{\cdot}C<\begin{matrix}CH{:}CH\\N{-}CH\end{matrix}>C{\cdot}}\right]\mathrm{Hg}(?)$, which does not melt at 230°. *Ethyl acetoacetate* 2-*chloro*-5-*pyridylhydrazone* (cf. A., 1925, i, 1316), m. p. 143°, when boiled in acetic acid solution, gives a *compound*, m. p. 175°, which gives a red coloration in aqueous solution with ferric chloride and with diazonium salts, and is probably of the structure $\mathrm{CH_2{\cdot}CO<\begin{matrix}C{=}N\\ \\ \end{matrix}>N{\cdot}C<\begin{matrix}CH{\cdot}CH\\CH{=}N\end{matrix}>CCl}$. 2-*Chloropyridine*-5-*arsinic acid*, m. p. 186°, is obtained by the interaction of diazochloropyridine chloride and potassium arsenite.

T. H. Pope.

Indole condensation of phenylhydrazones. A. Korczyński, W. Brydowna, and L. Kierzik (Rocz. Chem., 1927, **7**, 112—123).—See this vol., 255.

Manufacture of quinoline derivatives. Farbenfabr. vorm. F. Bayer & Co.—See B., 1927, 379.

Preparation of derivatives of 6-alkoxy-4-methylquinoline. Chem. Fabr. auf Aktien.—See B., 1927, 379.

Preparation of hydrocarbostyril and its derivatives. F. Mayer, L. van Zutphen, and H. Philipps (Ber., 1927, **60**, [*B*], 858—864).—β-Chloropropionyl chloride is converted by aromatic amines in boiling, anhydrous acetone into substituted β-chloropropionamides, which are transformed by aluminium chloride at temperatures above their

m. p. into hydrocarbostyrils. β-Chloropropionyl chloride thus yields the corresponding *anilide*, m. p. 119°, o-, m-, and p-*toluidide*, m. p. 78°, 90°, and 121°, respectively, o- and p-*chloroanilide*, m. p. 86° and 125°, respectively, 2 : 4-*dichloroanilide*, m. p. 103°, o-, m-, and p-*hydroxyanilide*, m. p. 125°, 132°, and 135°, respectively, p-*phenetidide*, m. p. 128°, p-*nitroanilide*, m. p. 208°, p-*aminoanilide*, m. p. 239°, *diphenylamide*, m. p. 96°; the *di*-β-*chloropropionyl* derivatives of *o*- and *m*-phenylenediamine, m. p. 170° and 239°, respectively, are described. β-Chloro-*n*-butyryl chloride affords similarly the corresponding *anilide*, m. p. 90°, o- and p-*toluidide*, m. p. 108° and 124°, respectively, o- and p-*chloroanilide*, m. p. 83° and 104°, respectively, 2 : 4-*dichloroanilide*, m. p. 109°, o-*hydroxyanilide*, m. p. 140°, and o-*aminoanilide*, m. p. 160°. 2-Keto-1 : 2 : 3 : 4-tetrahydroquinoline, m. p. 163°, and the following derivatives of it are described: 8-*methyl*-, m. p. 112°; 6-methyl-, m. p. 106°; 8-*chloro*-, m. p. 106°; 6-*chloro*-, m. p. 167—168°; 6 : 8-*dichloro*-, m. p. 147—148°; 8-*hydroxy*-, m. p. 195°; 5- or 7-hydroxy-, m. p. 230°; 6-*hydroxy*-, m. p. 237—238°; 1-*phenyl*-, m. p. 122°; 4-*methyl*-, m. p. 98°; 4 : 8-*dimethyl*-, m. p. 131°; 4 : 6-*dimethyl*-, m. p. 131°; 8-*chloro*-4-*methyl*-, m. p. 103°; 6-*chloro*-4-*methyl*, m. p. 172°; 6 : 8-*dichloro*-4-*methyl*-, m. p. 161°. 2 : 9-*Diketo*-, 3 : 9-*diketo*-, and 2 : 9-*diketo*-4 : 7-*dimethyl*-1 : 2 : 3 : 4 : 7 : 8 : 9 : 10-*octahydrophenanthrolins* have m. p. 365°, above 370°, and 242°, respectively. β-Chloropropion-*m*-toluidide is converted by aluminium chloride into a mixture of 2-*keto*-5- and -7-*methyl*-1 : 2 : 3 : 4-*tetrahydroquinolines*, from which products m. p. 131° and 160° are separated. β-*Chloropropionmethylanilide*, b. p. 150°/15 mm., loses hydrogen chloride when distilled under atmospheric pressure, and is converted into acrylmethylanilide, m. p. 76°; with aluminium chloride, it affords 2-*keto*-1-*methyl*-1 : 2 : 3 : 4-*tetrahydroquinoline*, b. p. 295—297°/760 mm., 160—161°/15 mm. β-*Chloropropionethylanilide*, b. p. 158—159°/15 mm., does not lose hydrogen chloride appreciably when distilled under atmospheric pressure; with aluminium chloride, it gives 2-*keto*-1-*ethyl*-1 : 2 : 3 : 4-*tetrahydroquinoline*, b. p. 150—155°/15 mm. β-*Chloro*-n-*butyrmethylanilide*, b. p. 265°/atm. pressure without appreciable decomposition, yields 2-*keto*-1 : 4-*dimethyl*-1 : 2 : 3 : 4-*tetrahydroquinoline*, b. p. 170°/15 mm. 2-Keto-1 : 2 : 3 : 4-tetrahydroquinoline is reduced by sodium and amyl alcohol to tetrahydroquinoline and transformed by sulphuryl chloride in benzene into *chloro*-2-*keto*-1 : 2 : 3 : 4-*tetrahydroquinoline*, m. p. 175—176°. H. WREN.

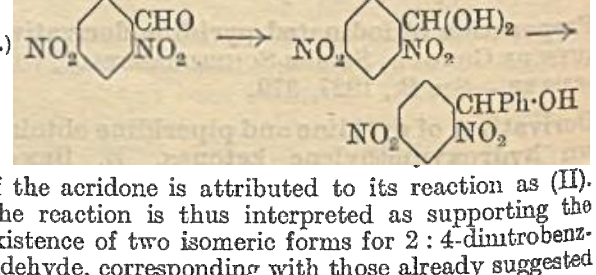
Synthesis of 2 : 4-dihydroxyquinolines. P. BAUMGARTEN and W. KARGEL (Ber., 1927, **60**, [*B*], 832—842).—Phenylmalonanilide is converted at 250—350°/15 mm., almost quantitatively, into aniline and 3-*phenyl*-2 : 4-*dihydroxyquinoline*, m. p. 319° [*sodium* salt; *monobenzoyl* derivative ((?) 4-*keto*-2-*benzoxy*-3-*phenyl*-3 : 4-*dihydroquinoline*), m. p. 243° (also +Ac·OH)]; phenylacetanilide is produced in minor amount. The same substances are formed when phenylmalonanilide is heated at the ordinary pressure, but are then accompanied by 2-*keto*-4-*anilo*-3-*phenyl*-1 : 2 : 3 : 4-*tetrahydroquinoline*, m. p. 295° (also +Ac·OH) (*hydrochloride*), identified by hydrolysis to 3-phenyl-2 : 4-dihydroxyquinoline. Simplification is introduced into the synthesis by the use of ethyl phenylmalonate and aniline as initial materials. By suitable variation of the components, the following compounds are obtained: 2 : 4-dihydroxy-3-phenyl-8-methylquinoline, m. p. 249° (also +Ac·OH) [*benzoyl* derivative, m. p. 263° after softening (also +Ac·OH)]; 2 : 4-*dihydroxy*-3-*phenyl*-1-*methylquinoline*, m. p. 222° (*benzoyl* derivative, m. p. 165°); 2 : 4-*dihydroxy*-3-*phenyl*-α-*naphthaquinoline*, m. p. 322° (also +Ac·OH) (*benzoyl* derivative, m. p. 335°); 2 : 4-*dihydroxy*-3-*benzylquinoline*, m. p. 194° (also +EtOH) (*benzoyl* derivative, m. p. 256°); 2 : 4-dihydroxy-3-ethylquinoline, m. p. 259°; 4-*keto*-2-*hydroxy*-3 : 3-*diethyl*-3 : 4-*dihydroquinoline*, m. p. 260° (*benzoyl* compound, m. p. 245°). Diethylmalondianilide has m. p. 218°.

Malonanilide when heated gives aniline, carbon dioxide, and small quantities of acetanilide and carbanilide, but is mainly converted into a dark, brittle mass from which 2 : 4-dihydroxyquinoline could not be isolated; a similar result is obtained when ethyl malonate and aniline are used. The unsubstituted ester can, however, react with a suitable amine, thus yielding, with α-naphthylamine, 2 : 4-*dihydroxy*-α-*naphthaquinoline*, m. p. 320° (decomp.) (also +Ac·OH); the *hydrochloride*, *benzoyl* derivative, m. p. 272°, and *nitroso*-compound, decomp. about 330°, are described. The compound is converted into α-naphthaquinoline by distillation with zinc dust. H. WREN.

Manufacture of pharmacetuical products [quinolines]. FAREBNFABR. VORM. F. BAYER & Co. —See B., 1927, 379.

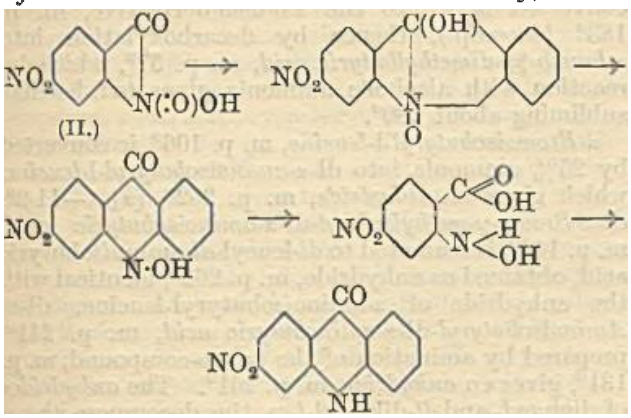
Derivatives of naphthaquinolines and naphtha-*iso*quinolines. C. S. GIBSON, K. V. HARIHARAN, K. N. MENON, and J. L. SIMONSEN (J. Indian Inst. Sci., 1927, 9A, 179—191).—See A., 1926, 1154.

New synthesis of acridones. I. TANASESCU (Bull. Soc. chim., 1927, [iv], **41**, 528—537).—In presence of sulphuric acid, 2 : 4-dinitrobenzaldehyde condenses with aromatic hydrocarbons and their electro-negative substituted derivatives, affording acridones. The presence of electropositive substituents in the aromatic nucleus causes the formation of the corresponding triphenylmethanes. In the case of benzene, the reaction affords, in addition to 2-nitroacridone, *di*-2 : 4-*dinitrobenzhydryl ether*, $(C_6H_3[NO_2]_2\cdot CHPh)_2O$, m. p. 167°. The formation of the latter is attributed to a normal reaction of the dinitrobenzaldehyde, *i.e.*, as (I), whilst the formation

(I.) 

of the acridone is attributed to its reaction as (II). The reaction is thus interpreted as supporting the existence of two isomeric forms for 2 : 4-dinitrobenzaldehyde, corresponding with those already suggested for *o*-nitrobenzaldehyde (A., 1926, 1247). Nitro-

benzene does not condense with 2 : 4-dinitrobenzaldehyde under the above conditions. Similarly, whilst



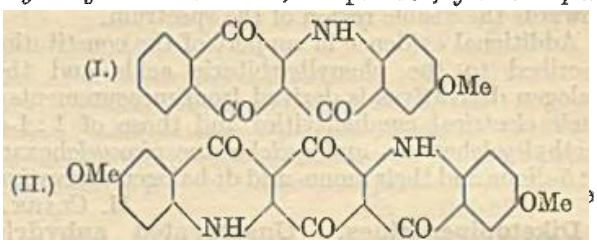
2-nitrodiphenylamine-6-carboxylic acid affords a nitroacridone (Ullmann, A., 1907, i, 846; 1908, i, 52), 2′-nitrodiphenylamine-6-carboxylic acid does not condense. Chlorobenzene affords 8(?)-*chloro*-2-*nitroacridone*, golden-yellow, m. p. above 360°; 8(?)-*bromo*-2-*nitroacridone*, brownish-yellow, is similarly obtained. Iodobenzene reacts similarly, but benzoic acid does not react. With phenol, the reaction is violent. Toluene affords 2 : 4-*dinitro*-4′ : 4″-*dimethyltriphenylmethane*, yellow, m. p. 280° (decomp.), and aniline 2 : 4′-dinitro-4′ : 4″-diaminotriphenylmethane, m. p. 132° (this vol., 139). Naphthalene, anthracene, acenaphthene, and phenanthrene react vigorously, affording dark-coloured products in which several mols. of hydrocarbon appear to have condensed with 1 mol. of 2 : 4-dinitrobenzaldehyde. Complex products are also obtained with these hydrocarbons when the condensation is effected in chloroform solution. The 2 : 4-dinitrobenzaldehyde can be replaced by other 2-nitrobenzaldehydes containing an electronegative substituent in the 4-position, the analogous 2-substituted acridone being obtained.

R. BRIGHTMAN.

Synthesis of 1-nitro- and 3-nitro-acridine and 1-methyl- and 3-methyl-acridine. H. JENSON and M. FRIEDRICH (J. Amer. Chem. Soc., 1927, **49**, 1049—1052).—Nitration of acridine by Graebe's method (Annalen, 1871, **158**, 275) affords two mononitro-derivatives, m. p. 216° (α) and m. p. 167° (β), together with a dinitro-derivative, reddish-yellow, m. p. not below 250°. The β-nitro-derivative is obtained by condensation of *o*-aminobenzaldehyde with *o*-bromonitrobenzene in nitrobenzene solution in presence of copper powder and sodium acetate, followed by treatment of the product with concentrated sulphuric acid at 100°, and is therefore 1-*nitroacridine*. The α-nitro-derivative is obtained similarly from *p*-bromonitrobenzene, and is therefore 3-*nitroacridine*. 1-Methylacridine and 3-methylacridine are obtained analogously from *o*-aminobenzaldehyde and *o*- and *p*-bromotoluenes.

F. G. WILLSON.

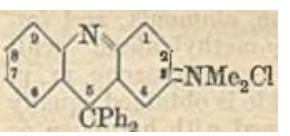
Hydroxyl derivatives of naphthacridonequinone and of benzodiacridonequinone. E. LEWICKA (Rocz. Chem., 1926, **6**, 881—889).—5-*Methoxy*-*o*-*toluidine* b. p. 248—249° [*hydrochloride*, m. p. 285° (decomp.), *acetyl* derivative, m. p. 134°], is prepared by the reduction of the corresponding nitro-compound, and yields on oxidation 2-amino-5-methoxybenzoic acid, which, on condensation with α-naphthaquinone, gives *α-naphthaquinone-5-methoxyanthranilic acid*, m. p. 262°. From this is obtained, by dehydration, *naphtha-3-methoxyacridonequinone* (I), which dyes cotton and wool red. Similarly, *α-naphthaquinone-5-hydroxyanthranilic acid*, m. p. 290°, yields *naphtha-*



3-*hydroxyacridonequinone*, also a red dye. *Benzoquinone-5 : 5′-dimethoxydianthranilic acid* [2 : 5-*di*-(4′-*methoxy*-2′-*carboxyanilino*)-p-*benzoquinone*], m. p. 300°, is obtained by substituting *p*-benzoquinone for α-naphthaquinone in the above reaction, and yields *benz*-3 : 3′-*dimethoxydiacridonequinone* (II), a brown dye for wool and cotton. *Benzoquinone-5 : 5′-dihydroxydianthranilic acid*, m. p. 340°, is prepared in an analogous manner, yielding on condensation *benz*-3 : 3′-*dihydroxydiacridonequinone*, also a brown vat dye.

R. TRUSZKOWSKI.

Carbazine syntheses. II. H. GOLDSTEIN and M. PIOLINO (Helv. Chim. Acta, 1927, **10**, 334—338).—By the action of magnesium phenyl bromide on methyl 2 : 4-diaminodiphenylamine-6-carboxylate (Goldstein and Rodel, A., 1926, 1138) is obtained 1 : 3-diamino-5 : 5-diphenyldihydroacridine identical with the product obtained by Kehrmann, Ramm, and Schmajewski (A., 1921, i, 600). Similarly, methyl 4′-dimethylaminodiphenylamine-2-carboxylate yields 3-dimethylamino-5 : 5-diphenyldihydroacridine, isolated as its *hydrochloride*, m. p. 295° (decomp.), which on oxidation (atmospheric or with ferric chloride) yields 5 : 5-*diphenyldihydroacridine*-3-*dimethylimmonium chloride* (annexed formula), (*perchlorate*), whilst methyl 4-amino-4′-dimethylaminodiphenylamine-2-carboxylate yields 5 : 5-diphenyl-7-amino-3-dimethylaminodihydroacridine, isolated as its *dihydrochloride* (*diacetyl* derivative, m. p. 222°) which on oxidation yields 3-*dimethylamino*-5 : 5-*diphenyldihydroacridine*-7-*immonium chloride*, from which, by the action of ammonia, the violet *base* is liberated.



J. W. BAKER.

Labile nature of the halogen atom in organic compounds. XIII. H. GRAHAM, A. K. MACBETH, and W. B. ORR (J.C.S., 1927, 740—746; cf. A., 1926, 846).—The absorption spectra of 1-phenylbarbituric and 1 : 3-diphenylbarbituric acids and their mono- and di-halogen derivatives afford further evidence for the view that the dihalogen derivatives have a diketonic structure, whilst the parent acid and the monohalogen derivatives exist in the enolic form. The stability of the latter halogen derivatives towards reducing agents is thus accounted for. In the spectra of the phenylbarbituric acids, the complex bands in

the absorption spectrum of barbituric acid itself are replaced by a principal band extending over $1/\lambda$ 3700—4200. The absorption spectra of 2-thiobarbituric and 2-thio-1 : 3-diphenylbarbituric acids present a series of bands similar to those of barbituric and 1 : 3-diphenylbarbituric acids, with the same simplification of absorption due to introduction of phenyl groups. The bands are all displaced, however, towards the visible region of the spectrum.

Additional evidence in support of the constitutions ascribed to the phenylbarbituric acids and their halogen derivatives is derived from measurements of their electrical conductivities and those of 1 : 1-dimethyl*cyclo*hexane- and *cyclo*hexane*spirocyclo*hexane-3 : 5-dione and their mono- and di-halogen derivatives.

M. CLARK.

Diketopiperazines. Unsaturated anhydride from leucylglycine anhydride. Synthesis of tertiary leucine. E. ABDERHALDEN and E. ROSSNER (Z. physiol. Chem., 1927, **163**, 149—184; cf. A., 1926, 603). *Anhydrides* of glycyl-*dl*-norleucine, glycyl-*dl*-aminoheptoic acid, and glycyl-*dl*-amino-*n*-octoic acid, prepared by heating the dipeptides for a short time in aniline at 170—180°, have m. p. 219—220°, 221—222°, and 222°, respectively. *dl*-Leucyl-*dl*-aminoheptoic acid yields an *anhydride*, m. p. 245°, when heated alone or in aniline or diphenylamine. *Leucyl*-dl-*amino*-n-*octoic anhydride*, m. p. 237°, and α- and β-dl-*leucyl*-dl-*phenylalanine anhydrides*, m. p. 215—217° and 254°, respectively, are similarly prepared.

Certain anhydrides of this type become unsaturated after heating for several hours in a solvent, *e.g.*, quinoline, in presence of animal charcoal. The products, which are probably formed by loss of two hydrogen atoms from adjacent carbon and nitrogen atoms, are separated from unchanged anhydride by hydrolysis of the latter with cold *N*-alkali. *dl*-Leucylglycine anhydride, heated with 30 parts of pure quinoline and 6 parts of dried animal charcoal for 5 hrs. at 230—240°, yields a compound, $C_8H_{12}O_2N_2$. m. p. 290° (darkens at 255°), which is decomposed by boiling 25% sulphuric acid into glycine, ammonia, and *iso*propylpyruvic acid (α-keto-γ-methylvaleric acid) (phenylhydrazone, m. p. 105°; semicarbazone, m. p. 10—11°). The dehydroanhydride is obtained equally well with animal charcoal charged with hydrogen or with oxygen. It gives with phenylcarbimide a *compound*, decomp. 281° (darkens at 230°), and with bromine a *compound*, $C_8H_{13}O_2N_2Br$, which is reconverted by treatment with phenylthiocarbimide into the dehydroanhydride. Evidence of the similar production of dehydroanhydrides is also obtained with anhydrides of α- and β-*dl*-leucyl-*dl*-norleucines (see below), α-*n*-*dl*-aminobutyric acid, and glycyl-*dl*-norleucine. Leucinimide, m. p. 265—266°, prepared by heating *dl*-leucyl-*dl*-leucine at 300—310°, decolorises permanganate almost instantly, whilst the imide of identical m. p. and mixed m. p., prepared from leucine methyl ester, does not. dl-α-*Bromo*-γ-*methylvaleryl*-dl-*norleucine*, m. p. 135° (sinters at 113°), obtained from bromo-γ-methylvaleryl bromide and norleucine, reacts with ammonia to form "α"-*leucylnorleucine*, m. p. 262°, and "β"-*leucylnorleucine*, m. p. 242°, both of which yield a normal anhydride, m. p. 242°.

tert.-Leucine (α-amino-ββ-dimethylbutyric acid) is synthesised from *tert.*-butylmalonic acid, which is converted first into the α-*bromo*-derivative, m. p. 183° (decomp.), thence by decarboxylation into α-*bromo*-ββ-*dimethylbutyric acid*, m. p. 57°, which by reaction with alcoholic ammonia gives *tert.*-leucine, subliming about 280°.

α-*Bromo*isobutyryl-l-*leucine*, m. p. 106°, is converted by 25% ammonia into dl-α-*amino*isobutyryl-l-*leucine*, which gives an *anhydride*, m. p. 262°, $[\alpha]_D$ −11·9°. dl-α-*Bromo*-γ-*methylvaleryl*-dl-α-*amino*isobutyric *acid*, m. p. 146°, is ammated to *dl*-leucyl-*dl*-amino*iso*butyric acid, obtained as anhydride, m. p. 262°, identical with the anhydride of α-amino*iso*butyryl-leucine. dl-α-*Amino*isobutyryl-dl-α-*aminobutyric acid*, m. p. 241°, prepared by amination of the *bromo*-compound, m. p. 131°, gives an *anhydride*, m. p. 261°. The *anhydrides* of diglycyl- and *dl*-dileucyl-*l*-cystine decompose above 250°.

C. HOLLINS.

Action of alcoholic potassium hydroxide on chloroacetyl-*p*-anisidine and -*p*-phenetidine: derivatives of piperazine. F. REVERDIN (Helv. Chim. Acta, 1927, **10**, 386—387).—When chloroacetyl-*p*-phenetidine is boiled for 1 hr. with 10% alcoholic potassium hydroxide solution, it is converted into 1 : 4-di-*p*-ethoxyphenyl-2 : 5-diketopiperazine (yield 36—37%), identical with that obtained by Bischoff and Nastvogel (A., 1899, 1011), thus confirming the structure previously assigned to the corresponding dimethoxy-compound obtained from chloroacetyl-*p*-anisidine (A., 1923, i, 320; cf. Halberkann, A., 1921, i, 562).

J. W. BAKER.

Transformations and isomerism of acyltetrahydroindazoles. K. VON AUWERS (Annalen, 1927, **453**, 211—238).—By analogy with the acylindazoles, the stable and labile acyltetrahydroindazoles are probably position-isomerides (cf. A., 1924, i, 328). Ethyl 2-keto*cyclo*hexylglyoxylate and phenylhydrazine give in alcoholic solution, (*a*) 4-*hydroxy*-2-*phenyl*-5 : 6 : 7 : 8-*tetrahydro*-3-*pyridazone*, m. p. 189—190°, which is converted by hydrochloric acid at 200° into 2-phenyltetrahydroindazole; (*b*) a mixture, in proportions varying greatly with the conditions, of ethyl phenyltetrahydroindazole-3-carboxylates, from which an acid, m. p. 194—195°, which must be the 2-*phenyl* derivative, since it cannot be esterified, and 1-*phenyltetrahydroindazole*-3-*carboxylic acid*, m. p. 163—164° (*methyl* ester, m. p. 109—110°), are obtained. On distillation, the former acid yields 2-phenyltetrahydroindazole, previously obtained from 2-benzoxymethylene*cyclo*hexanone. The constitution assigned to the latter and to the labile tetrahydroindazole-2-carboxylamide formed from it is accordingly correct. Direct acylation of tetrahydroindazoles takes place only in the 1-position, but the 2-derivatives may be prepared from hydroxymethylene*cyclo*hexanones and acylhydrazines. The 2-acyltetrahydroindazoles are, in general, slightly more stable than the corresponding acylindazoles, which they closely resemble. *Tetrahydroindazole*-3-*carboxylic acid*, m. p. 254°, from 2-keto*cyclo*hexylglyoxylic acid and hydrazine acetate, gives a 1-o-*nitrobenzoyl* derivative, m. p. 225—226°, the constitution of which follows from its ready conversion into a *methyl* ester, m. p. 193—194°.

When distilled, it affords 1-*o*-nitrobenzoyltetrahydroindazole, m. p. 148—149° (cf. *loc. cit.*), which is also obtained by direct acylation of tetrahydroindazole, but not by boiling benzaldehydesemicarbazone with *o*-nitrobenzoylhydrazine. The substance of m. p. 225—226° is formed, instead of the expected 2-nitrobenzoyl derivative, when 2-*keto*cyclo*hexylglyoxylic acid* o-*nitrobenzoylhydrazone*, m. p. 177—178°, is treated with acids. Similarly, with semicarbazide, 2-keto*cyclo*hexylglyoxylic acid gives tetrahydroindazole-3-carboxylic acid, and not its 2-carboxylamide. The displacement of the radical from the 2-position is probably due in both cases to the adjacent carboxyl group, since 2-*methyl*-6-*benzoxymethylene*cyclo*hexanone* o-*nitrobenzoylhydrazone*, m. p. 161°, passes smoothly into 2-o-*nitrobenzoyl*-7-*methyltetrahydroindazole*, m. p. 146—147°. The constitution of the stable tetrahydroindazolecarboxylamide, m. p. 187°, is confirmed by its formation from a direct substitution product, *tetrahydroindazole*-1-*carboxyl chloride*, m. p. 162—165°, and ammonia. In sodium hydrogen carbonate solution, semicarbazide and hydroxymethylene*cyclo*hexanone yield 2-*hydroxy*-Δ^1-cyclo*hexenylaldehyde semicarbazone*, m. p. 189°, which passes directly in presence of acids into the stable carboxylamide, m. p. 187°. The following derivatives of tetrahydroindazole: 2-o-*nitrobenzoyl*-, m. p. 179—180°; 1-m-*nitrobenzoyl*-, m. p. 140—142°; 2-m-*nitrobenzoyl*-, m. p. 118—118·5°; 1-*benzoyl*-, m. p. 58·5—60°, b. p. 208—210°/13 mm., $d_4^{99\cdot4}$ 1·1064, n_{He}^{102} 1·5697; 2-*benzoyl*-, liquid, rapidly isomerised at 200°; 1-*carbethoxy*-, b. p. 170°/18 mm., $d_4^{16\cdot5}$ 1·1306; n_{He}^{20} 1·5147; 2-*carbethoxy*-, b. p. (without perceptible isomeric change) 170°/18 mm., $d_4^{1\cdot}$ 1·1408, n_{He}^{20} 1·5141; of 7-methyltetrahydroindazole: 1-o-*nitrobenzoyl*-, m. p. 117—118°; 1-m-*nitrobenzoyl*-, m. p. 89—90°; 2-m-*nitrobenzoyl*-, m. p. 48—50° (cannot be isomerised); 1-*benzoyl*-, b. p. 202°/12 mm., d_4^{20} 1·139, n_{He}^{20} 1·5870; 2-*benzoyl*-, d_4^{20} 1·127, n_{He}^{20} 1·5804; 1-carbethoxy-, b. p. 161—163°/12 mm., d_4^{20} 1·109, n_{He}^{20} 1·5102; 2-carbethoxy-, b. p. 161—163°/12 mm., d_4^{20} 1·120, n_{He}^{20} 1·5093; and 2-*methyl*-6-*hydroxymethylene*cyclo*hexanone*-o-*nitrobenzoylhydrazone*, m. p. 137—140°, are described.

H. E. F. NOTTON.

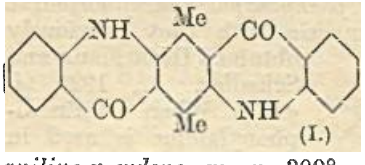
Heterocyclic compounds containing arsenic. I. Action of chloroacetamide on 3 : 4-diaminophenylarsinic acid. A. J. EWINS, G. NEWBERY, and R. W. E. STICKINGS (J.C.S., 1927, 851—855).—Chloroacetamide reacts with 3 : 4-diaminophenylarsinic acid, yielding a mixture of 3-*hydroxy*-1 : 4-*dihydroquinoxaline*-6-*arsinic acid*, m. p. not below 260° (*benzoyl* derivative m. p. above 290°), and 2-*hydroxy*-1 : 4-*dihydroquinoxaline*-6-*arsinic acid*, m. p. (decomp.) (*benzoyl* derivative, m. p. 251—252°). These results are not in agreement with those obtained by Lewis and Bent (A., 1926, 628). Reduction of 3-*nitrophenylarsinic acid* 4-*glycineamide* with ferrous hydroxide yields 3-hydroxy-1 : 4-dihydroquinoxalinearsinic acid with accompanying elimination of ammonia.

H. BURTON.

Synthesis in the glyoxaline series. Some derivatives of isoglyoxaline. P. C. MITTAR and N. N. SINHA (J. Indian Chem. Soc., 1926, **3**, 401—404).—Glyoxaline derivatives have been prepared by the action of oxalyl chloride, ethyl oxalate, and oxamate on amidines. From benzamidine is obtained 4 : 5-*diketo*-2-*phenyl*-4 : 5-*dihydroglyoxaline*, m. p. 174° (decomp.), which with phosphorus oxychloride yields 4-*chloro*-2-*phenyl*-5-*keto*isoglyoxaline, m. p. 215° (decomp.). Similarly, from *p*-toluamidine is obtained 2-p-*tolyl*-4 : 5-*diketo*-4 : 5-*dihydroglyoxaline*, m. p. not below 280°, which with phosphorus oxychloride yields 4-*chloro*-2-p-*tolyl*-5-*keto*isoglyoxaline, subliming at 260—265°.

J. W. BAKER.

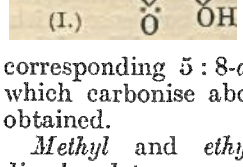
Linear dimethylquinacridone. W. LEŚNIANSKI and T. CZERSKI (Rocz. Chem., 1926, **6**, 890—896).—5-*Bromo*-2-*phenylaminoterephthalic acid*, m. p. 368°, is obtained by condensing aniline with 2 : 5-dibromoterephthalic acid. 2 : 5-Dibromo-*p*-xylene condenses with anthranilic acid to give 4-*bromo*-2 : 5-*dimethyldiphenylamine*-1′-*carboxylic acid*, m. p. 202°, and 2 : 5-*di*-o-*carboxyanilino*-p-*xylene*, m. p. 309°. The latter substance, when heated with phosphorus pentachloride and aluminium chloride, yields *lin. dimethylquinacridone*, (I), m. p. 330°.



(I.)

R. TRUSZKOWSKI.

2-Phenyltriazolephthalic acid: hydroxyl derivatives of 2-*N*-phenyl-ββ-naphthatriazolequinone. I. A. BERETTA [with R. MASSAROTTI and L. SCALIA] (Gazzetta, 1927, **57**, 173—178; cf. A., 1926, 848).—1-Phenyl-1 : 2 : 5-triazole-3 : 4-dicarboxylic anhydride, when heated with benzene and aluminium chloride, gives 4-*benzoyl*-1-*phenyl*-1 : 2 : *o*-*triazole*-3-*carboxylic acid*, m. p. 190°, but dehydrating agents do not close the ring to give the expected naphthaquinone derivative. By heating pyrocatechol with the anhydride and sulphuric acid, 5 : 6 (or 6 : 7)-*dihydroxy*-2-*phenyl*-ββ-*naphtha*-1 : 2 : 3-*triazole*-4 : 9-*quinone*, and, using quinol, the corresponding 5 : 8-*dihydroxy*-derivative (I), both of which carbonise above 360°, without melting, were obtained.

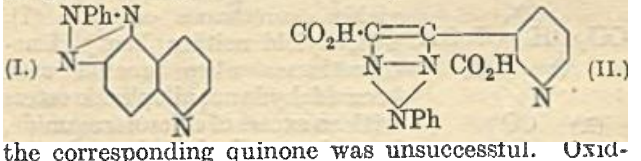


(I.)

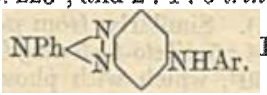
Methyl and *ethyl* 1-*phenyl*-1 : 2 : *o*-*triazole*-3 : 4-*dicarboxylates*, m. p. 89° and 41—42°, respectively, were prepared, and from the latter the *diamide*, m. p. 279°, from which, however, the phthalimide could not be obtained.

E. W. WIGNALL.

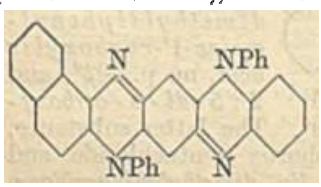
2-*N*-Phenyl-ψ-aziminoquinoline. A. BERETTA [with F. BENATI] (Gazzetta, 1927, **57**, 179—187).—When 5-amino-2-phenyl-1 : 3-benztriazole was heated with glycerol in presence of nitrobenzene and sulphuric acid, it condensed to give 2-*phenylpyridobenztriazole* (I), m. p. 161—161·5° (*hydrochloride*, m. p. 223°; *sulphate*, m. p. 268°; *dichromate*, darkens 180°, m. p. 208°; *picrate*, m. p. 262°, the two last carbonising). Attempted oxidation by chromic acid to the corresponding quinone was unsuccessful. Oxidation by alkaline permanganate gave 3-[α-*carboxy*-β-



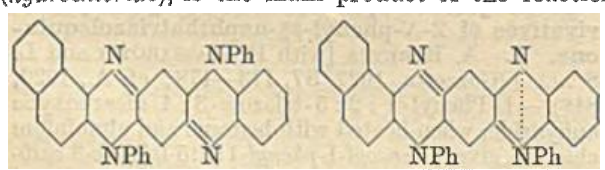
β-*pyridyl*]-1-*phenyl*-1 : 2 : 5-*triazole*-4-*carboxylic acid* (II), m. p. 189° (decomp.) (*barium* salt prepared).

5-Amino-2-phenyl-1 : 3-benztriazole reacts with the appropriate chlorobenzene derivatives to give 2 : 4-*dinitro*-, m. p. 223°, and 2 : 4 : 6-*trinitro*-, m. p. 225·5°, derivatives,  E. W. WIGNALL.

Fluorindine derivatives of naphthalene. F. KEHRMANN and R. LOGOZ (Helv. Chim. Acta, 1927, **10**, 339—345).—Hydroxy*iso*rosindone, subl. 240°, decomp. 287°, obtained by the condensation of dihydroxy-*p*-benzoquinone with phenyl-1 : 2-naphthylenediamine (Kehrmann and Prager, A., 1907, i, 447), when heated with *o*-phenylenediamine in boiling benzoic acid yields a *phenylnaphthaphenfluorindine* (annexed formula), isomeric with that previously



obtained (Kehrmann and Schedler, A., 1925, i, 441). When *o*-aminodiphenylamine is used in place of phenylenediamine, two isomeric *diphenylnaphthaphenfluorindines*, (I) and (II) are obtained, of which (II), green (*hydrochloride*), is the main product of the reaction.



(I.) (II.)

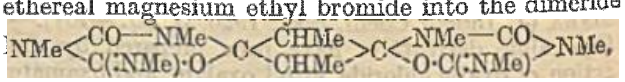
The latter, when treated with methyl sulphate, yields an *N*-methyl derivative isolated as its *chloroplatinate* (*hydrochloride*). Dinaphthadiphenazine, obtained by the oxidation of dinaphthafluorindine (*loc. cit.*), is reconverted into the latter on reduction with stannous chloride. Hydroxy*iso*rosindone condenses with 1 : 2-naphthylenediamine to yield *phenyldinaphthafluorindine*, $C_{10}H_6\langle{}^{N}_{NPh}\rangle C_6H_2\langle{}^{NH}_{N}\rangle C_{10}H_6$ (*hydrochloride*), which is probably a mixture of the two possible isomerides, and is also obtained, less readily, by the condensation of 2 : 3-dihydroxynaphthaphenazine with the hydrochloride of phenyl-1 : 2-naphthylenediamine. By the condensation of 6-acetamido-2 : 3-dihydroxynaphthaphenazine with *o*-phenylenediamine is obtained *acetamidonaphthaphenfluorindine* (*hydrochloride*), which readily oxidises in air to the azine, whilst with 1 : 2-naphthylenediamine it yields one of the two possible isomeric *acetamidodinaphthafluorindines*. J. W. BAKER.

ψ-Urethanes. I. H. K. SEN and C. BARAT (J. Indian Chem. Soc., 1926, **3**, 405—414).—The action of chloroformamide on ketones of the type $CCl_3{\cdot}CH(OH){\cdot}CH_2{\cdot}CO{\cdot}R$ yields ψ-urethanes of type (I), which yield neither benzylidenediurethanes when treated with benzaldehyde nor allophanic esters with an excess of chloroformamide, but when melted or heated with alcohol are converted into the trichloroethylidene-

CH_2
$CCl_3{\cdot}CH$ $CR{\cdot}OH$
(I.)

ketones, $CCl_3{\cdot}CH{:}CH{\cdot}CO{\cdot}R$. Thus from phenyl γγγ-trichloro-β-hydroxypropyl ketone (chloralacetophenone) is obtained a *ψ-urethane* (R=Ph), m. p. 155° (decomp.). *p*-Tolyl methyl ketone condenses with chloral in glacial acetic acid to yield p-*tolyl γγγ-trichloro-β-hydroxypropyl ketone*, m. p. 100°, giving a *ψ-urethane* ($R{=}C_6H_4Me$), m. p. 160° (decomp.), which yields p-*tolyl trichloroethylidenemethyl ketone*, m. p. 88—90°, when decomposed. βββ-*Trichloro-α-hydroxyethylacetonaphthone*, m. p. 90—92°, yields a *ψ-urethane* ($R{=}C_{10}H_7$), m. p. 125° (decomp.), which yields *trichloroethylideneacetonaphthone*, m. p. 105—106°. βββ-*Trichloro-α-hydroxyethylacetoveratrone*, m. p. 120—122°, reacts with great difficulty to form a ψ-urethane, the *product* obtained by the action of excess of chloroformamide having m. p. 80—100°, decomp. 105—108°. The yield of chloralacetone (Königs, A., 1892, 694) is improved by the substitution of 1% sodium carbonate solution for sodium hydroxide, but it is still much lower than that claimed by the earlier author. It yields a *ψ-urethane* (R=Me), m. p. 98° (decomp.). Chloroformamide reacts with methyl β-hydroxypropyl ketone and diacetone to yield directly ethylideneacetone (propenyl methyl ketone) and mesityl oxide, respectively. J. W. BAKER.

Carbimides. IV. 1 : 3 : 5-Oxdiazines. K. H. SLOTTA and R. TSCHESCHE (Ber., 1927, **60**, *[B]*, 1011—1020; cf. this vol., 548).—Whereas 2 : 4 : 6-triketo-3 : 5-dimethyl-1 : 3 : 5-oxdiazine has an exceedingly unstable ring, 2-methylimino-4 : 6-diketo-3 : 5-dimethyl-1 : 3 : 5-oxdiazine reacts normally with Grignard reagents. With magnesium methyl bromide it affords 2-*methylimino*-4-*keto*-3 : 5-*dimethyl*-6-*methylene* 1 : 3 : 5-*oxdiazine*, $CH_2{:}C\langle{}^{NMe\text{—}CO}_{O{\cdot}C(:NMe)}\rangle NMe$, m. p. 140°, which could not be caused to polymerise by protracted ebullition with the reagent. It is converted by an ammoniacal solution of hydrogen peroxide into trimethyl *iso*cyanurate. The *perchlorate*, decomp. 260°, additive *compound* with hydrogen peroxide, $C_7H_{13}O_4N_3$, decomp. 100°, and the *tetrabromo*-compound, decomp. 150—152°, are described. It is converted by boiling acetic anhydride into 2-*methylimino*-4-*keto*-3 : 5-*dimethyl*-6-*acetylmethylene*-1 : 3 : 5-*oxdiazine*, m. p. 158°, which yields a *perbromide* and an additive *compound* with hydrogen peroxide, and is quantitatively transformed by water into acetone and trimethyl *iso*cyanurate. 2-*Methylimino*-4-*keto*-3 : 5-*dimethyl*-6-*ethylidene*-1 : 3 : 5-*oxdiazine*, b. p. 165—168°/15 mm., m. p. 110°, is obtained in relatively poor yield by means of magnesium ethyl bromide. It yields an unusually stable *monohydrate*, *perchlorate*, decomp. 240°, *chromate*, *chloroplatinate*, and additive *compound* with hydrogen peroxide, decomp. 127°. It is oxidised by ammoniacal hydrogen peroxide or benzoyl peroxide to trimethyl *iso*cyanurate. With bromine in chloroform solution, it gives the *tetrabromo*-compound, $C_8H_{13}O_2N_3Br_4$, decomp. 148—150°. It is converted by protracted heating with ethereal magnesium ethyl bromide into the dimeride



decomp. 278°, which with perchloric acid and bromine yields derivatives of the monomeric form. With methylcarbimide in benzene at 100°, the monomeric variety gives the *compound* $NMe<^{CO\cdot CHMe}_{CO-NMe}>C<^{NMe-CO}_{O\cdot C(:NMe)}>NMe$, decomp. 228—230°. Catalytic reduction of 2-methylimino-4-keto-3 : 5-dimethyl-6-ethylidene-1 : 3 : 5-oxdiazine affords 2-*methylimino*-4-*keto*-3 : 5-*dimethyl*-6-*ethyl*-1 : 3 : 5-*oxdiazine*, b. p. 176°/12 mm., m. p. 40°, which gives a *tribromide*. m. p. 120° (decomp.), converted by boiling water into bromine and the ethylidene derivative. Boiling acetic anhydride converts 2-methylimino-4-keto-3 : 5-dimethyl-6-ethylidene-1 : 3 : 5-oxdiazine into the dimeric *acetyl* compound

$$NMe<^{CO\cdot NMe\cdot C\cdot CH_2\cdot CO\cdot CHMe\cdot C\cdot NMe\cdot CO}_{C(NMe)-O-CMeAc}>NMe \quad / O-C(NMe)$$

decomp. 235°, which is converted by boiling 2*N*-sodium hydroxide into the *compound* $CH<^{:CMe}_{C(OH)\cdot CMe}>C\cdot NHMe$, decomp. 262°. 2-Methylimino-4-keto-3 : 5-dimethyl-6-ethyl-1 : 3 : 5-oxdiazine and acetic anhydride give 2-*methylimino*-4-*keto*-3 : 5-*dimethyl*-6-*ethyl*-1 : 3 : 5-*oxdiazine*-6-*acetic acid*, $NMe<^{CO-NH}_{C(:NMe)\cdot O}>CEt\cdot CH_2\cdot CO_2H$, m. p. 186—188° (*methyl* ester, m. p. 101°; *ethyl* ester, m. p. 110°), which does not yield a perchlorate or add bromine.

Magnesium phenyl bromide and 2-methylimino-4 : 6-diketo-3 : 5-dimethyl-1 : 3 : 5-oxdiazine yield 2-*methylimino*-6-*hydroxy*-4-*keto*-6-*phenyl*-3 : 5-*dimethyl*-1 : 3 : 5-*oxdiazine*, decomp. 162°, which is completely decomposed by protracted heating with the Grignard reagent. The corresponding *perchlorate*, decomp. 286°, and the additive *compound* with hydrogen peroxide, decomp. 245°, are described. H. WREN.

Manufacture of new aromatic [heterocyclic] compounds and dyes therefrom [benzdithiazoles]. L. CASSELLA & Co.—See B., 1927, 325.

Synthesis of papaverine and allied compounds. C. MANNICH and O. WALTHER (Arch. Pharm., 1927, 265, 1—11).—The following analogues of papaverine have been prepared, by a simple modification of Pictet and Gams' method, for pharmacological investigation. All resemble, but none is so active as, papaverine. In Pictet and Gams' synthesis, acylamino-alcohols, $OH\cdot CHR\cdot CH_2\cdot NH\cdot CO\cdot R'$, are heated in xylene with phosphorus oxychloride; the corresponding methyl ethers, which can easily be obtained by Rosenmund's method (A., 1913, i, 462), condense in a similar way. ω-Nitromethylenedioxystyrene, when treated with sodium methoxide, yields β-*nitro*-α-3 : 4-*methylenedioxyphenylethyl methyl ether*, yellow prisms, m. p. 64°, which is satisfactorily reduced by coppered zinc dust and cold 85% formic acid to β-3 : 4-*methylenedioxyphenyl*-β-*methoxyethylamine*, an oil, b. p. 158—160°/13 mm. (*hydrochloride*, m. p. —113°). The *benzoyl* derivative, m. p. 90—91°, of this base affords, when treated with phosphorus oxychloride, 6 : 7-*methylenedioxy*-1-*phenylisoquinoline*, p. 123—124°; the *phenylacetyl* derivative, m. p. —124°, is similarly readily converted into 6 : 7-*methylenedioxy*-1-*benzylisoquinoline* (6 : 7-*methylenedioxyprotopapaverine*), m. p. 94°; the *homopiperonoyl* derivative, m. p. 127—128° (details of the preparation of homopiperonoyl chloride from piperonal by way of piperonyl chloride are given), likewise affords 6 : 7-methylenedioxy-1 : 3′ : 4′-methylenedioxybenzyl-*iso*quinoline [3′ : 4′ : 6 : 7-di(methylenedioxy)protopapaverine, cf. Buck, Perkin, and Stevens, A., 1925, i, 958], and the syrupy homoveratryl derivative gives the 3′ : 4′-dimethoxy-6 : 7-methylenedioxy-analogue, *i.e.*, Kondo's homoveratryldehydronorhydrastinine (J. Pharm. Soc. Japan, 1925, [519], 2). β-Nitro-α-3 : 4-dimethoxyphenylethyl methyl ether (Rosenmund, *loc. cit.*) is not an oil, but has m. p. 108—109°; it is readily reduced, like its congener, to β-methoxy-β-3 : 4-dimethoxyphenylethylamine, b. p. 164—167°/12 mm., of which the *phenylacetyl* derivative has m. p. 95°, and is converted into 6 : 7-*dimethoxy*-1-*benzylisoquinoline* (6 : 7-*dimethoxyprotopapaverine*), m. p. 69—70°, whilst the *homopiperonoyl* derivative, m. p. 88°, similarly yields 6 : 7-*dimethoxy*-1 : 3′ : 4′-*methylenedioxybenzyl*-*isoquinoline*, m. p. 123°. Papaverine is obtained when the *homoveratryl* derivative, m. p. 152°, suffers the same intramolecular condensation. This formation of an *iso*quinoline ring does not take place with unsubstituted phenylethylamine derivatives; thus, no papaverine analogue can be obtained from the *phenylacetyl* derivative, m. p. 84—85°, or the *homopiperonoyl* derivative, m. p. 75—76°, of β-methoxy-β-phenylethylamine (Rosenmund, *loc. cit.*).

W. A. SILVESTER.

Empirical formula of yohimbine. [MRS.] E. STEDMAN (Ber., 1927, 60, [*B*], 1009—1010).—The author's analyses of a series of esters of yohimboaic acid (cf. J.C.S., 1923, 123, 3003) and those of Spiegel agree with the formula $C_{21}H_{26}O_3N_2$ for yohimbine (see Spiegel, this vol., 163). H. WREN.

Microchemical differentiation of morphine and some important derivatives. H. W. VAN URK (Pharm. Weekblad, 1927, 64, 371—377).—The behaviour of morphine, codeine, dionine, heroine, and peronine towards a large number of alkaloid reagents is tabulated. Iodine, mercuric chloride, and the potassium and cæsium double iodides all give distinctive crystals with morphine and codeine; the latter may also be recognised by its picrolonate, thiocyanate, and chloroplatinate. Specific reagents for the other derivatives are: dionine, mercuric chloride; heroine, picric acid; peronine, ammonium formate and potassium thiocyanate. Sketches of many crystalline precipitates are given.

S. I. LEVY.

Aliphatic-aromatic arseno-compounds. I. Aryl arseno-, tetra-arseno-, and hexa-arseno-acetic acids. C. S. PALMER and R. H. EDEE (J. Amer. Chem. Soc., 1927, 49, 998—1007).—Aryl arsenoacetic acids, $R\cdot C_6H_4\cdot As{:}As\cdot CH_2\cdot CO_2H$, are obtained by reducing together arsinoacetic acid and the appropriate arylarsinic acid at a low temperature. When R = $\cdot NH\cdot CH_2\cdot CH_2\cdot OH$, $\cdot NH\cdot CH_2\cdot CH_2\cdot CH_2\cdot OH$, $\cdot NH\cdot CH_2\cdot CO_2H$, or $NH\cdot CH_2\cdot CO\cdot NH_2$, reduction with hypophosphorous acid yields the tetra-arseno-derivatives, $R\cdot C_6H_4\cdot[As{:}As]_2\cdot CH_2\cdot CO_2H$, but the arseno-compounds can be obtained by using stannous chloride. Formation of the tetra-arseno-derivatives is facilitated by addition of arsenious chloride, and if

sufficient of the latter be present, hexa-arseno-derivatives, $R{\cdot}C_6H_4{\cdot}[As{:}As]_3{\cdot}CH_2{\cdot}CO_2H$, can be obtained. For production of the unsymmetrical arseno-derivative it is necessary to arrange that this shall be precipitated as the least soluble of the possible products, otherwise one or both of the possible symmetrical derivatives may be precipitated. This indicates possibly that the unsymmetrical derivative is formed by rearrangement from the two symmetrical arseno-compounds which are the primary reduction products.

4-*Aminophenylarsenoacetic acid hydrochloride*, yellow, is obtained from sodium arsinoacetate and *p*-aminophenylarsinic acid, using dilute hydrochloric and hypophosphorous acids in presence of pyridine. Under different conditions, this reduction yields 4 : 4′-diaminoarsenobenzene sulphate and arsenoacetic acid, whilst mixtures of the symmetrical and unsymmetrical arseno-derivatives can also be produced. 4-*Acetamidophenylarsenoacetic acid hydrochloride*, yellow, is obtained analogously. 4-β-*Hydroxyethylaminophenylarsenoacetic acid hydrochloride*, orange, and 4-γ-*hydroxypropylaminophenylarsenoacetic acid hydrochloride*, orange-red, are obtained by reduction of mixtures of arsinoacetic acid and the appropriate phenylarsinic acid with stannous chloride, 4-*glycylphenylarsenoacetic acid*, orange, and 4-*aminoglycylphenylarsenoacetic acid hydrochloride*, similar, being obtained analogously. The following yellow to red derivatives of arsenoacetic acid were obtained by hypophosphorous acid reduction: 4-*hydroxyphenyl*-; 4-*acetoxyphenyl*-; *hydrochloride* of 3-*amino*-4-*hydroxyphenyl*-; *phenyl*-; p-*tolyl*-; and o-*chlorophenyl*-. The following red tetra-arsenoacetic acids, obtained as indicated above, are described: 4-*glycylphenyl*-; 4-*aminoglycylphenyl*-; 4-β-*hydroxyethylaminophenyl*-; 4-γ-*hydroxypropylaminophenyl*-; and 3-*amino*-4-*hydroxyphenyl*-. 3-*Amino*-4-*hydroxyphenylhexa-arsenoacetic acid*, reddish-brown, is described. F. G. WILLSON.

Isomerides of 3-amino-4-hydroxyphenylarsinic acid and its acetyl derivative (stovarsol). E. FOURNEAU, M. and MME. TREFOUEL and (MLLE.) G. BENOIT (Bull. Soc. chim., 1927, [iv], **41**, 499—514).—The ten isomeric aminohydroxyphenylarsinic acids have been prepared and their behaviour has been examined in regard to toxicity, maximum tolerated dose, and their effective curative dose on white mice infected with *Trypanosoma Brucei*. The margin between the toxic dose and the maximum tolerated dose is in some cases large, notably with 3-amino-4-hydroxy-, 2-amino-3-hydroxy- and 3-amino-6-hydroxy-phenylarsinic acids. 4-Amino-2-hydroxy- and 3-amino-4-hydroxy-phenylarsinic acids are sharply distinguished from the remaining isomerides by their high ratio of curative dose to maximum tolerated dose, the former giving the higher ratio. The 4-amino-2-hydroxy-isomeride is almost without action, however, in syphilis, although the 3-amino-4-hydroxy-compound is the most active arsenic compound known. For buccal administration, the doses of 4-amino-2-hydroxyphenylarsinic acid required are not greater than those required for intramuscular or intravenous injection. Acylation of the amino-group in this isomeride increases the ratio curative : tolerated dose, the maximum effect being observed with the acetyl derivative, the formyl and propionyl derivatives also showing marked exaltation. With isomerides containing amino-groups *o*- or *m*- with respect to the arsinic acid group, acylation diminishes or destroys their trypanocidal powers. Whilst the introduction of the glycineamide group in atoxyl diminishes its toxicity and increases its trypanocidal power, with 4-amino-2-hydroxyphenylarsinic acid the reverse is the case. The urethane derivative of this acid is without trypanocidal action as regards subcutaneous injection; the formyl derivative is superior to the acetyl derivative for subcutaneous injection, but inferior for oral administration.

3-*Amino*-2-*hydroxyphenylarsinic acid* (*acetyl* derivative) was prepared from 6-nitro-2-aminophenol by diazotisation, introduction of the arsinic group, and reduction of the 3-*nitro*-2-*hydroxyphenylarsinic acid* with ferrous sulphate and alkali or with sodium hyposulphite. 2-*Amino*-6-*hydroxyphenylarsinic acid* (*acetyl* derivative) was similarly prepared from 3-nitro-2-aminophenol (this vol., 555) through 6-*nitro*-2-*hydroxyphenylarsinic acid*. For the preparation of 3-*amino*-5-*hydroxyphenylarsinic acid*, 3 : 5-dinitroanisole was converted into 3 : 5-dinitrophenol by heating with sulphuric acid at 145°. Reduction of the phenol in acetic acid at 45° with stannous chloride and hydrochloric acid afforded 3-*nitro*-5-*acetamidophenol*, m. p. 265°, giving on hydrolysis with hydrochloric acid 3-*nitro*-5-*aminophenol*, m. p. 165°, from which 3-*nitro*-5-*hydroxyphenylarsinic acid* was prepared in the usual way. R. BRIGHTMAN.

Arsenic compounds of the quinoline series. A. BINZ and C. RATH (Annalen, 1927, **453**, 238—248).—Arsinic acids of known constitution (cf. Frankel and Lowy, A., 1913, i, 1228; Calvery, Noller, and Adams, A., 1926, 187) have been prepared from quinoline-diazonium salts. They are stable towards hydrogen peroxide, and convertible by normal methods into arsines, amphoteric arsinoxides, and amorphous arsenoquinoline hydrochlorides. The following are described: *quinoline*-5-*arsinic acid* ($+1H_2O$), decomp. 232°; yellowish-red 5 : 5′-*arsenoquinoline dihydrochloride*; *quinoline*-6-*arsinic acid* ($+1H_2O$), m. p. 260—262°; 6 : 6′-*arsenoquinoline dihydrochloride*; *quinoline*-8-*arsinic acid*, m. p. 230°; 8 : 8′-*arsenoquinoline dihydrochloride*; 8-*quinolylarsinoxide hydrochloride*; *dichloro*-8-*quinolylarsine hydrochloride*, m. p. 250° (decomp.); 8-*quinolylarsine*; 2-*methylquinoline*-3-*arsinic acid*, decomp. 220°; red 2 : 2′-*dimethyl*-3 : 3′-*arsenoquinoline dihydrochloride*; 2-*hydroxyquinoline*-6-*arsinic acid*; yellowish-white 2 : 2′-*dihydroxy*-6 : 6′-*arsenoquinoline*; *isoquinoline*-5-*arsinic acid* (from the (?)5-amino*iso*quinoline of Claus and Hoffmann, A., 1893, i, 366), and yellow 5 : 5′-*arseno*i*soquinoline*. H. E. F. NOTTON.

Mercurated benzidine compounds. A. BERNARDI and (SIGNA.) M. TARTARINI (Gazzetta, 1927, **57**, 223—226).—Benzidine and mercuric acetate react in glacial acetic acid to give a white precipitate (rapidly changing through yellow to brown) of *benzidine* 3(?)-*mercuriacetate*, decomp. 138—140°,

which forms a *hydrochloride*, $C_{14}H_{16}O_2N_2Cl_2Hg$, m. p. 239—241° Diacetylbenzidine heated with mercuric acetate at 120—160° gives a crystalline *substance*, $C_{32}H_{30}O_4N_4Hg,3H_2O$, which loses its "water of crystallisation" (the origin of which is unexplained) when heated at 130°, but when heated rapidly gives a product from which acetic acid extracts the *substance* $C_{18}H_{18}O_4N_2Hg$. E. W. WIGNALL.

Sulphur in proteins. III. Derivatives of *l*- and *i*-cystine. R. A. GORTNER and W. F. HOFFMAN (J. Biol. Chem., 1927, **72**, 433—448).—The product obtained by prolonged boiling of *l*-cystine with 20% hydrochloric acid (A., 1922, i, 429), and designated *i*-cystine, is perhaps *meso*-cystine; its various derivatives show physical differences from those of *l*-cystine. A sample of *l*-cystine prepared from a calculus had $[\alpha]_D^{25}$ —242·6°; this leads to the supposition that *l*-cystine isolated in the ordinary way by hydrolysis of a protein may be contaminated with some of the optically inactive *i*-cystine. *i-Cysteic acid* had m. p. 245° (decomp.). *Phenacyl* l-*cysteate*, m. p. 203—204°; *phenacyl* i-*cysteate*, m. p. 210°; *tetracarbethoxy*-l-*cystine*, m. p. 63°; *tetracarbethoxy*-i-*cystine*, m. p. 64°; *dibenzoyl*-l-*cystine*, m. p. 181°; *dibenzoyl*-i-*cystine*, m. p. 168—170°; *dibenzoyl*-"*stone*"-*cystine*, m. p. 160°; l-*cystine ethyl ester dihydrochloride*, m. p. 177—178°; i-*cystine ethyl ester dihydrochloride*, m. p. 169—170°; *di*-β-*naphthalenesulphonyl*-l-*cystine*, m. p. 203—204°; *di*-β-*naphthalenesulphonyl*-i-*cystine*, m. p. 215°; *phenylcarbimide* derivatives of l-*cystine*, m. p. 148—149°, i-*cystine*, m. p. 181°, "*stone*"-*cystine*, m. p. 132—133°; *phenylhydantoins* of l-*cystine*, m. p. 122—123°, i-*cystine*, m. p. 166°, "*stone*"-*cystine*, m. p. 112°. The sulphur in i-cysteine is less labile towards alkali than that in *l*-cysteine. *Benzoyl*-l-*cysteine* has m. p. 213°; *benzyl*-i-*cysteine*, m. p. 190°. All attempts to repeat the preparation of taurine from cysteic acid and of dithiodilactic acid from cystine according to Friedmann failed, as did also all attempts to resolve *i*-cystine.

C. R. HARINGTON.

Action of sodium carbonate on yeast-nucleic acid. H. O. CALVERY (J. Biol. Chem., 1927, **72**, —37).—From each of the fractions prepared from yeast-nucleic acid according to the method of Steudel and Peiser (Z. physiol. Chem., 1919, **108**, 42), were isolated guanine and adenine nucleotides, and, from the combined fractions, cystosine nucleotide; uracil nucleotide was not obtained. The fractions obtained by the above-mentioned workers were therefore mixtures of nucleotides formed from the original nucleic acid by the hydrolytic action of the warm sodium carbonate employed in the preparation.

C. R. HARINGTON.

Guanine nucleotide. M. V. BUELL and M. E. PERKINS (J. Biol. Chem., 1927, **72**, 21—26).—The mixed nucleotides obtained by hydrolysis of yeast-nucleic acid with 1% sodium hydroxide at the ordinary emperature were precipitated with lead acetate; a ter recovery, they were precipitated four times as ammonium salts, then again as lead salts. and finally as silver salts; on concentration of the solution obtained by decomposition of the latter with hydrogen u p e, guanine nucleotide crystallised out. The compound crystallised with $2H_2O$, which was lost on heating at 118°; $[\alpha]_D^{20}$ —13·5° in water (cf. Levene, A., 1920, i, 192). C. R. HARINGTON.

Group in thymus-nucleic acid responsible for the "nucleal" reaction. III. R. FEULGEN (Z. physiol. Chem., 1927, **165**, 215—223).—Partly polemical against Thannhauser and Blanco, (this vol., 268). After partial hydrolysis of thymus-nucleic acid, groups appear which give the so-called "nucleal" reaction (violet coloration with Schiff's reagent) and reduce alkaline silver and copper solutions. These reducing properties are due to an aldehyde group in thymic acid. which is unmasked by mild hydrolysis. Thymic acid reacts with 2 mols. of phenylhydrazine to form, not a salt, but a hydrazone. H. D. KAY.

Phosphorylation of proteins. C. RIMINGTON (Biochem. J., 1927, **21**, 272—281).—Proteins may be "phosphorised" by means of phosphorus oxychloride in carbon tetrachloride. The phosphorus apparently enters the protein in the form of an ester linking between phosphoric acid and a hydroxyl group. Phosphorised caseinogen contains 1·77% P, corresponding with a ratio P/N=0·130 "Re-phosphorised caseinogen," the product obtained by phosphorylating caseinogen from which the original phosphorus was removed by treatment with 1% sodium hydroxide for 24 hrs. at 37° (cf. Rimington and Kay, A., 1926, 970), contains 1·75% P and has a ratio P/N=0·124. Both substances are coagulable by rennin. Phosphorised globulin contains 0·71% P with P/N=0·051. It is precipitated by soluble calcium salts. The above phosphorised proteins lose phosphorus slowly as phosphoric acid under the action of pepsin or 0·25*N*-hydrochloric acid, but 0·25*N*-sodium hydroxide at 37° liberates the whole of the phosphorus as phosphoric acid in 24 hrs. Bone phosphatase liberates no inorganic phosphorus. Trypsin liberates rapidly the whole of the phosphorus of phosphorised globulin in the form of an organic acid-soluble substance which, as in the case of phosphorised caseinogen, is hydrolysed totally to phosphoric acid by bone phosphatase within a few hours. Trypsin liberates free phosphoric acid from phosphorised globulin extremely slowly.

S. S. ZILVA.

Phosphorus nucleus of caseinogen. S. POSTERNAK (Biochem. J., 1927, **21**, 289; cf. Rimington and Kay, A., 1926, 970).—The author has liberated a phosphorus nucleus from caseinogen by short tryptic digestion (Swiss Pat. 10,433: Chem. Zentr., 1925, **1**, 1371; Compt. Rend. Soc. Physiol. Geneve, 1926, **43**, 16, and this vol., 273). S. S. ZILVA.

Proteins. II. Benzoylated proteins. S. GOLDSCHMIDT and W. SCHON (Z. physiol. Chem., 1927, **165**, 279—294).—Caseinogen and egg-albumin may be benzoylated by the cautious addition of benzoyl chloride to the solution of the protein in sodium or potassium hydrogen carbonate. The insoluble benzoylproteins thus formed contain two kinds of benzoyl groups—those easily removed by cold dilute sodium hydroxide and those stable to this reagent. Caseinogen benzoylated under different conditions may contain from 10 to 15% of its weight of benzoyl groups. Cold

dilute sodium hydroxide removes more than half of this benzoyl content. H. D. KAY.

Preparation of polypeptides containing the phosphoric and ferric nuclei of ovovitelline. SWIGEL and T. POSTERNAK (Compt. rend., 1927, **184**, 909—911; cf. this vol., 273).—Hæmatogen, obtained by peptic digestion of yolk of egg, is hydrolysed by very active trypsin to a mixture of polypeptides. Of these, *γ-ovotyrin*, $C_{46}H_{84}O_{40}N_{12}P_4$, is the most soluble in presence of hydrochloric acid, and is separated by means of its *copper* salt; *α-ovotyrin*, $C_{21}H_{43}O_{24}N_7P_4$, is less soluble, and *β-ovotyrin* still less soluble. The latter can be separated into two fractions, $C_{21}H_{48}O_{26}N_8P_4$; and β_2, $(C_{24}H_{48}O_{26}P_4)_3Fe_2$, which can be dissolved in an alkali without separation of ferric hydroxide, although this is precipitated on boiling, and in solution the reactions of the ferric ion are given at once. The ovotyrins are all white powders, lævorotatory in solution; they represent different stages of degradation of ovovitelline. The substances α and γ are readily soluble in water; all give the biuret but not the Millon reaction, whilst γ gives also the Molisch reaction. β-Ovotyrin is partly pre-formed in the egg-yolk, and forms a large part of the ovovitellic acid of Levene and Alsberg (A., 1901, i, 300); it is more than doubled on keeping the yolks at 38—40° for 10 days, thus showing that they contain a proteolytic enzyme.

E. W. WIGNALL.

Peptone. V. A. BERNARDI and (SIGNA.) M. TARTARINI (Gazzetta, 1927, **57**, 227—232; cf. A., 1914, i, 443; 1915, i, 468; Bioch. e Ter. sperim., 1923, **10**, 215).—From Witte's peptone, substances of the formulæ $C_{51}H_{94}O_{24}N_{14}S$, $C_{67}H_{127}O_{37}N_{19}S$, and $C_{44}H_{83}O_{24}N_{11}S$ have been isolated, of which the first and third have the character of pure peptone free from protein matter. When the first is heated with 10% hydrochloric acid, neutralised, and precipitated with cupric hydroxide, the precipitate, blue, turning green at 100°, decomp. 218°, is copper aspartate. The aqueous solution after extraction with amyl alcohol gives a substance *A*, purified by mercuric acetate. The amyl alcohol extract gives a residue from which water extracts a solution *B*, and ammonia a solution *C*. All three substances give the triketohydrindene reaction and fail to give the biuret reaction. *A* and *C* alone give Millon's reaction, and *C* alone a picric acid reaction. It is thought that cupric hydroxide may separate from Witte's peptone substances which may belong to the diketopiperazine group. E. W. WIGNALL.

Anhydride nature of proteins. N. D. ZELINSKI and N. I. GAVRILOV (Biochem. Z., 1927, **182**, 11—17).

A review of the authors' method of catalytic hydrolysis of proteins under pressure and a defence of the view that the anhydride linking is an integral part of the protein molecule. Gelatin is stated to contain some 30—50% of anhydride nitrogen, albumin 35%, caseinogen 40%, gliadin 45%, and sturin 5—10%. J. PRYDE.

Autoclave hydrolysis of dipeptides and anhydrides of amino-acids. N. D. ZELINSKI and N. I. GAVRILOV (Biochem. Z., 1927, **182**, 18—25).—In general, anhydrides of amino-acids are hydrolysed by dilute acids under pressure, so that those derived from homologous acids of higher mol. wt. are hydrolysed less readily than those of lesser mol. wt. Increase in the concentration of acid hastens the hydrolysis. During the neutral aqueous hydrolysis of dipeptides, anhydride formation takes place; the larger the dipeptide molecule the more readily it occurs, whilst increase of the dipeptide concentration in any given instance increases the extent of anhydride formation. In weakly acidic solutions, anhydride formation is lessened, and in *M*-acid it ceases. During the acid hydrolysis of proteins under pressure there is therefore no risk of anhydride formation at the cost of peptides if acid and protein are present in equimolar proportions. On the other hand, some of the pre-existing anhydrides are decomposed, especially those of low mol. wt. Thus diketopiperazine itself has not yet been isolated from such hydrolysed proteins. In acid solution the decomposition of anhydrides leads directly to amino-acids; dipeptides are not intermediates. In neutral soluton, the dipeptides participate in the equilibria. J. PRYDE.

Dynamics of autoclave hydrolysis of proteins by dilute acids. N. I. GAVRILOV, E. STACHEJEVA, A. TITOVA, and N. EVERGETOVA (Biochem. Z., 1927, **182**, 26—34).—An investigation of the course of hydrolysis of proteins under pressure in which the influence of time, temperature, acid, and protein concentrations is recorded and from which conclusions are reached in support of Zelinski's views on the constitution of proteins (cf. preceding abstracts)

J. PRYDE.

Hydrolysis of silk fibroin with 25% formic acid. N. D. ZELINSKI and K. P. LAWROWSKI (Biochem. Z., 1927, **183**, 303—306).—Silk fibroin treated with 25% formic acid in an autoclave at 180° is completely hydrolysed in a manner analogous to that with 4—5% mineral acid, the amino-acid anhydrides of the protein being further hydrolysed to the free amino-acids, which are isolated in the case of tyrosine, glycine, and alanine as the ester hydrochlorides.

P. W. CLUTTERBUCK.

Sericin. N. ALDERS (Biochem. Z., 1927, **183**, 446—450).—Sericin, prepared from raw silk by an improved method, had an ash content of 3·9%, gives the biuret, xanthoprotein, and Millon reactions, but not the Fehling test, the total nitrogen being 15·9%, the monoamino-nitrogen 12·59%, nitrogen of bases 1·51%, acid amide nitrogen 1·68%, and contains approximately, tryptophan 1%, tyrosine 7%, cystine 1%, arginine 5%, and lysine 1%.

P. W. CLUTTERBUCK.

Alcohol-soluble proteins in mixed solvents. II. D. B. DILL (J. Biol. Chem., 1927, **72**, 239—247).—Zein behaves similarly to gliadin (A., 1925, i, 1478) in that its solutions in aqueous-alcoholic mixtures show a "turbidity temperature" which varies with the nature of the solvent, but not with the concentration of protein, and, further, in that, for a given solvent mixture, there exists a critical temperature above which there is no upper limit to the solubility of the protein. The "turbidity temperature" is regarded as the f. p. of a compound of the protein with alcohol and water in certain proportions. Curves

are given showing the solubility of zein in mixtures of water with methyl, ethyl, and propyl alcohols, and of both zein and gliadin in mixtures of water with *tert.*-butyl alcohol. The range of solubility is lower in the case of zein than in that of gliadin.

C. R. HARINGTON.

Optical rotatory power and dispersion of proteins. L. F. HEWITT (Biochem. J., 1927, **21**, 216—224).—The extraction of lipins from proteins increases their rotatory power. Crystallised and non-crystalline serum-albumins behave similarly in their optical activity. The various serum-proteins have distinct rotatory values. Serum-albumin, egg-albumin, and lactalbumin have rotatory dispersions dominated by an absorption band at about 2760 Å. Serum-globulins, caseinogen, and gelatin have different rotatory dispersions from the albumins. Pseudo- and eu-globulins retain their characteristic rotations and other properties after extraction with alcohol and ether at −4°, and with ether at the ordinary temperature for 24 hrs. S. S. ZILVA.

Limited applicability of Nessler's reagent for determination of nitrogen. B. SJOLLEMA and L. SEEKLES (Biochem. Z., 1927, **183**, 240—244).—A number of compounds, in particular caffeine and theobromine, when treated with sulphuric acid containing potassium and copper sulphates, yield an appreciable quantity of methylamine; less of the latter is formed using a mixture of sulphuric acid, phosphorus pentoxide, and mercury. Determination of nitrogen by this method is impossible.

C. R. HARINGTON.

Determination of carbonyl in aldehydes and ketones. G. W. ELLIS (J.C.S., 1927, 848—851).—A modification of the method described by Strache (A., 1892, i, 546; ii, 1530). The aldehyde or ketone (about 0·1 g.) is treated with excess of a solution of phenylhydrazine, the concentration of which is determined by oxidation (Fehling's solution) to nitrogen and benzene. The excess of phenylhydrazine is then determined in the same manner. A simple apparatus arranged so that the oxidation can be done under reduced pressure, thus eliminating dissolved nitrogen, is described. The nitrogen is measured saturated with benzene and water vapours.

H. BURTON.

Biochemistry.

Regulation of respiration. Tissue acidity, blood acidity, and the co-ordination of the dual function of hæmoglobin during suspended ventilation. A. B. HERZMAN and R. GESELL (Amer. J. Physiol., 1927, **80**, 416—426).—Changes in acidity of the arterial and venous blood were studied continuously by the manganese dioxide electrode. The relations of blood acidity to the end of apnœa, induced by asphyxia or by over-ventilation, were followed and the results discussed in relation to changes in acidity of the tissues and the respiratory centre.

R. K. CANNAN.

Gas exchange of nerve during stimulation. W. O. FENN (Amer. J. Physiol., 1927, **80**, 327—346).—A modification of Thunberg's micro-respirometer is described, adapted to the determination of the oxygen absorbed and the carbon dioxide produced by nerve with a sensitivity of about 4×10^{-5} c.c. oxygen. The average resting oxygen consumption of the lateral line nerve of the dogfish was 1·35 mm.^{3} and the carbon dioxide production 1·1 mm.^{3}, the mean resting respiratory quotient being 0·83. The average increase on stimulation was 21% and the respiratory quotient of the extra metabolism was 0·78. These values for the quotient are probably low, owing to an error in the determination of the carbon dioxide. With increased surface, as with the smaller nerves, there was a distinct tendency towards an increase in resting and active metabolism.

R. K. CANNAN.

Effect of hydrogen-ion concentration on the respiratory exchange of the tissues. M. COMEL (Atti R. Accad. Lincei, 1927, [vi], **5**, 307—310).—Experiments on the respiration of pulped frog muscle in solutions containing either mixed phosphates or citrate and hydrochloric acid show that the consumption of oxygen is virtually constant for values of p_H between 7·86 and 6·24, but diminishes when 5·31 is reached. The carbon dioxide evolved increases in quantity over the p_H range 7·86—7·35, then remains constant to 6·24, and subsequently diminishes. The respiratory quotient rises as p_H falls from 7·86 to 7·15, the value then remaining at 1 until p_H=5·31. With the hibernating frog, for values of p_H above 7·15, the consumption of oxygen and the output of carbon dioxide remain almost equal, the quotient rising slightly. For values of p_H below 5·31, both oxygen consumed and carbon dioxide evolved fall considerably, the quotient increasing markedly. The results obtained similarly with frog's liver, although analogous, are more uniform and exhibit sharper differences.

It appears that the fundamental factor in the maintenance of a high respiratory exchange is a hydrogen-ion concentration below the isoelectric point, dissociation of protein anions being thus permitted. It may be, however, that the results obtained are due to a specific action of the phosphate ion in enhancing the respiratory exchange.

T. H. POPE.

Precipitation of serum-proteins by acids and salts of heavy metals. L. LORBER (Biochem. Z., 1927, **183**, 16—22).—The precipitation of the proteins of blood-serum by any acid reaches a maximum at a concentration of $N/160$; in the case of sulphosalicylic acid, which has a specific precipitating effect on protein, a second maximum is reached at a concentration of $N/2·5$. In the case of the salts of heavy metals, the same minimum concentration of $N/160$ is required for maximum precipitation of protein; but, whilst in the cases of lead nitrate and aluminium sulphate the degree of precipitation falls with higher concentrations of salt, in those of copper sulphate

and zinc sulphate the maximum precipitation is maintained as more salt is added. In the above experiments, therefore, the precipitation of the proteins appears to be determined by the base-binding power of the substance added, and not by the final p_H. C. R. HARINGTON.

Analysis, salting out, and specific refraction of human blood-plasma proteins and comparative viscosity of serum. W. STARLINGER, K. SPÄTH, and E. WINANDS (Biochem. Z., 1927, **183**, 245—273).—The objections of Arnd and Hafner (A., 1926, 421) and of Petschacher, Berger, and Schretter (Z. ges. exp. Med., 1926, **50**) to the authors' method of protein determination are discussed and dismissed on the grounds of further experimental work. The error in eighty-two double determinations of total serum-protein and of the protein fraction precipitated by ammonium sulphate was ±0·06 g.-%. The non-agreement between the results obtained by half-saturation with ammonium sulphate when compared with those by full saturation with magnesium sulphate is confirmed with twelve pathological sera, but results by half-saturation with sodium sulphate were not completely reproducible. The error in refractometric determinations is not so large with normal as with pathological sera. P. W. CLUTTERBUCK.

Content of fibrinogen not spontaneously coagulable in the plasma of the dog. II. E. ZUNZ (Bull. Soc. chim. Belg., 1927, **36**, 89—96; cf. Vol. jubil. Charles Richet, Paris, 1926, 94—98).—A method for the determination of spontaneously non-coagulable fibrinogen in normal plasma and during anaphylactic or peptone shock is described which depends on coagulation by means of carbon dioxide followed by 1% aqueous calcium chloride, the fibrinogen in normal plasma being also determined by Grain's method. This improved method of comparison confirms the conclusion previously reached that anaphylactic or peptone shock is not invariably accompanied by any very considerable or consistent diminution in content of fibrinogen not spontaneously coagulable. C. HOLLINS.

6-Amino-2-oxypurine (oxyadenine) [in blood]. M. V. BUELL and M. E. PERKINS (J. Biol. Chem., 1927, **72**, 745—749).—From the protein-free filtrate of pig's blood, the purine compounds were precipitated with uranyl nitrate, hydrolysed with sulphuric acid, and purified first by means of the copper salts and finally by the silver salts; after removal of the silver as chloride, the solution deposited a sparingly soluble *hydrochloride*, $C_5H_5ON_5,HCl,2H_2O$; the free base and its salts agreed in all respects with the 6-amino-2-oxypurine synthesised by Fischer (A., 1898, i, 48). C. R. HARINGTON.

Serum electrolytes. II. Electrolyte composition and p_H of the serum of a poikilothermous animal at different temperatures. J. H. AUSTIN, F. W. SUNDERMAN, and J. G. CAMACK (J. Biol. Chem., 1927, **72**, 677—685).—The blood of alligators maintained at 35° was compared with that of others kept at 9°. At the higher temperature, the concentrations of protein, hydrogen ions, lactic acid, dextrose, and phosphate and the tension of carbon dioxide were increased; the total base was slightly diminished and the hydrogen carbonate and residual base markedly so; the change in p_H was such that the base bound per unit of protein remained unaltered. C. R. HARINGTON.

Biological importance of acid-soluble organic phosphorus of blood. H. JOST (Z. physiol. Chem., 1927, **165**, 171—214).—The greater part of the organic acid-soluble phosphorus of the red corpuscle (horse) is present as the diphosphoric ester of glyceric acid, confirming Greenwald's findings. A crystalline brucine salt has been prepared. The synthesis of this ester, which takes place, under certain conditions, in blood, is intimately associated with glycolysis, and is not hindered by anaerobic conditions. It is suggested that diphosphoglyceric acid and glycerophosphoric acid are simultaneously produced from hexose by the Cannizzaro transformation of an intermediate triosephosphoric acid. Diphosphoglyceric acid is readily hydrolysed by kidney extracts, the optimum reaction being on the alkaline side of p_H 8. An important part of the urinary phosphate is probably produced in this way. H. D. KAY.

Inorganic phosphorus content of blood with reference to calcium concentration. A. GROLLMAN (J. Biol. Chem., 1927, **72**, 565—572).—Whilst in normal mammalian blood the inorganic phosphorus is completely diffusible, this is not so with the blood of lower animals. The difference is due to the higher calcium content of the latter blood, since an artificial increase of the calcium content of mammalian blood, brought about by administration of parathyroid extract, or by direct addition of calcium chloride to the shed blood, causes part of the inorganic phosphorus to become non-diffusible. C. R. HARINGTON.

Diffusibility of calcium in human blood-serum. R. F. LOEB and E. G. NICHOLS (J. Biol. Chem., 1927, **72**, 687—694).—Blood-serum was dialysed through collodion sacs against solutions containing varying amounts of sodium and calcium chlorides; the final equilibrium ratio, calcium in serum : calcium in outer solution, was greatest when the calcium chloride and sodium chloride present in the outer solution were least. It therefore follows that for significant comparison of the diffusibility of calcium in pathological conditions, the total concentrations of calcium and of sodium chloride in the systems studied must be comparable. C. R. HARINGTON.

Effect of ingestion of calcium lactate on serum-calcium. W. BAUER and M. W. ROPES (J. Amer. Med. Assoc., 1926, **87**, 1902—1904).—Ingestion of calcium lactate (5 g. and 10 g.) is followed by an increase (14% and 28%, respectively) in the serum-calcium. CHEMICAL ABSTRACTS.

Electrolytic equilibrium of the blood. Effects of the intravenous injection of calcium salts. Importance of the liver. L. CONDORELLI (Arch. Farm. sperim. Sci. aff., 1926, **42**, 193—207).—Normal dogs react to the intravenous injection of calcium salts by rapidly fixing the calcium, putting into circulation large quantities of sodium united to carbon dioxide, increasing the proportion of magnesium in the blood by about 100% and that of the inorganic phosphorus considerably, and by diminishing that of

chloride. When sufficient calcium to cause death is injected, a marked rise in the potassium of the blood is observed, the proportion of potassium being much greater in the portal blood than elsewhere. In these phenomena, which tend to regulate the electrolytic equilibrium of the blood, the liver plays an important part, but is not the only organ concerned. The pronounced differences observed between venous and arterial blood from the same vascular region, as regards the electrolytic composition of the blood, are related to the exchanges occurring between blood and tissues. It is evident that the animal organism has at its disposal a certain amount of sodium which, in case of need, may be circulated to re-establish disturbed electrolytic equilibrium of the blood. T. H. POPE.

Analysis. VI. Determination of calcium in blood-serum. L. PINCUSSEN and P. SCHIMMELPFENG (Biochem. Z., 1927, **183**, 42—44).—The method of Kramer and Tisdall (A., 1921, ii, 595) frequently gives low results owing to the short period allowed by these authors for the precipitation of the calcium as oxalate; if this period be increased to 24 hrs., precipitation is always complete.

C. R. HARINGTON.

Colorimetric determination of potassium in 0·2 c.c. of blood. S. YOSHIMATSU (Tôhoku J. Exp. Med., 1926, **8**, 174—179).—The potassium is precipitated from undiluted serum or from a solution of the blood-ash in acetic acid by means of sodium cobaltinitrite; the precipitate is dissolved in nitric acid, reduced with dimethylglyoxime and sodium sulphide, and determined colorimetrically. The accuracy, using 0·2 c.c. of blood or 1 c.c. of serum, is ±5%. CHEMICAL ABSTRACTS.

Determination of non-protein nitrogen in human serum with special reference to the nitrogen of urea and of the so-called ureic substances. E. PEANO (Rev. sud-americana endocrinol. immunol. quimioterap., 1926, **9**, 784—803).—In the determination of non-protein-nitrogen in serum by the hypobromite method, deproteinisation by Fosse's method is preferred. After deproteinisation, the urea-nitrogen is best determined by the xanthhydrol method, and the residual nitrogen in the filtrate by the hypobromite or the Kjeldahl method. In normal sera the ratio of urea- to residual nitrogen is 1·60—1·80, and that of urea- to non-protein-nitrogen is 0·70. CHEMICAL ABSTRACTS.

Determination of the amino-nitrogen of the blood. L. CANNAVÒ (Arch. Farm. sperim. Sci. aff., 1926, **42**, 225—234).—For the amino-nitrogen of the Van Slyke's method gives results almost always slightly higher than those obtained by Bang's method, probably because the nitrous acid reacts not only with amino-acids, but also with polypeptides, carbamide, etc. For the amino-nitrogen in the blood of a normal man after fasting for 24 hrs., values between 1 and 12·0 mg. per 100 c.c. were obtained by the former and between 5·8 and 11·9 by the latter method; e normal value is assumed to be about 9 mg. ormal values were obtained with patients suffering m syphilis, diabetes, tuberculosis, malaria, neuralgia, acute articular rheumatism, blennorrhagic umatism, gastric ulcer, and heart disease. The amino-nitrogen falls below normal in pernicious anæmia and typhus, and rises above normal in hepatic cirrhosis and, especially, acute glomerular nephritis.

T. H. POPE.

Experimental alteration of tryptic activity of blood-serum. O. STEPPUHN and X. UTKIN-LJUBOWZOW. **Blood proteases.** L. UTKIN-LJUBOWZOW (Biochem. Z., 1927, **183**, 90—102, 103—112).—The tryptic activity of blood-serum is not affected by removal of the pancreas; it is increased by production of a sterile abscess and is reduced by extirpation of the spleen. It is concluded that the enzyme is not identical with pancreatic trypsin and that it is contained in the leucocytes.

The blood-sera of rabbits and dogs contain two proteolytic enzymes: a tryptase which has its optimum activity at p_H 7, and a peptase with an optimum at p_H 2·5—2·7. The activity of the tryptase is reduced very rapidly on the acid side, but more slowly on the alkaline side of its optimum p_H.

C. R. HARINGTON.

The specific activity of hæmolytic serum-albumin is not connected with the total protein content. M. PIETTRE (Compt. rend., 1927, **184**, 952—954; cf. A., 1926, 635, 856).—A solution of hæmolytic serum-albumin was fractionated by alcoholic precipitation and by regulated heating in acid and alkaline solution. Removal of 32—41% of the serum-albumin caused no sensible diminution of hæmolytic activity. B. W. ANDERSON.

Measurement of percentage hæmolysis. II. E. PONDER (Proc. Roy. Soc., 1927, **B**, **101**, 193—217).—An analysis of the percentage hæmolysis curves, obtained by the radiometer and selenium cell methods, for simple lysins, acting alone, with accelerators, and with inhibitors, has been made. For systems involving lysins, *e.g.*, saponin and sodium taurocholate, acting alone, the form of the curve is explained by the assumption that a unimolecular reaction proceeds among a population the resistances of which are distributed according to a frequency curve. Accelerators and inhibitors alter the resistance of the population to the lysin, the alteration being described by an expression containing the single resistance constant *R*.

W. ROBSON.

Buffering of the tissues as indicated by carbon dioxide capacity of the body. R. J. BROCKLEHURST and Y. HENDERSON (J. Biol. Chem., 1927, **72**, 665—675).—The total carbon dioxide capacity of all tissues of the body other than the blood is less than that of the latter alone; the tissues can therefore be buffered to a small extent only. C. R. HARINGTON.

Action of liver pulp on ammonium cyanate. R. FOSSE and N. ROUCHELMANN (Compt. rend., 1927, **184**, 1021—1023).—At 38° 1 kg. of dog's liver pulp prevents the transformation of 6·5 g. of ammonium cyanate into urea, the duration of the experiment being 24—96 hrs. Coagulated liver pulp acting similarly prevents the transformation of 5 g. per kg. of pulp. E. A. LUNT.

Co-zymase content of animal tissues. H. VON EULER and D. RUNEHJELM (Z. physiol. Chem., 1927, **165**, 306—313).—The tissues are finely minced and boiled with a definite volume of water. The extract

is filtered and added to a suspension of washed yeast in phosphate buffer solution, which also contains dextrose and sodium hexosediphosphate. Carbon dioxide production is measured at intervals. The most active extracts are those prepared from kidney, heart muscle, and liver. Spleen, skeletal muscle, lung, and pancreas extracts are less active. H. D. KAY.

Composition of the muscle of the crab, *Grapsus nankin*. K.-H. LIN (J. Biochem. [Japan], 1926, **6**, 409—415).—The muscle of *Grapsus nankin* contains alcohol-coagulable protein-nitrogen 15·41 (heat-coagulable, 15·05), fat 0·21, ash 4·88, sulphur 0·98, phosphorus 0·58%. The distribution of the amino-acids was: cystine 1·74, arginine 7·54, histidine 2·12, lysine 9·74, tryptophan 1·48, tyrosine 5·62%.

CHEMICAL ABSTRACTS.

Cutaneous framework of insects. Dihydroxyphenylalanine in the wing cases of may-bugs. H. SCHMALFUSS and H. P. MÜLLER (Biochem. Z., 1927, **183**, 362—368).—3 : 4-Dihydroxyphenylalanine is isolated from the wing-cases of the may-bugs *Melolontha melolontha*, L., and *M. hippocastani*, F.

P. W. CLUTTERBUCK.

Preparation of lecithin. P. A. LEVENE and I. P. ROLF (J. Biol. Chem., 1927, **72**, 587—590).—Practical details are given for the preparation of lecithin from egg-yolk, brain, and liver.

C. R. HARINGTON.

Oil-red-*O*-pyridine, a rapid fat stain. F. PROESCHER (Stain Tech., 1927, **2**, 60—61).—The stain is made by adding 3—5 g. of oil-red-*O* to 100 c.c. of 70% solution of pyridine in water. After 1 hr. at the ordinary temperature with occasional shaking, the solution is saturated. It should be protected from the light and filtered before use. Frozen sections, after fixation in formaldehyde, are immersed in 50% pyridine for 3—5 min. and then in the stain for 3—5 min. Sections from the central nervous system should be stained for 20—30 min. The stain is superior to sudan-III. H. W. DUDLEY.

Snake (*Agristroden Blowhoffi*) venom. H. WADA (Japan Med. World, 1926, **6**, 308—315).—An aqueous solution of the venom is neutral to litmus, foams when shaken, is negative to the Fehling, Nylander, and Trommer tests, positive to the sulphosalicylic acid, Heller, and Millon tests, and yields white precipitates with phosphotungstic acid, lead acetate, and silver nitrate. CHEMICAL ABSTRACTS.

Action of mercuric chloride and hydrogen peroxide on bile pigments. W. F. VON OETTINGEN and T. SOLLMANN (J. Biol. Chem., 1927, **72**, 635—641).—The bluish-green colour produced by the action of mercuric chloride on bilirubin is due to the formation of mercury salts of the mixed oxidation products of the pigment; other oxidising salts, *e.g.*, copper sulphate, produce colour changes of a similar type. The oxidation of bilirubin by hydrogen peroxide is accelerated by high concentrations of hydrochloric acid and by raising the temperature; it is inhibited by cyanide, quinine, and caffeine. The effect of metallic salts on the hydrogen peroxide oxidation is variable and bears no relationship to their individual direct effects on the pigment.

C. R. HARINGTON.

Chloride content of the blood of milk-giving animals during milking. A. KRESTOWNIKOV (Biochem. Z., 1927, **183**, 307—309).—The chloride content of the blood of cows and goats does not alter appreciably during milking. P. W. CLUTTERBUCK.

Circulation of phosphorus in nature. M. EGOROV (Ukraine Chem. J., 1926, **2**, [Tech. Part], 74—80).—Whilst the cycle of nitrogen in nature is well known, that of phosphorus is scarcely recognised. The author has previously shown that air contains phosphorus, and that horses' fæces will give up 3·68—18·73% of its combined phosphorus when exposed in air. Although it was supposed that the phosphorus is eliminated as the hydride, yet no results proving this could be obtained. A step towards the solution of this problem has been taken by the use of glowing powdered magnesium, and by activated carbon. Air was drawn over fæces moistened with water, and passed through sodium hydroxide, lead acetate, concentrated sulphuric acid, and finally over activated carbon. Under these conditions, the dry fæces yielded 10% of its phosphorus (as P_2O_5). E. ROTHSTEIN.

Colorimetric determination of iodine in urine. S. YOSHIMATSU and H. SAKURADA (Tohoku J. Exp. Med., 1926, **8**, 107—112).—The determination (±3%) is based on the formation of a dark brown solution when silver iodide, dissolved in potassium cyanide solution, is reduced with sodium sulphide.

CHEMICAL ABSTRACTS.

Determination of bromine in presence of chlorine [in urine]. F. OTTENSOOSER (Arch. exp. Path. Pharm., 1927, **122**, 77—81).—To one portion of urine an excess of silver nitrate is added, the precipitate filtered off, and the silver in the filtrate determined volumetrically. The precipitates of silver chloride and silver bromide obtained by adding silver nitrate to another portion are weighed. From these two results the amounts of chlorine and of bromine present can be calculated. W. O. KERMACK.

Colloidal reactions of the cerebrospinal fluid. W. SCHMITT (Kolloid-Z., 1927, **41**, 334—347).—The importance of the use of the gold and gum-mastic reactions in diseases of the central nervous system is emphasised, and a *resume* is given of views held by previous investigators as to the nature of the reactions. L. L. BIRCUMSHAW.

Mineral salt content of the blood in disease. A. S. BLUMGARTEN and G. L. ROHDENBURG (Arch. Int. Med., 1927, **39**, 372—384).—From the analyses of blood from 173 patients suffering from various diseases, the following figures are deduced for quantities present in 100 c.c. of whole blood: sodium 120—180 mg., potassium 130—170 mg., calcium 6—11 mg., magnesium 2·98—4 mg.; total salts 250—300 mg. Certain diseases are associated with deviations above or below these normal concentrations. In particular, carcinoma is accompanied by low magnesium and calcium contents, and leucæmia and purpura hæmorrhagica by a low potassium and high sodium and calcium contents. W. O. KERMACK.

Cholesterol, lecithin, and fatty acids in blood of new-born mice with inherited anæmia. S. B. DE ABERLE, W. M. HOSKINS, and M. BODANSKY

(J. Biol. Chem., 1927, 72, 643—648).—The blood of mice suffering from inherited anæmia has 35·25% reduction in cholesterol, 4·52% reduction in lecithin, and 8·03% increase in fatty acids, as compared with the blood of normal mice from the same litters.

C. R. HARINGTON.

Fatty acids of the spleen after castration and their quantitative variation during aseptic autolysis. L. CANNAVÒ (Arch. Farm. sperim. Sci. aff., 1926, 42, 139—144).—With castrated dogs, the quantity of total fatty acids in the spleen is mostly considerably greater than with the control animals. When the spleen is subjected to autolysis, with the castrated dogs the fatty acids increase in amount after 24 hrs., this increase being either maintained or gradually lost, or alternately rising and falling, during the next few days; with normal dogs, the fatty acids increase for about 48 hrs. and then gradually fall.

T. H. POPE.

Blood-sugar in the normal and diabetic [subject]. C. D. SHAPLAND (Lancet, 1926, ii, 589—594).—When ingested by a fasting young subject, sucrose produces a definite blood-sugar curve similar to that given by dextrose; with diabetics the curve, like that of dextrose, differs from the normal. In advanced age and in long-standing obesity, the curve tends to approach the diabetic type. In diabetes the renal threshold for sugar tends to become raised. Normal variations of blood-sugar may amount to 0·078% of sugar.

A. A. ELDRIDGE.

Carbohydrate metabolism in diphtheria. F. J. HECTOR (Lancet, 1926, ii, 642—645).—In severe diphtheria, during toxæmia and acidosis, the concentration of the fasting blood-sugar is abnormally low, there is a marked defect in the storage mechanism, and the ability of the tissues to utilise dextrose is diminished.

A. A. ELDRIDGE.

Spleens from Gaucher's disease and lipoid-histiocytosis. W. BLOOM and R. KERN (Arch. Int. Med., 1927, 39, 456—461).—Chemical and microchemical analyses are given of spleens from cases of Gaucher and of lipoid-histiocytosis (Niemann's variety).

W. O. KERMACK.

Total acid-base equilibrium of plasma in health and disease. VIII. Hydrogen carbonate and chloride in the serum of patients with heart ailure. IX. High serum hydrogen carbonate in heart failure. Asphyctic anoxæmia. J. P. ETERS, H. A. BULGER, and A. J. EISENMAN (J. Clin. Invest., 1927, 3, 497—510, 511—520).—VIII. The carbon dioxide content and capacity, the chloride-ion concentration, and the total choride and hydrogen carbonate-ion concentration of the blood in cardiac disease are abnormally variable; two types of abnormality are associated, respectively, carbon dioxide and high chlorine values.

IX. [illegible] changes in the lungs are associated with [illegible] hydrogen carbonate values in cardiac patients.

CHEMICAL ABSTRACTS.

[illegible] deficiency in experimental obstructive jaundice. W. C. BUCHBINDER and R. KFR[illegible] J. Physiol., 1927, 80, 273—277).—In puppies subjected to ligation of the common bile duct and in cases of human jaundice low values for serum-calcium were found.

R. K. CANNAN.

Glycolysis in normal and in leucæmic blood. M. FALCON-LESSES (Arch. Int. Med., 1927, 39, 412—420).—The sugar content of normal blood kept at body temperature decreases rapidly, and where the initial concentration of dextrose is less than 0·01 g. per 100 c.c., it is complete within 6 hrs. In the case of blood from patients suffering from myelogenous leucæmia, the glycolysis takes place more rapidly, being complete usually within 2 hrs. It is doubtful whether this is due merely to an increase in the number of leucocytes, as the immature nature of these cells may be an important factor. In blood from a case of pernicious anæmia, glycolysis was slower than in normal blood, but in blood from a case of erythræmia it was more rapid. Experiments on plasma and on blood in which the corpuscles had been damaged by the addition of water indicate the importance of the presence of intact cells during glycolysis.

W. O. KERMACK.

Special action of nickel on normal human sera. A. SIEGLER (Compt. rend., 1927, 184, 954—956).—Both normal and syphilitic human sera gave a positive Bordet–Wassermann reaction after ultrafiltration through collodion mounted on a nickel filter sheath, the nickel apparently acting as a catalyst. This change in serum in presence of nickel does not take place in a vacuum.

B. W. ANDERSON.

Tellurium and its curative action on syphilis. C. LEVADITI, M. and MME. NICOLAU, and Y. MANIN (Ann. Inst. Pasteur, 1927, 41, 369—442).—A detailed study has been made of the effects of administering tellurium to rabbits, its distribution in various organs, and its mode of elimination. It exercises a marked curative action on various experimental spirochætoses, including syphilis. The compounds used include sodium tellurite, potassium tellurite, tellurium trioxide, tellurium di-iodide, quinine tellurium iodide, dimethyl telluride, diphenyl telluride, and 4-ethyl*cyclo*telluropentanedione, as well as "metallic" tellurium in finely-divided and colloidal conditions. Details are given for the determination of small quantities of tellurium in organs and body-fluids.

W. O. KERMACK.

Tellurium in the treatment of human syphilis. L. FOURNIER, C. LEVADITI, and L. GUÉNOT (Ann. Inst. Pasteur, 1927, 41, 443—457).—Tellurium administered either as tellurium trioxide, tellurium iodide, quinine tellurium iodide, or as the element in a finely-divided condition has a marked curative action on human syphilis, but the treatment is complicated by the occurrence of undesirable reactions in certain cases.

W. O. KERMACK.

Mineral metabolism in experimental tetanus. J. M. KRINIZKI (Biochem. Z., 1927, 183, 81—89).—Injection of tetanus toxin, in amount sufficient ultimately to kill the animal, causes a marked reduction in the blood-calcium and a slight increase in the potassium. If the calcium of the blood be artificially raised by transplantation of bone, the same or a greater fall takes place as the result of tetanus intoxication, and the symptoms of the latter are not in any way modified. The only change observed in the

blood-sugar in these experiments was a terminal hypoglycæmia. The results suggest a possible relationship between the symptoms of tetanus and functional failure of the parathyroid glands.

C. R. HARINGTON.

Plasma calcium in tuberculous adults. E. M. GRIESHEIMER and C. C. VAN WINKLE (Amer. Rev. Tuberculosis, 1927, **15**, 270—277).—Tuberculosis is not characterised by a demineralisation. Ingestion of milk, but not that of cod-liver oil or exposure to light, increases the plasma calcium. More "active" patients show lower calcium values.

CHEMICAL ABSTRACTS.

Tuberculosis. VIII. Identification of a skin-reacting substance in tuberculous sera. F. EBERSON (Amer. Rev. Tuberculosis, 1927, **15**, 127—135).—Tuberculous serum contains a heat-sensitive skin-reacting substance, independent of tuberculin or its related substances. The compound, probably a toxin, is destroyed by heating at 60—65° for 20—45 min.

CHEMICAL ABSTRACTS.

Inhibitive reaction of tuberculosis serum. Nature of the inhibitive substance. D. PERLA (Amer. Rev. Tuberculosis, 1926, **14**, 706—717).—The inhibitive reaction of tuberculosis serum is not specific; it is dependent on an increase of the protective colloidal constituents of the serum.

CHEMICAL ABSTRACTS.

Lipoid equilibrium of blood-serum. C. ACHARD, A. GRIGAUT, and A. LEBLANC (Compt. rend., 1927, **184**, 843—845).—Extraction of blood-serum with 20 times its volume of a mixture of 3 parts of 95% alcohol and 1 part of ether affords the following normal values: total fats 7·50, cholesterol 1·60, lecithin 1·70%, iodine value 45. The lipæmic constant, cholesterol/fatty acids=0·38, corresponds with the lipocytic coefficient of Mayer and Schæffer. The iodine value of the total fats of the liver is normally about 110, but in cirrhotic or fatty livers may fall below 60. The iodine value of the fatty acids from serum also affords an indication of the general nutritive condition of the organism in typhoid fever and pneumonia. In such cases, the iodine value may fall considerably and return to normal only some weeks after cessation of the fever. The ratio (iodine value : 100) × total fats − 3·375 is termed the lipo-iodine capacity, and may be as low as 1·02 in typhoid fever.

R. BRIGHTMAN.

Basal metabolism as determined by the respiratory exchange. F. A. PICKWORTH (Proc. Roy. Soc., 1927, **B**, **101**, 163—185).—I. A new method, involving the use of an air-tight chamber and a modified Haldane air-analysis apparatus, for the determination of the basal metabolic rate is described, by which emotional disturbances are diminished and muscular relaxation in the subject is attained. Figures so obtained are claimed to approximate more closely to the real rate. Tables are given for calculating results.

II. Reduction of the magnitude of certain variable factors, *e.g.* muscular tonus and attention, in the determination of the basal metabolism of normal subjects by the use of the above technique, yields results at least 20% lower than those obtained by the bag method. Figures showing the effect of such factors as the relaxation of mind and body, sleep, fatigue, diet, irritation, and hot baths are given.

W. ROBSON.

Relationship of blood-sugar concentration, specific dynamic action, and rate of oxidation of a number of carbohydrates. K. SCHIRLITZ (Biochem. Z., 1927, **183**, 23—41).—Starch, lævulose, sucrose, maltose, dextrose, and lactose exhibited specific dynamic actions of descending degree, ranging from 9·25% with starch to 1·15% with lactose. In the case of dextrose in particular, the specific dynamic effect occurs before there is evidence of oxidation of the extra sugar, and cannot therefore be connected with the catabolism of the latter. There is no constant relationship between the concentration of blood-sugar and the rate of oxidation of carbohydrate or the degree of specific dynamic action.

C. R. HARINGTON.

Origin of acetaldehyde in bacterial and animal metabolism. M. D. WHETHAM (Austral. J. Exp. Biol., 1927, **4**, 35—56).—The use of acetoin as an indication of the formation of acetaldehyde during fermentation is recommended. It can be determined quantitatively by oxidation to diacetyl and by subsequent precipitation as nickel dimethylglyoxime.

Neuberg's pyruvic acid–aldehyde theory of carbohydrate breakdown, established for yeast fermentation, is held to need further examination in the case of animal and bacterial cells. *Bacillus lactis aerogenes* does not produce acetoin from pyruvate, lactate, or succinate, and abundant evidence is also cited in the case of other bacterial and animal cells against the formation of aldehyde from pyruvate. Lusk's theory for the breakdown of carbohydrate in muscle (dextrose ⟶ methylglyoxal ⟶ acetaldehyde + formic acid) is discussed as an alternative hypothesis.

E. A. LUNT.

Lactic acid as the intermediate product in anaerobic carbohydrate exchange in the animal cell. J. STOKLASA (Biochem. Z., 1927, **183**, 461—476).—Lactic acid, in anaerobic respiration of muscle, arises as the first product of carbohydrate exchange, and from it are formed alcohol and carbon dioxide, the alcohol next giving rise to acetaldehyde, acetic acid, and carbon dioxide. By the action of β- and γ-rays, the production of carbon dioxide is inhibited and of lactic acid is increased, whilst the action of α-rays of ionium or of radium emanation causes an increase in the oxidative phase, lactic acid completely disappearing.

P. W. CLUTTERBUCK.

Lactic acid content of the blood after the administration of lævulose. A. LANYI (Magyar Orvosi Archivum, 1926, **27**, 566—571).—After the administration of lævulose to men or dogs, the lactic acid content of the blood increases and reaches a multiple of normal values. Dextrose does not cause any such increase. The lævulose is more easily transformed into an enol form, and it is more easily assimilated by the organism. The increase of lactic acid lasts 3 hrs. Normal values are restored after 6 hrs.

CHEMICAL ABSTRACTS.

Chemical and colloid-chemical changes in muscle during fatigue. G. EMBDEN and H. JOST

(Z. physiol. Chem., 1927, **165**, 224—254).—The ability of isolated frog's muscle, fatigued by repeated induction shocks, to esterify phosphoric acid in presence of sodium fluoride is considerably less than that of unfatigued muscle. This is also true of the muscle while still in the intact animal when it is fatigued to such an extent that recovery from the fatigue is complete in a few hours. The change in colloidal conditions which occurs in the muscle during fatigue, and is responsible for these changes in the esterifying power of the minced tissue, is therefore reversible. The breakdown and resynthesis of lactic acid are brought about by the same enzyme. The lactic acid content of the fatigued muscle in the intact animal is not markedly increased above the resting value, but in all cases the glycogen is much diminished immediately after a period of stimulation, and even 24 hrs. later has not risen again to its original value. H. D. KAY.

Time-relationships of the formation of lactic acid during muscular contraction. G. EMBDEN, E. LEHNARTZ, and H. HENTSCHEL (Z. physiol. Chem., 1927, **165**, 255—278).—Pairs of isolated frog's muscles (semi-membranosus), one of each pair in oxygen, the other in hydrogen or nitrogen, were stimulated indirectly at short intervals for 30 min. The oxygen consumption of the first during this time was determined, and the lactic acid content of each at the end of the 30 min. The quotient excess lactic acid in second muscle/lactic acid burnt in the first muscle (calculated from oxygen uptake) is usually considerably greater than the values obtained by Meyerhof. The difference in lactic acid content of the oxygenated and unoxygenated muscle is due not merely to its partial disappearance in the former as a result of oxidation and resynthesis into glycogen, but also to the actual production of a greater amount of lactic acid in the unoxygenated muscle. A considerable portion of the lactic acid formed under these anaerobic conditions is produced, not during the period of contraction, but after the contraction is over. H. D. KAY.

Ephedrine, pseudoephedrine, and β-phenylethylamine with reference to their effects on the pupil and on the blood-pressure. K. K. CHEN (Arch. Int. Med., 1927, **39**, 404—411).—β-Phenylethylamine does not dilate the pupils of rabbits' and cats' eyes. When injected into dogs in small doses it raises the arterial blood-pressure, but when given by mouth to man it does not exert its pressor action. Pseudoephedrine hydrochloride, a dextrorotatory stereoisomeride of ephedrine hydrochloride, dilates the pupils of man when applied locally, raises arterial blood-pressure in dogs when injected, and slightly increases systolic blood-pressure in man when given by the mouth. W. O. KERMACK.

Influence of hydrogen-ion concentration on the solubility of uric acid. A. JUNG (Arch. exp. Path. Pharm., 1927, **122**, 95—120).—The effect of the variation of the hydrogen-ion concentration on the solubilities of uric acid and of sodium urate is in general in harmony with the view that uric acid dissolves in water as a colloidal electrolyte. The influence of certain compounds, *e.g.*, atophan, on the solubility of uric acid is largely accounted for by the change in the hydrogen-ion concentration. Administration of acid to animals favours the elimination of uric acid. W. O. KERMACK.

Biochemistry of complex salt solutions. I. Biological action of Wiesbaden hot-spring water. II. Influence of ferrous and manganous ions on respiration and fermentation of yeast. K. HARPUDER (Biochem. Z., 1927, **113**, 45—57, 58—62).—I. Wiesbaden hot-spring water alters the isoelectric point of proteins; it inhibits the hæmolysis of red blood-corpuscles by chloroform and by acid, but not by alkali or other hæmolytic agents; it increases the activity of amylase, pepsin, and serum-lipase, the catalytic oxidation of amino-acids on charcoal, the growth, respiration, and fermentation of yeast, and the process of phagocytosis.

II. Ferrous sulphate depresses the respiration of baker's yeast in concentrations above $1\times10^{-4}M$; that of brewer's yeast is not affected. The fermenting power of baker's yeast is raised by concentrations between 1×10^{-6} and $1\times10^{-5}M$, and depressed by concentrations above $1\times10^{-3}M$; brewer's yeast is not affected below $1\times10^{-3}M$-ferrous sulphate, above which concentration its fermenting power is depressed. Manganous sulphate up to $1\times10^{-3}M$ had no effect on brewer's yeast or on the respiration of baker's yeast; the fermenting power of the latter was increased by concentrations between 1×10^{-6} and $1\times10^{-3}M$. C. R. HARINGTON.

Biochemistry of irradiation. IV. Changes in the total mineral balance under the influence of ultra-violet light. C. KROETZ (Arch. exp. Path. Pharm., 1927, **120**, 351—358).—The effect of the short waves of a quartz lamp on healthy adults is recorded. With an experimental diet providing sufficient calories and vitamins, with a high calcium and phosphorus content and a low total base content, such rays lead to a "mineralisation" of the body. Phosphorus and magnesium show increases, chlorine, sodium, and calcium (the last with a fluctuation) reductions, potassium no important change. The indicated changes of the ion-balance are accompanied by a progressive increase of the renal water excretion. W. ROBSON.

Toxicology of the alkyl halides. C. BACHEM (Arch. exp. Path. Pharm., 1927, **122**, 69—76).—Comparison of methyl bromide, methyl iodide, ethyl bromide, and ethyl iodide shows that the methyl are more toxic than the ethyl compounds, and that the iodides are more toxic than the bromides. W. O. KERMACK.

Influence of parasympathetic poisons on blood-sugar. II. Effect of eserine and pilocarpine on adrenaline hyperglycæmia. III. Lowering of the blood-sugar level through parasympathetic stimulation. T. SAKURAI (J. Biochem. [Japan], 1926, **6**, 465—485, 487—498).—II. The hyperglycæmia caused by subcutaneous injection of 0·1—0·2 mg. of adrenaline is inhibited by eserine or pilocarpine; the slight hyperglycæmia caused by 0·05—0·1 mg. of adrenaline is unaffected by eserine.

III. Ergotoxin prevents adrenaline and diuretin hyperglycæmia, but has no noticeable influence on

the blood-sugar. The administration of ergotoxin with pilocarpine or choline lowers the blood-sugar. It is concluded that parasympathetic stimulation causes a fall in the blood-sugar level.

CHEMICAL ABSTRACTS.

Experimental phosphorus poisoning with particular reference to blood-sugar. I. IVANČEVIC (Arch. exp. Path. Pharm., 1927, **122**, 24—43).—The disappearance of glycogen from the liver of dogs after phosphorus poisoning is caused partly by the transport of dextrose to the periphery, and partly by the increased metabolism of it in the liver. Soon after the injection of phosphorus, small increases in the concentration of dextrose in the blood may be observed, and this is followed by hypoglycæmia, presumably when all the available liver-glycogen has disappeared. W. O. KERMACK.

Autolysis. VI. P. RONA and E. MISLOWITZER (Biochem. Z., 1927, **183**, 122—134).—During autolysis of liver, the proportion of the total phosphorus which is colloidal (*i.e.*, precipitable with mercuric chloride) is progressively diminished; coincidently with this, the non-colloidal fraction shows an increase first in the organic phosphorus compounds easily hydrolysed by acid, and, later, in those more resistant to hydrolysis. The easily hydrolysable organic phosphorus compounds apparently consist of hexosephosphates.

C. R. HARINGTON.

Enzymic formation of lactic acid in muscle extract. III. Lactic acid formation from fermentable hexoses. O. MEYERHOF (Biochem. Z., 1927, **183**, 176—215).—The previously observed (this vol., 75) formation of lactic acid from polysaccharides, by an enzyme contained in muscle extract, takes place also with hexoses, but much more slowly. By extraction of baker's yeast with water containing toluene and precipitation of the extract with alcohol, there was obtained a substance which, on addition to the muscle extract, greatly accelerated the formation of lactic acid from hexoses. This activator is readily destroyed by heat or by treatment with acid or alkali; in neutral solution at 0°, however, it can be preserved indefinitely. Treatment of a hexose with muscle extract in presence of this activator leads to rapid formation of lactic acid parallel with a disappearance of inorganic phosphate (*i.e.*, synthesis of hexosediphosphate). At the point when all the inorganic phosphate has been used up, the velocity of formation of lactic acid falls sharply, and subsequently runs parallel to the liberation of inorganic phosphate; that is to say, in the second stage lactic acid and phosphoric acid are being formed in equimolecular quantities from the hexosediphosphate. If, after the end of the first stage, a further addition of inorganic phosphate be made, the original velocity of lactic acid formation is restored. The presence of small amounts of arsenate has little effect on the first stage of the reaction, but accelerates the splitting of the hexosediphosphate. The glycolytic process is inhibited to some extent by fluoride, cyanide, and hydrogen sulphide, but only by relatively high concentrations of the last two substances.

In alcoholic fermentation by yeast, the equation of Harden and Young (A., 1912, ii, 670) is followed only when the substrate is a hexose; with polysaccharides, the rate of formation of hexosediphosphate exceeds that of fermentation; the accelerating effect of arsenate on the fermentation of glycogen is therefore explained by its effect on the splitting of the hexosediphosphate. Whilst in the case of hexoses fermentation and esterification are suppressed equally by fluoride, in that of glycogen the fermentation is suppressed much more than the esterification. Hexosediphosphate can be fermented just as well by acetone-yeast when the latter has been washed free from co-zymase, but under these conditions the fermentation is not accelerated by arsenate. Co-zymase appears, therefore, to be concerned with the synthesis of the hexosediphosphate, and not with the second stage of the fermentation reaction, which must consist, as in the case of muscle, in a direct splitting of the hexosediphosphate into phosphoric acid and degradation products of the hexose.

C. R. HARINGTON.

Lactic acid-forming enzyme of muscle. K. MEYER (Biochem. Z., 1927, **183**, 216—239).—Boiled muscle-juice containing the co-enzyme of the lactic acid-forming enzyme (cf. this vol., 75) was freed from glycogen by addition of alcohol, and from phosphate by treatment with barium chloride and colloidal ferric hydroxide. Addition of such a purified co-enzyme solution to a dialysed extract of muscle failed to produce a system which would form lactic acid from glycogen; the system could, however, be completed by addition of inorganic phosphate, which is not only necessary to the reaction, but also bears a quantitative relationship to the amount of lactic acid produced. The co-enzyme of lactic acid formation appears probably to be also a co-enzyme of respiration, but this question could not be finally determined owing to the impossibility of eliminating oxidation of protein in the system employed. The inhibiting effects of oxalate and fluoride on the lactic acid formation are markedly altered by the nature of the medium, and appear to bear no relationship to the calcium content of the solution. The best purification of the enzyme was effected by successive precipitation with acid sodium acetate solution (p_H 4·4) and recovery from the precipitate with dilute alkaline phosphate solution. (In the case of rabbit muscle, complete precipitation was obtained only on the further addition of potassium chloride with the acetate.) In this way, a preparation was obtained which was 10 times as active in forming lactic acid as the muscle extract, and 30 times as active as the original chopped muscle. C. R. HARINGTON.

Leucocyte lipase. M. SHODA (Okayama Igakkai Zasshi, 1926, 744—753).—The hydrolysis of tributyrin by the leucocytes from the abdominal cavity of the rabbit is promoted by deoxycholic acid, less so by cholic acid. The lipase may be concentrated and purified in exactly the same way as pancreatic lipase (Willstatter); in this state it is more energetically activated by bile acids. CHEMICAL ABSTRACTS.

Hydrogen-ion concentration during fat hydrolysis by pancreatic steapsin and bile acids. Relation between the structure of bile acids and the lipolytic activity. M. SHODA (J. Biochem.

[Japan], 1926, **6**, 395—407).—The fat-splitting activity of pancreatic lipase is promoted by the bile acids in the descending order: deoxycholic, cholic, gallodeoxycholic, hyodeoxycholic acid. The optimum p_H is 8·04, 8·04, 8·04, 8·04—9·18, respectively. For cholic and gallodeoxycholic acids, in acid or alkaline medium, the effect increases with the amount of acid used. For hyodeoxycholic acid at p_H 7·163—5·906, the effect decreases with increase in the amount of acid; with deoxycholic acid at p_H 5·906—5·288, resynthesis occurs. A structural genetic relationship is indicated for gallodeoxycholic and cholic acids and hyodeoxycholic and deoxycholic acids, respectively. When the hydroxyl group is in position 7 in the second ring, the lipolytic function is activated, and when it is in position 13 in the third ring it is inhibited. CHEMICAL ABSTRACTS.

Action of the principal components of tobacco smoke on peptic digestion. G. VASCELLARI and V. PENNATI (Arch. Farm. sperim. Sci. aff., 1926, **42**, 145—166).—The peptic action was followed by Mett's and Grützner's methods, the former yielding the more definite and trustworthy results. The peptic digestion of egg-albumin (fibrin) is retarded markedly by 1 part of nicotine per 200 (400) parts of the enzyme solution, appreciably by 1 : 1000 (—), and not at all by 1 : 2000 (1 : 600). The peptic digestion of albumin (fibrin) is arrested by 1 : 200 (1 : 200) of pyridine or 1 : 20 (1 : 20) of ammonia, retarded by 1 : 1000 (1 : 400) of pyridine or 1 : 1000 (1 : 200) of ammonia, and unaffected by 1 : 2000 (1 : 600) of pyridine or 1 : 2000 (1 : 400) of ammonia.

T. H. POPE.

Effect of different preparations of the quinine group on the enzymic functions of the organism. VII. Importance of the actual reaction of the medium in the investigation of enzymic processes. J. A. SMORODINZEV and A. N. ADOWA (Biochem. Z., 1927, **183**, 274—282).—The actual p_H of the medium during tryptic digestion of caseinogen in presence of quinine can be determined by the quinhydrone method, the indicator method proving unsatisfactory. Solutions of quinine hydrochloride, concentrations 0·05—0·0008M, give p_H values 6·20—5·97. Addition of quinine hydrochloride, in concentrations of 0·06—0·11%, does not change the actual reaction of Gross' digestion mixture, higher concentrations (0·5%), however, displacing the p_H to the acid side. Quinine hydrochloride inhibits tryptic digestion of caseinogen, an effect to be distinguished from its action through change of p_H. Addition of carbamide does not change either the p_H or the rate of digestion, and the influence of carbamide salts is entirely due to their effect on the p_H of the medium. High concentrations of quinine hydrochloride–carbamide displace the p_H to the acid side, whilst the inhibitory effect of small concentrations is explained by the action of quinine itself, and is not due to any change in p_H (cf. Biochem. Z., 1927, **181**, 149; A., 1926, 94, 202, 433, 640).

P. W. CLUTTERBUCK.

Raffinase. V. I. ISAJEV (Chem. Listy, 1927, **21**, 101—108, 141—148).—The optimum p_H for preparations of raffinase from malt is between 4·2 and 4·8, as for invertase. The temperature coefficient of the reaction is 1·5—1·8. Various antiseptics, such as sodium fluoride, chloroform, thymol, and toluene, very slightly retard the reaction of hydrolysis to lævulose and melibiose, whilst previous treatment of the enzyme extract with kaolin slightly accelerates hydrolysis, probably owing to selective adsorption of anti-catalysts. The optimum temperature for the action of raffinase is 40—45°. The addition to the reaction mixture of boiled extract slightly retards the reaction, whilst glycerol has a much stronger inhibitory action. The velocity of hydrolysis increases with concentration of enzyme, whilst the contrary is the case with greater concentration of substrate, owing to the greater concentration of end-products. That the products of reaction have an inhibitory effect is shown by the fact that the addition of lævulose and melibiose, separately or together, retards the velocity of hydrolysis. Dextrose, although not a product of this reaction, exerts a similar influence; this points to the identity of raffinase with invertase.

R. TRUSZKOWSKI.

So-called succino-dehydrase. A. BACH and D. MICHLIN (Ber., 1927, **60**, [*B*], 827—832; cf. Thunberg, A., 1918, i, 140, ii, 87; 1920, i, 784).—Bach's observation that enzymic reduction at the expense of water molecules and enzymic oxidation by molecular oxygen are two completely independent processes occasioned by different enzymes appears difficult to reconcile with the existence of "succino-dehydrase" (cf. *loc. cit.*), which causes dehydrogenation of succinic acid by means of methylene-blue and molecular oxygen. It is found that under the influence of succinic acid, about 300 times as much oxygen is absorbed by muscle as corresponds with the amount of reduced methylene-blue. Hydrocyanic acid has no influence on the methylene-blue reduction, whereas it restricts the absorption of oxygen. Inorganic buffer solutions (mixtures of phosphates and borates) at about p_H 7·4 and neutral salt solutions facilitate methylene-blue reduction, but do not affect the absorption of oxygen. The two processes must therefore be regarded as differing fundamentally from one another. Since the methylene-blue reduction ("residual reduction") occasioned by inorganic buffer solutions is of the same order of magnitude as the reduction caused by neutral succinate solutions, the supposed dehydrogenation of succinic acid in the methylene-blue experiment appears very doubtful.

Urease. I. H. VON EULER and E. BRUNIUS (Biochem. Z., 1927, **183**, 1—15).—No evidence could be obtained of the existence, in solutions of urease prepared from soya or Jack beans, of a specific co-enzyme, as suggested by Onodera (A., 1916, i, 228). The best purification of the enzyme was effected by adsorption on kaolin from 0·03N-acetic acid solution, recovery of the enzyme from the adsorbate by means of dilute sodium carbonate or ammonia, and dialysis of the resulting solution for 15 hrs.; this method yielded a preparation 5 times as active as the starting material. Aluminium hydroxide is also an efficient adsorbent, but, in this case, it is not possible to recover the enzyme in good yield.

C. R. HARINGTON.

Zymase in extracts from green tobacco leaves. A. FODOR and R. COHN (Z. physiol. Chem., 1927, **165**, 295—305).—Glycerol extracts of ripe, green tobacco leaves, free from cells and bacteria, will decompose added dextrose at 37° in phosphate buffer at p_H 6·4 with liberation of carbon dioxide. The extracts behave like weak zymase preparations. If the green leaves are kept for some days before the glycerol extracts are made, the zymase activity is diminished. Press juice from the leaves is inactive.

H. D. KAY.

Influence of carbon monoxide and light on indophenol oxydase of yeast-cells. D. KEILIN (Nature, 1927, **119**, 670—671).—None of the four different iron-porphyrin compounds of living yeast cells is responsible for the inhibition of respiration caused by carbon monoxide (Warburg, A., 1926, 1277), but the indophenol reaction of yeast is inhibited by boiling, by potassium cyanide, and by carbon monoxide. Warburg's respiratory ferment is thus a polyphenol or an indophenol oxydase system. The carbon monoxide–oxydase compound is dissociated and the oxydase re-activated by light. Carbon monoxide inhibits the indophenol oxydase of mammalian muscle, and the oxidation of pyrocatechol by an aqueous extract of oatmeal flour or of dry potato oxydase preparation. A. A. ELDRIDGE.

Alcoholic fermentation of dextrose solutions exposed to the action of ultra-violet rays. R. DE FAZI (Atti R. Accad. Lincei, 1927, [vi], **5**, 344—348).—Exposure of dextrose solutions to the rays from a quartz mercury-vapour lamp for periods up to 6 hrs. does not alter the optical rotation, but subsequent alcoholic fermentation of the solutions proceeds more rapidly and under purer conditions than with the untreated sugar solutions. The effect of the ultra-violet rays appears to be bactericidal.

T. H. POPE.

Action of surface-active materials on yeast fermentation. VII. H. ZELLER (Biochem. Z., 1927, **183**, 369—388).—Acetone, ether, and turpentine in moderate doses do not inhibit, whilst formamide accelerates fermentation. Methyl, ethyl, and amyl alcohols, paracetaldehyde, and amylene hydrate (concentrations of 1 : 40—1 : 80) inhibit with a preceding acceleration in smaller doses. Quinine and chloral hydrate (1 : 400—1 : 8000), chloralformamide (1 : 400), camphor (1 : 800), guaiacol and bromoform (1 : 1600), benzene and aniline (1 : 3200), toluene creosote, chloroform, and psicain (1 : 4000), thymol and cresol (1 : 8000) inhibit without preceding acceleration in smaller doses. Lysol (1 : 1600), hexetone (1 : 800), formaldehyde (1 : 4000), morphine (1 : 800), and eserine (1 : 2700) inhibit, but accelerate in smaller doses. Naphthalene and naphthol (1 : 16,000) inhibit, but in smaller doses accelerate as much as amyl and sodium nitrites, the inhibitory dose for the latter being 1 : 8000. Cantharidin (1 : 400,000) inhibits without any preceding acceleration. P. W. CLUTTERBUCK.

Combined action of two substances on yeast fermentation. VIII. H. ZELLER (Biochem. Z., 1927, **183**, 389—407).—The inhibitory actions on yeast fermentation of toluene, benzene, chloroform, carbon disulphide, and benzoic acid are additive, and phenol increases the inhibition of mercuric chloride, benzoic acid, and chloroform. Saponin and tannin partly decrease the inhibitory action of chloroform. Cantharidin inhibits very powerfully, the inhibition being partly prevented by addition of zinc acetate, calcium chloride, and sodium citrate, and wholly by ammonium acetate. Oxalic acid decreases the inhibition by toluene, but increases that by phenol. The effect on the rate of fermentation is also determined of adding sodium chloride or citrate, ammonium acetate, calcium chloride, chloral, or mercuric chloride, followed by arsenic, chloral, Witte's peptone, or mercuric chloride, and also when the order of addition is reversed. Fermentation is three times as rapid when peptone is followed by mercuric chloride as when this is followed by peptone, twice as rapid when sodium citrate is followed by mercuric chloride or when this is followed by ammonium acetate as *vice versa*, and is 1·5 times as rapid when sodium chloride is followed by arsenic, when sodium citrate is followed by arsenic, or when chloral is followed by ammonium acetate as when the order of addition is reversed. P. W. CLUTTERBUCK.

Acceleration of alcoholic yeast fermentation by animal charcoal. H. IVEKOVIC (Biochem. Z., 1927, **183**, 451—460).—The more rapid decomposition of sugar by yeast in presence of animal charcoal is caused by the acetaldehyde produced, which stimulates the reaction, and by the decreased concentration of carbon dioxide and alcohol, which are removed by adsorption. The withdrawal of alcohol amounts to 16—18%. P. W. CLUTTERBUCK.

Formation of pure *l*-lactic acid by fresh and dry yeast and of *dl*-lactic acid by yeast maceration juice. C. NEUBERG and M. KOBEL (Biochem. Z., 1927, **182**, 470—487).—The conversion of methylglyoxal into lactic acid by top and bottom fresh yeasts, dried yeast, and cell-free yeast maceration juice is followed quantitatively under varying conditions, with and without addition of sugar. Fresh yeasts react very much more slowly than the dried yeast and the maceration juice, and the reactions are accelerated by the presence of sugar. Whereas the reaction is quantitative without addition of sugar, in its presence about 5% of the aldehyde is reduced to *l*-propyleneglycol. Whereas with fresh yeast and dried yeast the lactic acid isolated as the zinc salt was almost pure (95%) *l*-lactic acid, that with maceration juice was inactive. P. W. CLUTTERBUCK.

Control of "bios" testing and the concentration of "bios." R. J. WILLIAMS, J. L. WILSON, and F. H. VON DER AHE (J. Amer. Chem. Soc., 1927, **49**, 227—235).—The activity of "bios" preparations largely depends on the strain of yeast from which the preparation was separated. The authors have chosen a strain of *Saccharomyces cerevisiæ* which can be easily duplicated. Their culture medium is suitable for this strain. Seeding should be small and growth period short if accurate testing of "bios" is to be secured. Under these conditions, there is no optimum concentration of "bios" for growth. The preparation of a very active material from a yeast extract is described. By treatment with fuller s

earth, an extract yields two fractions, each of which shows little activity alone, but the mixture produces growth approximating to that of the original extract. R. K. CANNAN.

Chemistry of bacteria. XIV. *Bacillus lactis aërogenes*. D. M. HETLER (J. Biol. Chem., 1927, **72**, 573—585).—*Bacillus lactis aerogenes* was grown on a synthetic medium; figures are given for the nitrogen and phosphorus distribution in various extracts of the de-fatted bacteria; the results obtained show a marked difference, according as the bacteria had been autoclaved or not; the difference could, in general, be ascribed to hydrolytic changes during this process. The nitrogen distribution of the alkali-soluble protein of the bacteria indicates that this protein is of a different nature from that which was similarly prepared (A., 1926, 1277) from tubercle bacilli. C. R. HARINGTON.

Bacterial decomposition of sugars on a trickling filter. J. H. WATKINS (Proc. Iowa Acad. Sci., 1925, **32**, 96).—A study of the ability of the organisms to utilise sugar without acid production, and to decompose lactic acid. CHEMICAL ABSTRACTS.

Formation of organic acids from sugars by *Aspergillus niger*. F. CHALLENGER, V. SUBRAMANIAM, and T. K. WALKER (Nature, 1927, **119**, 674; cf. this vol., 228).—When *Aspergillus niger* is grown on dextrose as the sole source of carbon, the solution contains saccharic acid. A. A. ELDRIDGE.

Fixation of molecular nitrogen by *Azotobacter agile*. S. KOSTYTSCHEV, A. RISKAL'CHUCK, and O. SHRETZOVA (Bull. Bur. Agric. Microbiol. [Russia], 1926, **1**, 91—108).—The process is one of reduction. *Azotobacter*, when grown in a nitrogen-free culture solution, contained ammonium- and amino-nitrogen; nitrate was reduced to ammonia. The reduction is apparently catalytic. CHEMICAL ABSTRACTS.

Proteolytic action of certain specific organisms on milk proteins in milk and synthetic butter. G. SPITZER, E. H. PARFITT, and W. F. EPPLE (J. Dairy Sci., 1927, **10**, 15—32).—The production of titratable acidity was usually maximal during the first 15 days. Organisms producing a high percentage of ammonia were usually also active in producing amino-acids and peptones. In synthetic butter there was a continuous increase in acidity, and during storage a continuous increase in amino-acids and peptones. The presence of dextrose and galactose may largely account for the retarded proteolysis of the proteins in milk. CHEMICAL ABSTRACTS.

Hydrogen sulphide production by bacteria. MULSOW and F. S. PAINE (Proc. Iowa Acad. Sci., 1925, **32**, 63—70).—The sulphur metabolism of bacteria is easily disturbed by a change in the nature or concentration of the sulphur compound. Sodium phite, sodium thiosulphate, and potassium sulphate, ut sodium sulphate, suffer bacterial reduction o hydrogen sulphide. CHEMICAL ABSTRACTS.

Formation of volatile sulphur compounds by ria. L. H. ALMY and L. H. JAMES (J. Bact., 1926, 12 —331).—A method for determining the of production hydrogen sulphide by bacteria in h th cultures is described. With *Proteus vulgarus*, five commercial peptones yielded hydrogen sulphide in the ratios 1 : 7 : 15 : 19 : 24; the gas was produced faster under aerobic conditions. Cystine gave practically the theoretical yield in 24 hrs. With *P. vulgarus*, *Salmonella aertrycke*, or *Bacillus coli*, mercaptans were not formed. CHEMICAL ABSTRACTS.

Mechanism of immunisation. IV. Dialysis experiments. B. SBARSKY and K. NIKOLAEV (Biochem. Z., 1927, **183**, 419—425).—A study of the dialysis of diphtheria toxin with and without addition of glycine and tyrosine indicates that the influence of amino-acids on the toxin is due, not to any chemical reaction with it, but to a protective action within the organism. P. W. CLUTTERBUCK.

Decomposition of toxins by soil organisms. W. A. GARDNER (Alabama Agric. Exp. Sta. Bull., 1926, No. 225, 1—38).—Vanillin, coumarin, pyridine, resorcinol, cinnamic acid, quinone, quinol, caffeine, piperidine, and benzidine are decomposed by soil organisms. The distribution of the organisms concerned is indicated. CHEMICAL ABSTRACTS.

Stain solubilities. I. Data in the literature. W. C. HOLMES (Stain Tech., 1927, **2**, 44—49).—The solubilities of 26 commonly used stains are given. H. W. DUDLEY.

Acid-fuchsin as a stain—a refinement in manufacture. J. T. SCANLAN, R. W. FRENCH, and W. C. HOLMES (Stain Tech., 1927, **2**, 50—55).—Rosaniline sulphonated between 80° and 85° gives the best results in staining by Van Gieson's method. The best mixture of acid-fuchsin and picric acid is 1 part of 1% aqueous solution of the former to 20 parts of a saturated aqueous solution of the latter. Details for the preparation and use of acid-fuchsin are given. H. W. DUDLEY.

Fate of sugar in the animal body. IV. Tolerance of normal and insulin-treated rats for dextrose and lævulose. C. F. CORI and G. T. CORI. **V. Seasonal ketonuria in fasting rats.** G. T. CORI and C. F. CORI (J. Biol. Chem., 1927, **72**, 597—614, 615—625).—IV. Dextrose can be injected into normal rats at a maximum rate of 2·5 g. per kg. per hr. without causing glycosuria; this maximum limit is not affected by a previous period of fasting during the winter, but is much lowered by similar treatment in the summer. The tolerance of mice for dextrose is about the same as that of rats when the sugar is injected intravenously; but whilst in the rat the maximum rate of absorption of dextrose from the intestine is below the maximum rate of utilisation, the reverse is the case in the mouse. The maximum tolerance of rats for lævulose is 0·35 g. per kg. per hr. when injected into the femoral vein, and 0·7 g. when injected into a mesenteric vein, under fasting conditions; under normal conditions, the rate is 0·65 g. Dextrose and lævulose are utilised at equal rates when injected in excess of the maximum tolerance. Injection of insulin raises the maximum tolerance of rats for dextrose by 20% and that of rabbits by 40%, but has no effect on the tolerance for lævulose.

V. The acetone excretion of fasting rats is 3 times as great in the summer, when the tolerance for dextrose is low (see above), as in the winter. This is not a

temperature effect. The lowered tolerance for dextrose is due to failure in oxidation and not in glycogen storage; it can be raised by administration of insulin, and appears, therefore, to be associated with decreased functional activity of the pancreas.

C. R. HARINGTON.

Effect of injected dextrose on tolerance. E. M. JORDAN (Amer. J. Physiol., 1927, **80**, 441—449).—Injection of dextrose into dogs at a rate exceeding the tolerance level tended to raise the tolerance of the animal. From the effects of insulin on animals subjected to continuous injection of dextrose at different rates, it is concluded that dextrose stimulates the secretion of insulin. R. K. CANNAN.

Action of insulin. II. A. BALTZER, E. GRAFE, and F. PARTSCH (Arch. exp. Path. Pharm., 1927, **120**, 359—370).—Applying Warburg's method to thin sections of the liver, the authors conclude that the action of insulin with regard to glycolysis, glycogenolysis, and respiration is the same whether experimental material is taken from a normal, depancreatised, or phloridzinised animal, provided that the organ is already poor in glycogen. W. ROBSON.

Action of insulin. II. Antagonism between insulin and adrenaline. B. VON ISSEKUTZ (Biochem. Z., 1927, **183**, 283—297).—A method is described for following the formation of sugar, acids, and carbon dioxide during perfusion of the surviving rabbit's liver. Liver rich in glycogen forms a considerable amount of sugar and acid, the falling as low as 5 unless sodium hydroxide is added to the perfusion liquid. Adrenaline accelerates both sugar and acid formation, the former action becoming important only when the p_H is below 7·5. Insulin does not, however, cause either glycogen synthesis or inhibition of sugar formation, but it decreases the formation of acid, probably accelerating its oxidation. Adrenaline cannot accelerate the formation of either sugar or acid in presence of insulin.

P. W. CLUTTERBUCK.

Action of insulin on the gastric secretion of diabetics. L. CANNAVÒ (Arch. Farm. sperim. Sci. aff., 1926, **42**, 134—138).—Insulin exerts no action on the acidity of the gastric secretion of diabetics.

T. H. POPE.

Blood-calcium as affected by insulin. J. C. BROUGHER (Amer. J. Physiol., 1927, **80**, 411—415).—In normal or parathyroidectomised dogs the blood-calcium was increased for about 2 hrs. after injection of insulin. R. K. CANNAN.

Effects of lowered body-temperature and of insulin on the respiratory quotients of dogs. W. H. FINNEY, S. DWORKIN, and G. J. CASSIDY (Amer. J. Physiol., 1927, **80**, 301—310).—Amytal anæsthesia greatly reduces the metabolic rate and causes a temporary fall in the respiratory quotient of dogs. Lowering the body temperature of an animal in which shivering has been suppressed reduces the quotient to values as low as 0·32. Although insulin will abolish shivering and so reduce the quotient, yet, when it is administered to dogs in which shivering has been prevented by other means, there follows a definite rise in the respiratory quotient.

R. K. CANNAN.

Influence of insulin on liver- and muscle-glycogen in the rat under varying nutritional conditions. A. D. BARBOUR, I. L. CHAIKOFF, J. J. R. MACLEOD, and M. D. ORR (Amer. J. Physiol., 1927, **80**, 243—272).—Standard white rats are suitable animals for such studies owing to the small variation in the concentrations of glycogen in liver and tissues when the animals are kept on a standard *régime*. When sub-convulsive doses of insulin were administered to rats which had been starved for 48 hrs., there was an immediate reduction in the glycogen of both liver and muscles. The muscle-glycogen remained depressed as long as the blood-sugar, but in the case of the liver an increase to, or above, the normal concentration occurred before recovery from hypoglycæmia. During active absorption of carbohydrate, large doses of insulin notably retarded the rate of deposition of glycogen in the liver, but stimulated that in the muscles. Smaller doses—sufficient to prevent alimentary hyperglycæmia—still retarded the accumulation in the liver and prevented any important increase in the muscles. The fate of the sugar disappearing from the blood of normal animals under the influence of insulin is considered.

R. K. CANNAN.

Decrease in sugar metabolism and destruction of insulin by ultra-violet irradiation. W. E. BURGE and G. C. WICKWIRE (J. Biol. Chem., 1927, 72, 827—831).—The normal rate of utilisation of dextrose, lævulose, and galactose by *Paramœcium caudatum* is depressed by irradiation with ultra-violet light. This effect is abolished by addition of insulin to the medium, and is thought to be due to the destruction of insulin in the living cells by the irradiation. Such a destruction has been shown to occur *in vitro*.

C. R. HARINGTON.

Dissolution of insulin into two new active substances. C. FUNK (Science, 1927, **65**, 39—40).—On fractionation, insulin yields insulin-*A* and -*B*; the former, which is present in the greater proportion, decreases the blood-sugar of normal rabbits, decreases the blood-sugar of rabbits having a high initial blood-sugar value, but increases that of rabbits with low initial blood-sugar values, or has no effect. Insulin-*B* causes lasting increases in blood-sugar and dilution of the blood with large retention of water.

A. A. ELDRIDGE.

Importance of minute chemical constituents of biological products. Nickel, cobalt, and insulin. G. BERTRAND (Science, 1926, **64**, 629—630).—An address delivered before the American Chemical Society on September 9, 1926.

Thyroid apparatus. Rôle of thyroid and parathyroid glands in chemical differentiation of bone during growth. XLIV. Ash, organic matter, and water. XLV. Calcium, magnesium, and phosphorus. F. S. HAMMETT (J. Biol. Chem., 1927, 72, 505—525, 527—544).—XLIV. The bones of rats which have been subjected to thyroidectomy at an early stage of growth show a higher content of water and organic matter and a lower content of ash than those of normal rats of the same age; the relationships are reversed, however, if the comparison be made with normal rats of the same size, and the

changes are therefore to be ascribed to a general retardation of growth rather than to a lessened degree of ossification. Parathyroidectomy at all stages of growth in the female reduces the degree of ossification and has the same effect in the male before puberty; in the male after puberty, the effect is reversed.

XLV. Parathyroidectomy in young rats causes a decrease in the calcium and phosphorus and an increase in the magnesium of the bones, as compared with those of normal rats; the effect on the magnesium is the most marked. Similar, but less definite changes were observed when the thyroid was removed simultaneously with the parathyroids.

C. R. HARINGTON.

Fat-soluble vitamins. XXVII. Determination of vitamin-*A*. H. STEENBOCK and K. H. COWARD (J. Biol. Chem., 1927, **72**, 765—779).—In the determination of vitamin-*A*, vitamin-*D* is best supplied by irradiation of the basal diet or by addition of irradiated cholesterol, and occurrence of ophthalmia forms a better criterion of depletion of the animal's store of vitamin-*A* than cessation of growth. Yellow maize is comparatively rich in vitamin-*A*, which is contained chiefly in the endosperm; whole wheat, white maize, and oats are poor in vitamin-*A*.

C. R. HARINGTON.

Influence of light and heat on formation of vitamin-*A* in plant tissues. K. H. COWARD (J. Biol. Chem., 1927, **72**, 781—799).—The process of germination of grains is not accompanied by formation of vitamin-*A*, but the latter is present, in small amount, in seedlings grown in the dark to a height of 10—12 cm., the amount being lower the higher the temperature during growth. Exposure of the seedlings to the light of a mercury-vapour lamp markedly increases their vitamin-*A* content, the effect being due to the visible rays; no deleterious effect on the vitamin was observed as the result of prolonged irradiation. C. R. HARINGTON.

Action of light on cod-liver oil. P. R. PEACOCK (Lancet, 1926, ii, 328—330).—When cod-liver oil is exposed to white light, its fluorescence gradually disappears ("delumination"); before delumination is complete, the arsenic chloride test for vitamin-*A* fails. Deluminated oil, when kept in the dark, slowly regains its fluorescence, but the vitamin-*A* is permanently destroyed. There is a change in the absorption spectrum corresponding with the change in fluorescence. A. A. ELDRIDGE.

Vitamins-*A*, -*B*, and -*C* in green plant-tissues other than leaves. E. J. QUINN, M. P. BURTIS, and E. W. MILNER (J. Biol. Chem., 1927, **72**, 557—563).—Green French beans and green peppers contain about the same amount of vitamins-*A* and -*B* as lettuce, but less than spinach. The vitamin-*C* content of green peppers is 4 times as high as that of French beans, and is as great as that of any other plant-tissue hitherto examined. C. R. HARINGTON.

Vitamin-content of wheat- and rye-germ. A. SCHEUNERT (Biochem. Z., 1927, **183**, 113—121).—Wheat- and rye-germ contain moderate amounts of vitamins-*A* and -*B*, the quantity of both being slightly greater in rye; vitamin-*C* is absent in both cases.

C. R. HARINGTON.

Fat-soluble vitamin content of egg-yolk in relation to diet. R. M. BETHKE, D. C. KENNARD, and H. L. SASSAMAN (J. Biol. Chem., 1927, **72**, 695—706).—The fat-soluble vitamin content of egg-yolk varies with the vitamin content of the hens' diet; administration of 2% of cod-liver oil caused a 500% increase in the concentration of vitamins-*A* and -*D* in the egg-yolk. C. R. HARINGTON.

Influence of the p_H of the nutrient medium on the amount of vitamin-*B* formed by *Bacillus vulgatus*. A. SCHEUNERT and M. SCHIEBLICH (Annalen, 1927, **453**, 249—258).—In continuation of previous work (Biochem. Z., 1923, **139**, 57) *Bacillus vulgatus* has been grown in a modification of Maassen's solution containing carbamide, sucrose, citrates, and inorganic salts, precautions being taken against initial introduction of vitamin-*B*. Preliminary sterilisation renders the solution alkaline. If the p_H of the solution when inoculated is 7·0, a thick, greyish-red bacterial skin is rapidly formed, but above p_H 7·6 the growth is greenish-white in colour. Measurement of the rate of growth of albino rats on a vitamin-*B*-free basal diet to which the air-dried bacterial mass is added indicates that vitamin-*B* is present in cultures of the first type, but only slightly, or not at all in those of the second. *B. vulgatus* is therefore capable of synthesising vitamin-*B*, but only at hydrogen-ion concentrations around p_H 7·1. All cultures were free from vitamin-*A*. H. E. F. NOTTON.

Formation of vitamin-*B* by *B. vulgatus* Migula in vitamin-free media. A. SCHEUNERT and M. SCHIEBLICH (Biochem. Z., 1927, **184**, 58—66).—Dried *B. vulgatus* (0·2—0·4 g.) which had been grown on a medium free from vitamin and containing only mineral salts, synthetic malic acid, and a maize starch shown in animal experiments to be free from vitamin, was sufficient to maintain growth of rats over an experimental period of 62 days. The bacillus, therefore, must be able to synthesise vitamin-*B*.

P. W. CLUTTERBUCK.

Antirachitic substances. VI. Distribution and possible origin of vitamin-*D*. C. E. BILLS (J. Biol. Chem., 1927, **72**, 751—758).—The widespread occurrence of vitamin-*D* in the liver oils of fish, together with its increase with the age of the fish and its excess over the vitamin content of the diet, suggest that the vitamin may be synthesised by the fish. The vitamin-*D* content of catfish oil was not affected either by exposure of the fish to irradiation or by exclusion of light. C. R. HARINGTON.

Condition of chlorophyll in the living plant. Rôle of iron in carbon dioxide assimilation by green plants. K. NOACK (Biochem. Z., 1927, **183**, 135—152, 153—175).—Chlorophyll is adsorbed from aqueous solution by colloidal aluminium hydroxide, but the adsorbate fails to show the red fluorescence characteristic of the chloroplasts of plants; the red fluorescence is, however, observed in preparations obtained by adsorbing chlorophyll from solution in light petroleum by means of dry colloidal aluminium hydroxide or dry lipin-free globin. By fractional centrifugation of a mixture of green leaves ground up with water and calcium carbonate, the disintegrated

chloroplasts were obtained as a green mass, which, on treatment with water, gave a colloidal solution exhibiting red fluorescence. Addition of ammonium sulphate or salts of heavy metals produced a precipitate which retained the fluorescence; the latter was, however, lost on short heating, either of the original solution or of the precipitate, at 100°. On the other hand, more prolonged heating of the solution caused a restoration of the fluorescence. It therefore appears that the red fluorescence is dependent on the existence of chlorophyll in the molecular disperse condition, either adsorbed on protein, as in the above solution before heating, or dissolved in lipins as in the same solution after prolonged heating; in the living plant, it is probably adsorbed on the proteins of the chloroplasts.

The photo-oxidation of benzidine by eosin, previously shown to be accelerated by manganous salts, is also accelerated by ferrous salts, but in much smaller concentration; concentrations of ferrous salts equal to the optimum concentrations of manganous salts cause complete inhibition of the reaction. Copper salts are active in still lower concentrations. A similar accelerating effect of iron salts is observed in the photo-oxidation of benzidine by chlorophyll. The accelerating effect of the iron in these reactions is abolished by the presence of hydrogen sulphite or cyanide. By analogy, therefore, it is thought that the function of the fluorescent chlorophyll in the chloroplasts of plants may be the activation of iron, which presumably plays a part in the process of carbon dioxide assimilation. C. R. Harington.

Composition of honey-dew. E. Schoofs (Bull. Soc. chim. Belg., 1927, **36**, 119—123).—A sample of honey-dew contained 56% of dextrin and gummy materials, 14% of reducing sugar (the osazone, m. p. 204·5°, confirms that this is mainly dextrose), 2·6% of sucrose, 2·98% of proteins, 2·92% of inorganic matter (largely phosphates), 3·19% of vegetable debris, and 2·2% of substance soluble in concentrated alcohol. A preliminary extraction with light petroleum gave 0·097% of a fatty substance, m. p. 61°. C. Hollins.

Absorption of ions by citrus and walnut seedlings. A. R. C. Haas and H. S. Reed (Hilgardia, 1926, **2**, 67—106).—The seedlings remove more cation than anion from solutions of single calcium salts; calcium salts are readily absorbed in absence or deficiency of sodium and potassium. Acid culture solutions do not always tend to become neutral, or neutral solutions to become acid. Chemical Abstracts.

Mode of formation of sucrose in the beet. H. Colin (Compt. rend., 1927, **184**, 835—837).—In view of the presence of only traces of pentoses in the mixture of reducing sugars present in the leaves and stem of the beet (cf. Colin and Franquet, this vol., 599), the dextrorotatory power of the mixture is attributed to excess of dextrose. Condensation of the reducing sugars to sucrose is connected with the life processes of the plant, and does not take place in the boiled pulp. The vascular rings of the stem are richer in sucrose than the parenchyma and contain only traces of reducing sugar. R. Brightman.

Acids formed by species of *Rhizopus*. T. Takahashi and T. Asai (Proc. Imp. Acad. Tokyo, 1927, **3**, 86—89).—Confirmation is obtained of the view that gluconic acid is an intermediate product in the degradation of dextrose by *Rhizopus*. The cultivation of either of two species at 25—30° for 45—75 days in solutions containing calcium gluconate, together with a little free gluconic acid and ammonium sulphate or peptone, produces formic, acetic, fumaric, and succinic acids, ethyl alcohol, and acetaldehyde. A similar culture oxidises calcium acetate to succinic acid in 60 days. J. M. Gulland.

Fission of α-aminophenylacetic acid by *Oidium lactis*. M. Chikano and T. Kitano (Z. physiol. Chem., 1927, **164**, 217—225).—By the action of *Oidium lactis* on *dl*-α-aminophenylacetic acid, the *d*-acid is converted into a mixture of *l*-mandelic acid and phenylglyoxylic acid, and eventually into benzoic acid. Phenylglyoxylic acid and *l*-mandelic acid are interconvertible by the same means. Phenylglyoxal in similar manner yields benzoic acid and an unidentified substance, m. p. 62°. Benzoic acid is not attacked by the fungus. C. Hollins.

Relation of soil to plant cell sap. M. M. McCool (Michigan Agric. Exp. Sta., Quarterly Bull., 1926, **9**, 60—64).—The cell sap of plants grown on fertilised soil shows greater f. p. lowering than the sap of plants from check plots. The phosphorus content of cell sap appears to be affected by soil type as well as by fertilisation. It further appears that the inorganic phosphorus content of cell sap varies with the time of day, the amount being greater in the morning than later in the day. Chemical Abstracts.

Factors controlling the rate of nitrification of organic materials. A. L. Whiting (J. Amer. Soc. Agron., 1926, **18**, 854—876).—In general nitrogenous materials containing much total or water-soluble nitrogen are easily nitrified. Green or young plants nitrify more rapidly than dry or old ones. The relation of carbon to the production of nitrates in the early stages of nitrification is in question. Chemical Abstracts.

Deficiencies of nitrogen metabolism in plants. R. C. Burrell (Bot. Gaz., 1926, **82**, 320—328).—Plants deficient in magnesium are not characteristic in appearance or chemical composition. Deficiency of potassium causes marked physical differences and an accumulation of starch in the leaves. Deficiency of calcium produces small, yellow plants and comparatively small root development; nitrate accumulates in the leaves. Chemical Abstracts.

Physiological acidity of ammonium nitrate. D. Prianischnikov (Biochem. Z., 1927, **182**, 204—214).—Plants normally take up ammonia more rapidly than nitric acid from a solution of ammonium nitrate, and the nutrient solution therefore becomes increasingly acidic the larger the root mass of the plant. Exceptions occur when the synthetic power of the plant, *e.g.*, the formation of asparagine and glutamic acid from ammonia, is impaired, as when the carbohydrate supply is exhausted, or if it is diminished and at the same time nitrogen is present in excessive quantity. Similar conditions arise if acids or anæsthetics are present. J. Pryde.

Importance of carbon dioxide for the plant cell. Experiments with *Aspergillus niger*. A. RIPPEL and H. BORTELS (Biochem. Z., 1927, **184**, 237—244).—*Aspergillus niger* develops poorly in an atmosphere deprived of carbon dioxide, and it is concluded that carbon dioxide is itself necessary to the plant cell. P. W. CLUTTERBUCK.

Relation of the protein content of maize to its specific gravity. F. T. SHUTT (Dep. Agric. Canada Rep. Dom. Chem., [1925], 1926, 34).—The highest individual specific gravity of the samples was associated with the highest percentage of protein. CHEMICAL ABSTRACTS.

Physiological studies of the grape. I. Anatomy and distribution of primary chemical constituents. II. Enzymes. III. Respiration. IV. Transpiration. V. Factors affecting the keeping quality. VI. Bursting of berries. VII. Diurnal variations in humidity, temperature, and root pressure. F. J. DE VILLIERS (Dep. Agric. Union S. Africa Sci. Bull., 1926, **45**, 6—15; 15—28; 28—49; 49—62; 62—74; 74—79; 79—85).—I. Reducing sugars are more or less uniformly distributed throughout the fruit, except near the primary and secondary vascular strands. Tannins disappear from the mesophyll during maturation and become confined to the regions of the vascular tissues and sub-epidermal layers. The pigment of the berry of *Vitis vinifera* is œnin; pigmentation depends on cell acidity, the action of an oxidising enzyme, and on light.

II. During maturation, catalase activity increases and finally diminishes slightly; oxydase activity decreases. The catalase of grapes is very sensitive to changes of p_H. Enzyme activity is maximal at 40°.

III. An accurate method for measuring the rate of respiration of fruit is described. The rate of respiration decreased as maturity was approached; removal of 40% of the water did not affect metabolism. The thermal coefficient of the respiratory activity of grapes corresponds approximately with that for a unimolecular reaction. CHEMICAL ABSTRACTS.

Influence of early and late planting and sprouting on the yield and dry matter content of potatoes. F. T. SHUTT (Dep. Agric. Canada Rep. Dom. Chem., [1925], 1926, 42). CHEMICAL ABSTRACTS.

Correlation between specific gravity, total solids, and starch content of potatoes. F. T. SHUTT (Dep. Agric. Canada Rep. Dom. Chem., [1925], 1926, 65). CHEMICAL ABSTRACTS.

Chemistry of tea leaves. II. Isolation of guanine nucleotide and cystosine nucleotide. H. O. CALVERY (J. Biol. Chem., 1927, **72**, 549—556; c. A., 1926, 982).—The mixed nucleotides from tea eaves were purified through the lead salts in the usual way and converted into the ammonium salts. eatment of the solution with alcohol yielded an insoluble fraction from which guanine nucleotide was isolated by the method of Buell and Perkins (this vol., 584), and a soluble adenine fraction from which, by means of the brucine salt, cytosine nucleotide was prepared. C. R. HARINGTON.

Coumarin content and nutritive value of selected types of sweet clover. F. T. SHUTT (Dep. Agric. Canada Rep. Dom. Chem., [1925], 1926, 37—42).—The coumarin content in autumn cuttings in the year of seeding was 0·81—1·08% (leaf) and 1·23—1·43% (stalk); for the first and second cuttings in the second year, the values were: 0·25—1·06, 0·57—1·06% (leaf), and 0·28—1·04, 0·35—1·24%, respectively. The percentages of protein, fibre, ash, etc. are also recorded. CHEMICAL ABSTRACTS.

Lignin. I. Metalignin, a new type of alkali lignin. C. DORÉE and E. C. BARTON-WRIGHT (Biochem. J., 1927, **21**, 290—300).—A new type of lignin—*metalignin*—$C_{20}H_{20}O_6$, m. p. 186°, has been obtained from spruce. The sawdust was previously well extracted with benzene, alcohol, and water in succession. It was then digested with a 5% solution of sodium hydroxide for 36 hrs. to remove hemicelluloses. The purified sawdust was finally treated in an autoclave with a 4% sodium hydroxide solution at 8 atm. for 1 hr. The metalignin was then precipitated with hydrochloric acid. The *monobenzoyl*, *monoacetyl*, and *methyl* derivatives, and the *dioxime* were prepared. Metalignin, which differs in its solubility in organic solvents from lignins previously described, contains one hydroxyl, two methoxyl, and two carbonyl groups, and apparently two double linkings. It agrees in composition with the α-lignin of Klason (A., 1920, i, 821). The above method of extraction of lignin is not quantitative (cf. Mehta, A., 1926, 209). S. S. ZILVA.

Comparative plant chemistry. XVI. Latex-bearing plants. II. J. ZELLNER [with E. HUPPERT, R. KLAPHOLZ, K. M. KNIE, O. POLLATSCHEK, A. SPITZER, J. RICHLING, and M. STEIN] (Monatsh., 1926, **47**, 681—707).—The whole of the air-dried plant, *Taraxacum officinale*, Wigg., was examined (cf. Power and Browning, J.C.S., 1912, **101**, 2411). The light petroleum extract (3·15%) gave the following products when hydrolysed: ceryl alcohol, α- and β-lactucerol, stearic, palmitic, oleic, linoleic, and phosphoric acids, also glycerol and choline, indicating the presence of lecithin. The alcohol extract (9·49%) contained phlobaphens, tannin (2·81%), and dextrose (3·33%), lævulose being absent. The aqueous extract (35·13%) contained polysaccharides precipitable by alcohol (1·79%), tartaric acid, sulphate, phosphate, and chloride. Soluble mineral matter (7·56%), crude fibre (16·13%), total nitrogen (1·55%), total ash (14·78%), and free acid (2·07%) were also present. The latex contained 69·1% of water. The petroleum extract of the dried latex contained caoutchouc and a mixture of esters, from which, after hydrolysis, pure α-lactucerol (taraxasterin), m. p. 217°, $[\alpha]$ +97·4° [acetate, m. p. 250°; propionate, m. p. 221° (decomp.); benzoate, m. p. 257°(decomp.)], and impure β-lactucerol, m. p. 155° (acetate, m. p. 210°), were isolated. The alcohol extract contained inactive inositol, reducing sugars, and a bitter principle.

The light petroleum extract of the latex of *Lactuca sativa*, L., was apparently free from caoutchouc, but contained esters of α- and β-lactucerol from which the latter was obtained pure. The alcohol extract contained inositol.

Caoutchouc, α- and β-lactucerol, ceryl alcohol, and

traces of acetic acid and solid fatty acids were obtained in a similar way from the latex of *Sonchus asper*, L. (cf. A., 1926, 646), whilst the alcohol extract contained inositol and mannitol.

Tragopogon pratensis, L., is relatively rich in latex. The light petroleum extract of this contained caoutchouc, ceryl alcohol (?), and *substances*, (*a*), m. p. 193°, (*b*), m. p. 280°, and (*c*), m. p. 118—120°, which are hydrolysed to amorphous resin acids and (*a*) α-lactucerol, (*b*) β-lactucerol, and (*c*) a mixture of the two, respectively. The alcohol extract contained inositol, mannitol, tannin-like substances, and a *compound*, m. p. 120°.

The fresh latex, obtained in small yield from *Cichorium endivia*, contains oxydases. Caoutchouc, ceryl alcohol, α- and β-lactucerol, probably in combination with higher fatty acids, and inositol were also present. Extraction with cold 2% sodium hydroxide gave a protein-like substance.

The latex of *Cichorium intybus* contains 64% of water. Light petroleum extracted (*a*) caoutchouc, (*b*) a mixture of esters from which *substances*, m. p. 118—120°, m. p. 175°, and m. p. 194°, were separated. Hydrolysis of the whole mixture gave α- and pure β-lactucerol, m. p. 152°, [α] +48·2° or 49·5° (acetate, m. p. 282°), with acetic and stearic acids. Alcohol extracted a bitter *principle*, m. p. 215°, [α] +56·2°, apparently identical with lactucin (Kromayer, Arch. Pharm., 1861, **155**, 6), a *compound*, $C_{20}H_{32}O_{16}$, m. p. 104°, a *compound*, m. p. 205°, [α] +87·3°, potassium hydrogen oxalate, potassium trihydrogen oxalate, mannitol, and invert-sugar containing an excess of lævulose.

The latex of *Scorzonera hispanica*, L., contained caoutchouc, α- and β-lactucerol as acetates, inositol, and lactucin. The presence of both α- and β-lactucerol in all the specimens hitherto examined is noteworthy, although pure samples of both have not yet been isolated from any one plant. This is probably due to the great difficulty of separating them from one another, and this fact also accounts for the differing physical constants recorded by previous authors for these substances and their acetates. The so-called lactucons (*loc. cit.*) are now shown to contain esters of resin acids and the higher fatty acids as well as acetates.

H. E. F. Notton.

Chemical constituents of native (Austrian) herbs. J. Zellner [with J. Falkowsky, H. A. Spitzer, and E. Taschner] (Arch. Pharm., 1927, **265**, 27—41; cf. A., 1925, i, 763).—*Galeopsis ochroleuca*, Lam., as dried for the market, contains: light petroleum extract, 3·62%; ether extract, 3·12%; alcohol extract, 15·30%; water-soluble matter, 25·26%, of which mineral matter accounts for 1·13%; polysaccharides, 3·12%; reducing sugars, 1·69%; free acids (as KOH), 2·45%; protein, 15·31%; fibre, 20·16%; ash, 5·19%. Of the light petroleum extract, 22·72% is not hydrolysable, and consists of a paraffinic hydrocarbon, m. p. 69°, similar to that already found in *Tussilago*. There are also present a phytosterol, m. p. 135°, oleic, stearic, and other fatty acids, resins, resin acids, and phlobaphens. That portion of the alcohol extract which is soluble in water contains a bitter glucoside (fructoside), yielding on hydrolysis a compound closely resembling menyanthin (*loc. cit.*), to the presence of which the medicinal value of the herb may be due. Pectins, tannins, and other compounds are also present. *Impatiens noli tangere*, L. (air-dry), contains: light petroleum extract, 4·67%; ether extract, 2·03%; alcohol extract, 9·41%; water-soluble matter, 28·14%, of which mineral matter accounts for 10·58%, and polysaccharides, 1·20%; reducing sugars, 4·30%; free acids (as KOH), 0·73%; total nitrogen, 2·69%, equivalent to protein, 16·84%; fibre, 25·0%; methylpentosans, 12·05%; ash, 12·02%. There are present in the extracts obtained by using organic solvents, carotene, ceryl alcohol, a sterol, m. p. 165—166°, possibly stigmasterol, fatty acids (palmitic and stearic), glycerol, and phosphoric acid. The aqueous extract contains invertase. Resin acids, phlobaphens, tannins, dextrose, and lævulose, choline, and polysaccharides (yielding galactose and pentoses on hydrolysis) were also isolated. A commercial sample of dried roots of *Bryonia dioica*, Jacq., gave the following results (cf. for *Bryonia alba*, L., Girardet, A., 1924, i, 1269). From the light petroleum extract, ceryl alcohol, phytosterol (m. p. 134—135°), another sterol (m. p. 159°; C, 84·83%; H, 12·79%), possibly stigmasterol, or the parent compound of bryonol (cf. Power and Moore, J.C.S., 1911, **99**, 937; and also Silber, Dissertation, Erlangen, 1894); carotene, fatty acids (saponification value, 2·05; iodine value, 61·7), including oleic, palmitic, and myristic acids; glycerol and phosphoric acid were also isolated. The ether extract contained, besides unidentified compounds, a substance ($C_{10}H_{16}O$) of m. p. 300—301°, showing the reactions of phytosterol, and resembling urson or caryophyllin (cf. Trier, "Chemie der Pflanzenstoffe," 1924, 575). This compound apparently undergoes dehydration when treated with acetic anhydride, being converted into two *compounds*, of m. p. 173° and 231—232° ($C_{30}H_{46}O_5$), respectively. However, no sure indication that a hydroxyl group is present was obtained. The compound, provisionally termed *α-bryon*, is apparently simultaneously oxidised and nitrated when treated with nitric acid, for the product is a strong *acid*, m. p. 121—122°, containing nitrogen. A trichloroethylene extract of the root yields another compound (m. p. 292—293°), which also is a sterol and resembles, but is not identical with, the above α-bryon. This is termed *β-bryon*, and has the composition $(C_{10}H_{16}O)_n$, where n is possibly 4. The (di)*acetyl* derivative has m. p. 227—228°, and the (mono)*methyl*, m. p. 162—163°. When β-bryon is treated with nitric acid, an amorphous acid of m. p. about 166° is produced. The powdered root, after this extraction with trichloroethylene, now yields to 80% alcohol two more compounds, together with other substances. The first of these is a bitter compound, m. p. 128°, soluble in water, apparently bryogenin (Silber, *loc. cit.*); the second (m. p. 81—83°) is amorphous, insoluble in water, and has the properties of an alkaloid. It is hydrolysed by alcoholic potassium hydroxide to tiglic acid and a base resembling cevadin or sabadillin. The name bryonicin, already used by Konninque and Maquart (Ber., 1871, **4**, 921), has been given to this compound. Tannins and invert-sugar are also obtained from extracts of *Bryonia*.

W. A. Silvester.

Japanese plants. VIII. Occurrence of free pentose in bamboo shoots. S. KOMATSU and Y. SASAOKA (Bull. Chem. Soc. Japan, 1927, 2, 57—60).—From 10 litres of juice, freshly expressed from shoots of *Phyllostachys quilioli*, crystalline dextrose (43 g.) and *l*-xylose (5·4 g.) were isolated, this being the first direct extraction of crystalline pentose from vegetable tissue. The juice also contained glycuronic acid and pectins. B. W. ANDERSON.

Alleged free pentoses of leaves. H. COLIN and R. FRANQUET (Bull. Soc. Chim. biol., 1927, 9, 114—116).—The observations of Davis and Sawyer (B., 1916, 374) that the leaves of the potato and beet contain free pentoses to the extent of more than 5%, and even up to 25%, of the total sugars is not confirmed. The tests used for the detection of free pentose are the reaction with β-naphthol and the furfuraldehyde test. The results indicate that if pentoses are present in the leaf in the free state, the amount is very small. A. WORMALL.

Distribution of glucosides in western Canadian plants. D. R. MCCULLAGH (Trans. Roy. Soc. Canada, 1926, III, 20, [v], 331—338).—A number of native plants of western Canada have been studied by means of Bourquelot's enzymic methods. Extracts of the fresh plant-tissue have been subjected to the action of invertase and then emulsin, and in each process the ratio between the increase in reducing power and the change in optical activity has been measured. The ratios or indices obtained give definite indications of the presence of certain glucosides. Sucrose is present in nearly all the 13 plant species examined. β-Glucosides, hydrolysable by emulsin, are present in 11 of the species, and of this number 8 contain glucosides which have possibly not yet been isolated. The results from two plants suggest either the presence of tri- or tetra-saccharides or of glucosides of lævorotatory sugars.
A. WORMALL.

New glucoside in the root of *Peucedanum decursivum*, Maxim. I. J. ARIMA (J. Chem. Soc. Japan, 1927, 48, 88—93).—By extracting the root (500 g.) of Nodake (*P. decursivum*, Maxim) with 2 litres of cold 1% sulphuric acid for 1—2 days, a new glucoside, *nodakenin*, $C_{20}H_{24}O_9$ ($+H_2O$), m. p. 215°, $[\alpha]^{20}$ +56·6°, was isolated in 0·4% yield from 95% alcohol. Hydrolysis decomposes it into 1 mol. of dextrose and 1 mol. of *nodakenetin*, $C_{14}H_{14}O_4$, m. p. 185°, $[\alpha]_D^{20}$ −22·4° (*acetyl* derivative, m. p. 129—130°); nodakenetin contains a hydroxyl group, a stable lactone ring, and a double linking. K. KASHIMA.

Glucofrangulin. Reply to Bridel and Charaux. E. CASPARIS and R. MAEDER (Bull. Soc. Chim. 324—326; cf. Casparis, J. Suisse de Pharm., 1926, 49; Bridel and Charaux, Bull. Soc. Chim. biol., 1926, 8, 655—663).—Polemical.
W. O. KERMACK.

d-Mannitol from *Gardenia turgida*. M. O. [illegible]ST and N. RAO (J. Indian Inst. Sci., 1927, 9A, 207).—See A., 1925, i, 1295.

Presence of free methyl salicylate in some American species of *Polygala*. E. T. WHERRY (J. Washington Acad. Sci., 1927, 17, 191—194).—Twenty-seven species and sub-species of the genus *Polygala* native to the eastern United States have been found, with a single exception, to contain some substance, probably the glucoside gaultherin, from which methyl salicylate is readily set free.
E. A. LUNT.

Mineral constituents of the cotton plant. J. S. MCHARGUE (J. Amer. Soc. Agron., 1926, 18, 1076).—Copper, iron, manganese, zinc, calcium, magnesium, phosphorus, potassium, sodium, sulphur, and nitrogen are present (total, 185 lb. per acre). Nitrogen, calcium, and potassium are present in the (nearly equal) largest quantities; the proportion of sodium is greater than that of phosphorus or magnesium. Copper (0·4 lb. per acre), manganese (0·1 lb. per acre), and zinc (0·16 lb. per acre) are probably vitally concerned in the production of cotton.
CHEMICAL ABSTRACTS.

Effect of phosphorus on composition of tomato plants. J. H. MACGILLIVRAY (J. Agric. Res., 1927, 34, 97—127).—The effect of phosphorus starvation on tomato plants (grown normally from seed for about 8 weeks and then transplanted to sand and supplied with nutrient solutions) is to decrease the percentage of phosphorus in all parts of the plant, although, as in plants with an ample supply of phosphorus, the regions of growth contain the highest percentage. There is a re-utilisation of the phosphorus present, and, regardless of treatment, about half the total amount is found in the fruit. The size and number of the fruits are decreased by phosphorus starvation, a high proportion of the flowers falling. There is an increase in the percentage of total nitrogen, confined mainly to water-soluble nitrogen, excluding nitrates; the coagulable nitrogen shows a decrease. The plants grown in absence of phosphorus showed a large increase in the percentage of sugars present; they approximately trebled their dry weight in 52—55 days of growth. C. T. GIMINGHAM.

Phosphate ion as a promoter catalyst of respiration. C. J. LYON (J. Gen. Physiol., 1927, 10, 599—615).—The effect of phosphates on the rate of production of carbon dioxide by *Elodea canadensis* appears to depend on the potential of the phosphate ion. Quantitative experiments verify an equation deduced theoretically on this basis. The effect of phosphates on other enzyme actions such as the oxidation of pyrogallol by hydrogen peroxide in presence of per oxydase and the hydrolysis of a number of esters by lipase preparations is shown to conform to a similar equation. W. O. KERMACK.

Arsenate as a catalyst of oxidation. C. J. LYON (J. Gen. Physiol., 1927, 10, 617—622).—Arsenate exerts a catalytic effect on the oxidation of pyrogallol by atmospheric oxygen, on the catalytic oxidation of pyrogallol by metallic iron, and on the production of carbon dioxide by *Elodea canadensis*.
W. O. KERMACK.

Effect of ethylene on the enzymes of pineapples. L. O. REGEIMBAL and R. B. HARVEY (J. Amer. Chem. Soc., 1927, 49, 1117—1118).—The total sugars of pineapples are decreased, and the direct-reducing sugars increased, by ripening with ethylene or propylene, the latter being the more effective, due

to increase in the activity of the invertase. The activity of the proteolytic enzymes is also increased by the above treatment. F. G. WILLSON.

Toxic principle of *Erythrophlæum lasianthum*. P. KAMERMAN (S. African J. Sci., 1926, **23**, 179—184).—An alkaloid has been isolated from this tree the bark and pods of which are used by "medicine men" under the name Um-Kwangu. It is apparently identical with erythrophleine isolated by Power and Salway from "sassy bark." The physiological action, toxicity, properties, and concentrations in the bark and pods are recorded. R. K. CANNAN.

Toxicity of genus *Cotyledon*, cause of the disease "krimpsiekte." P. KAMERMAN (S. African J. Sci., 1926, **23**, 185—187).—From the leaves was obtained a material which was not an alkaloid or glucoside, but resulted in "krimpsiekte" when given to goats. It is suggested that it belongs to the picrotoxin group of nerve poisons.
R. K. CANNAN.

Sikimitoxin, the toxic principle of *Illicium religiosum*, Sieb. (Mang-t'sao). T. Q. CHOU (Chinese J. Physiol., 1927, **1**, 213—218).—A white, amorphous substance of indefinite m. p. has been isolated from *Illicium religiosum*. It contains no nitrogen, is soluble in cold water, and is feebly acidic. The substance has been called sikimotoxin, being distinct from Eijkman's sikimin. 0·2 Mg. per g. body-weight is the minimum lethal dose for a cat.
R. K. CANNAN.

Poisonous principle from Chinese rhododendron, *Rhododendron Hunnewellianum*. T. Q. CHOU (Chinese J. Physiol., 1927, **1**, 157—160).—The toxic principle isolated from the Chinese drug Nao-Yang-Hua, $C_{19}H_{31}O_6$, m. p. 273°, $[\alpha]_D^{25}$ −52·5° in alcohol, is probably identical with andromedotoxin, which has been isolated from other species of this genus, and with asebotoxin from *Andromeda japonica*. A second toxic substance, m. p. 255°, was isolated in small mount. R. K. CANNAN.

Iodine, arsenic, iron, calcium, and sulphur content of Chinese medicinal algæ. B. E. READ and G. K. GOW (Chinese J. Physiol., 1927, **1**, 99—108).—The concentrations of iodine, arsenic, iron, and calcium in various algæ employed medicinally in China were found to be exceptionally high. There is some evidence that some of the calcium occurs as the soluble calcium salt of an ethereal sulphate.
R. K. CANNAN.

Biochemistry of rust diseases of cereals. I. Adsorption of copper from copper compounds by rust spores (*Tilletia tritici* [Bjerk.]) of wheat. J. BODNAR, I. VILLANYI, and A. TERENYI (Z. physiol. Chem., 1927, **163**, 73—93).—Rust spores from wheat grain adsorb in 5 min. about 1·14% of copper from dilute copper sulphate, chloride, or nitrate solutions, and slightly more in 24 hrs. or from solutions of higher concentration. From copper acetate solutions, the quantity of copper adsorbed increases much more with rise in concentration and with time, rising to 4·28% from a 1% solution in 24 hrs. The adsorbed copper is not removed by treatment with water, but is completely extracted by hot 10% hydrochloric acid. The copper in the salt solutions is replaced by alkali metals, calcium, magnesium, and, to a slight extent, hydrogen, and the sulphate, chloride, etc. content of the solutions remains unaltered. The adsorption of the copper is of a chemical nature, the copper combining partly with phosphoric acid and partly with proteins. C. HOLLINS.

Influence of salt content of colloids on their *E.M.F.* in relation to bio-electric currents. R. BEUTNER and A. MENITOFF (J. Biol. Chem., 1927, **72**, 759—763).—The *E.M.F.* set up by interposition of a colloidal gel between two different salt solutions is reduced almost to zero by addition of salt to the colloid; the *E.M.F.* is therefore produced at the junction of salt solution with salt-free colloid, and its magnitude and direction will be determined by the relative velocities of the ions of the salts diffusing from the aqueous solution into the gel. C. R. HARINGTON.

Electrodialysis in biochemistry. II. C. DHERÉ (Kolloid-Z., 1927, **41**, 315—326).—A review of the application of electrodialysis to the purification of proteins, enzymes, antibodies, and hormones, etc., with special reference to the electric charge on "free" proteins. L. L. BIRCUMSHAW.

Distilled water in biology. E. CANALS and M. MOUSSERON (Bull. Soc. Chim. biol., 1927, **9**, 203—207; cf. Canals and Genevet, A., 1925, ii, 847).—Water distilled in a copper still and then distilled twice from chromic acid in glass vessels is not satisfactory for biological purposes. A. WORMALL.

Nephelometric determination of arsenic. G. DENIGES (Bull. Soc. Chim. biol., 1927, **9**, 343—344).—The advantages appear doubtful of the alterations introduced by Delaville and Belin (this vol., 376) into the method for the nephelometric determination of arsenic previously proposed by the author.
W. O. KERMACK.

Determination of small amounts of arsenic in insect tissue. D. E. FINK (J. Biol. Chem., 1927, **72**, 737—743).—By a modification of the electrolytic method of Lawson and Scott (A., 1925, i, 996) 0·00002 mg. of arsenious oxide or 0·001 mg. of arsenic oxide can be detected in biological material, without previous destruction of organic matter.
C. R. HARINGTON.

Determination of 1—15 mg. of dextrose. B. VON ISSEKUTZ and J. VON BOTH (Biochem. Z., 1927, **183**, 298—302).—The Hagedorn–Jensen micro-method is adapted for the determination of 1—15 mg. dextrose.
P. W. CLUTTERBUCK.

Effect of potassium iodide in the Shaffer-Hartmann micro sugar reagent. W. A. DE LONG (J. Biol Chem., 1927, **72**, 731—735).—The sensitivity of the reagent of Shaffer and Hartmann (A., 1921, ii, 417) for the determination of dextrose is reduced by the presence of potassium iodide; in determining small amounts of dextrose, therefore, it is better to add the iodide subsequently to the reduction.
C. R. HARINGTON.

BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

JULY, 1927.

General, Physical, and Inorganic Chemistry.

Orbits and light-radiation of hydrogen electrons. T. ENGSET (Ann. Physik, 1927, [iv], **82**, 1017—1024).—An extension of earlier theoretical work (this vol., 181). R. A. MORTON.

Reversibility of spectral lines. M. KIMURA (Japan. J. Phys., 1927, **4**, 75—80).—From a review of the known reversals occurring in the spectra of magnesium, calcium, zinc, cadmium, mercury, aluminium, thallium, and indium, it is shown that in the non-luminous vapours of these metals lower members of the spectral series are most easily absorbed, whilst higher members are more easily absorbed in the vapour produced by a spark discharge under water. The hypothesis that an electric field increases the probability of a large orbital transition and decreases that of a small one is advanced to interpret these results. It involves the conclusion that the order of reversibility of series lines depends on the intensity of the electric field in which the absorbing atom is placed. Confirmatory evidence is cited from data on the reversibility of lines in the heavy-current arc spectra of aluminium and thallium. R. W. LUNT.

Ratio of the numbers of resonating electrons for the potassium doublets. V. K. PROKOFIEV (Phil. Mag., 1927, [vii], **3**, 1010—1025).—It has been shown, from measurements of the dispersion of potassium vapour in the regions of the first and second doublets of the principal series, that the ratio of the numbers of resonating electrons corresponding with the two doublets is 110 : 1, and is independent of the density of the vapour. The corresponding measurements of this ratio for the individual lines of each doublet are 1·995 for the red and 2·046 for the violet doublet. These results are 20—50% lower than those obtained by Bevan (A., 1911, ii, 349) and by Baxter (Phil. Mag., 1921, [vi], **42**, 289), and it is suggested that these observers worked at greater distances than has the author from the absorption lines, which are outside the absorption bands always seen in the red end of the spectrum at high vapour density. A. E. MITCHELL.

Multiplets in three-electron systems of the first long period. R. C. GIBBS and H. E. WHITE (Physical Rev., 1927, [ii], **29**, 655—662).—The triad of multiplets of V III designated $^4F_{2,3,4,5}{}^{3,4,5,6}$, $_{2,3,4,5}{-}^4F'_{2,3,4,5}$, and $^4F_{2,3,4,5}$ $^4D_{1,2,3,4}$ and multiplet $^4F_{2,3,4,5}{-}^4F_{2,3,4,5}$ have been identified. In the V III multiplets, the initial state is given by one $4p$ electron and two $3d$ electrons; in the final state, one electron is in a $4s$ orbit and the other two are in $3d$ orbits. A comparison of the data for one-, two-, and three-electron systems of scandium, titanium, and vanadium shows that the addition of first one and then a second d electron causes, not only an increase in the multiplicity, but also successive shifts in the radiated lines towards the longer wave-lengths by approximately the same frequency interval. A. A. ELDRIDGE.

Line absorption spectra of the alkaline-earth elements. O. H. WALTERS and S. BARRATT (Phil. Mag., 1927, [vii], **3**, 991—993).—Observations of the line absorption spectra of the vapours of calcium, strontium, barium, and magnesium show the possibility of transitions of the series electron from its normal $1S$ orbit to orbits of the P, p_2, D, and F types. The transition to a D orbit has been observed in calcium and strontium vapours. Transition to an F orbit has been found in barium vapour. It is thus evident that the selection rule of unit change in azimuthal quantum number does not hold, and that changes of 2 and 3 occur in the absence of any applied field. The series $1S—mP$ is the most readily absorbed. The widths of these lines are sensitive to the partial pressure of the metal vapour, the behaviour being analogous to that of the corresponding series of the alkali metals. The $1s—mp_2$ and the $1S—mD$ lines are weakly absorbed, and their observation is difficult. Only the first three members of the $1s—mF$ series of barium are strongly in evidence. A. E. MITCHELL.

Screening constants from optical data. O. LAPORTE (Physical Rev., 1927, [ii], **29**, 650—654).—The screening constants of copper, rhodium, palladium, and gold, computed from the optical data, are in agreement with those obtained from X-ray data. A. A. ELDRIDGE.

Line absorption of the non-luminous vapours of selenium and tellurium. M. KIMURA (Japan. J. Phys., 1927, **4**, 81—84).—The spectrum obtained by filling a small cavity in the anode of a carbon arc (40 amp.) with selenium or tellurium has been examined; it is found that the group of lines 1960, 2040, 2063, 2075 are self-reversed for selenium, and 2081, 2143, 2147, 2209, 2259, 2383, 2386 Å. for tellurium. The cadmium line 2259 is absorbed by tellurium vapour at 1600° (presumed to contain some monatomic tellurium); so also at 2143 is the wing of the line 2144 broadened by a condensed discharge; it is therefore concluded that tellurium vapour absorbs the lines 2259 and 2143. Similar observations on selenium vapour showed that it absorbs the lines 1960 and 2040, and it is thought that the former can be identified with the $1S—2P$ line. R. W. LUNT.

Large displacements and broadening of the lines of bromine and iodine. K. ASAGOE (Japan. J. Phys., 1927, 4, 85—102).—The broadening and displacement of a number of lines of the spectra of bromine and iodine have been determined in the range 6500—2270 Å. as functions of the pressure of the vapour and the current density. The displacement increases as these two factors increase, the largest amount recorded being 2 Å. The modes of broadening can be classified into three types as with chlorine (this vol., 2). R. W. LUNT.

Secondary radiation and polarisation of resonance radiation in cadmium. W. A. MACNAIR (Physical Rev., 1927, [ii], 29, 677—682).—When cadmium vapour containing a trace of mercury is illuminated by light of wave-length 2288 Å., only the cadmium line 2288 Å. appears in the secondary radiation if the vapour is stagnant, but if the metal is distilling, the mercury line 2536·7 Å. and the cadmium lines 2288 and 3261 Å. appear. It is suggested that unstable molecules of CdHg are present in the distilling vapour. In order to account for the polarisation (35%) of the cadmium resonance radiation (3261 Å.) in zero magnetic field, it is necessary to assign effective radii to the colliding atoms which are 30 times as great as the radii effective in ordinary collisions. A. A. ELDRIDGE.

Stages in the excitation of the spectrum of indium. J. G. FRAYNE and C. W. JARVIS (Physical Rev., 1927, [ii], 29, 673—676).—Electronic excitation of indium vapour gave the following lines (Å.): 3·3 volts, 4511·31, 4101·76; 4·2 volts, 3258·56, 3039·35 in addition; 6·9 volts, 3051·19, 2957·01, 2932·63, 2858·30, 2836·91, 2775·35, 2753·88 in addition; 13·2 volts, 2710·26, 2601·75, 2560·15, 2523·08, 2306·07 in addition. The resonance lines were less intense than the corresponding lines due to the metastable atoms. A. A. ELDRIDGE.

Structure of the La II spectrum. W. F. MEGGERS (J. Opt. Soc. Amer., 1927, 14, 191—204).—Existing data on the spark spectrum of lanthanum have been correlated and a system of terms has been applied covering many of the observations.
L. F. GILBERT.

New lines in the arc spectrum of gadolinium between 3100 and 2200 Å. S. PINA DE RUBIES (Anal. Fís. Quím., 1927, 25, 90—93).—Data are given for 250 new lines between 3064·9 and 2217 Å. in the arc spectrum of gadolinium at normal pressure.
G. W. ROBINSON.

Possible abnormal spectral series of mercury. R. G. LOYARTE and A. T. WILLIAMS (Physikal. Z., 1927, 28, 383—387).—Investigations on the excitation potentials of mercury atoms have disclosed a constant difference of 1·4 volts (Franck and Einsporn, Z. Physik, 1920, 2, 18; Loyarte, A., 1926, 1073). The regularity can be explained spectroscopically by the assumption of an abnormal arc spectrum for the mercury atom, based on a deep $1S'$ term 174,940 1, combining with terms of the form where x may be 1^3P_2, 1^3P_1, 1^3P_0, and $1P_1$, n 1, 2, 3, 4, 5, 6, or 7, and $\Delta\nu$ a displacement constant corresponding with 1·4 volts. Mercury vapour excited by means of electron impacts has been examined spectroscopically. In addition to other lines (normal triplet series etc.), abnormal lines at 2045 and 1973, designated $1^1S—a^3P_0^1$, $1^1S—a^3P_1^1$, are disclosed, and it is thought very probable that they are the first terms of two abnormal mercury series. R. A. MORTON.

Broadening of the mercury resonance line by the addition of foreign gases. W. ORTHMANN and P. PRINGSHEIM (Z. Physik, 1927, 43, 9—15).—By the addition of foreign gases, the breadth of the absorption line corresponding with the resonance radiation of mercury vapour becomes 2·5 times the normal Doppler breadth. The line-breadth of the resonance radiation has been shown by absorption measurements to be the same for broadened and unbroadened primary radiation. This result is discussed theoretically (cf. A., 1926, 224).
R. A. MORTON.

Modified scattered X-radiation due to superposition. C. G. BARKLA (Nature, 1927, 119, 778—779).—Systematic examination of the radiation scattered from various thicknesses of scattering substance shows that a perfectly regular development of the modified scattered radiation can be traced to the superposition of unmodified radiation from thin layers. A. A. ELDRIDGE.

Soft X-ray spectra. T. H. OSGOOD (Nature, 1927, 119, 817).—Using the anti-cathode of an X-ray tube as a source of radiation, and a concave glass grating mounted at a large angle of incidence, some 15 lines between 40 and 200 Å. have been photographed. Strontium, barium, and platinum are possible causes of the observed spectra. The most prominent of the lines which have been fitted into the scheme of X-ray levels is the $M_{I,\,II}$ doublet of strontium (159, 160·1 Å.). The spectrum of aluminium contains a kind of band with sharp limit at 166·6 Å., shading off towards the longer wave-lengths. A. A. ELDRIDGE.

X-Ray isochromats of copper taken in different directions relative to the cathode stream. W. W. NICHOLAS (Physical Rev., 1927, [ii], 29, 619—631).—Measurements of the variation with potential of the intensity of monochromatic X-rays of wave-lengths 0·823—0·247 Å. for directions making angles of 36°, 90°, and 144° with the cathode stream show that an isochromat of frequency ν is linear from $(5/4H)\nu$ to $2H\nu$, where $H\nu$ is the quantum voltage for excitation of frequency ν. The intercepts on the intensity axis at $H\nu$ are tabulated. The energy distribution in the X-ray continuous spectrum from a thick and a thin target, respectively, is investigated.
A. A. ELDRIDGE.

Selective displacement of 0·0153 A. in X-ray spectral lines. V and VI. F. H. LORING (Chem. News, 1927, 134, 291—292, 321—322; cf. this vol., 391).—V. A new method is given for the derivation of the displacement value based on the relationship of Δ_H to Δ_{H_α}.

VI. The inter-relationships between the displacement value and various constants is further discussed. The question of the absolute constancy of the Planck, Rydberg, and other constants is raised.
R. A. MORTON.

Precision measurements of the *K*-series of molybdenum and iron. A. LARSSON (Phil. Mag., 1927, [vii], **3**, 1136—1160).—A detailed description is given of a precision spectrograph intended for wave-length measurements over the range 0·4—2·5 Å. The method of measurement is described, and the results of measurements of the *K*-series of iron and molybdenum are given. Absolute measurements in the first order gave for molybdenum for the wave-lengths of $K\alpha_1$ and $K\beta_1$, the values of 0·707831 and 0·630978 Å., respectively. The corresponding value for the line $FeK\alpha_1$ was 1·932066 Å. Relative measurements in the first order of the lines $MoK\alpha_2$, $MoK\beta_2$, $MoK\beta_3$, and $FeK\alpha_2$ gave the wave-lengths of 0·712089, 0·619698, 0·631579, and 1·935987 Å., respectively. Relative measurements in the second order gave the wave-length of the line $MoK\alpha_2$ as 0·712115 Å. Similar measurements in the third order gave the wave-lengths of the lines $MoK\alpha_2$ and $MoK\beta_3$ as 0·712116 and 0·631547 Å., respectively. The accuracy of the measurements is discussed, and the results are compared with those of other observers.

A. E. MITCHELL.

Positions of the *K*-absorption limits of vanadium in various of its compounds. S. B. HENDRICKS and R. W. G. WYCKOFF (J. Physical Chem., 1927, **31**, 703—712).—Data for the *K*-absorption limits of vanadium in many of its compounds are given and discussed. The lower the valency the longer, in general, are the wave-lengths of the absorption edges. Pronounced variations occur in compounds of the same valency type, and the positions of the absorption edges depend on factors other than the numerical value of the valency. These factors are briefly discussed. L. S. THEOBALD.

Theory of the Compton effect. G. WENTZEL (Z. Physik, 1927, **43**. 1—8).—The Compton effect has hitherto been studied by means of the wave mechanics only for the limiting case of free-electron scattering. A theory applicable to weakly-bound electron scattering has now been developed which shows satisfactory agreement with experiment.

R. A. MORTON.

Photo-electric threshold for germanium. G. B. WELCH (J. Opt. Soc. Amer., 1927, **14**, 233).—Germanium was exposed to monochromatic radiations of measured intensities in the range 2550—2375 Å., and the consequent photo-currents were determined. Extrapolation of the curve formed by plotting currents per unit intensity of radiation against the wave-lengths used until it cuts the wave-length axis give the photo-electric threshold of germanium as probably 2590—25 Å. L. F. GILBERT.

Changes in the photo-electric threshold of mercury. H. K. DUNN (Physical Rev., 1927, [ii]. **29**. 693—700).—Kazda's value (2735 Å.; A., 1926, 3) for the long wave-length limit of the flowing surface of mercury is confirmed. Hydrogen in contact with the surface does not change the photo-electric behaviour, but when the mercury is condensed in presence of hydrogen the variations in the photo-electric threshold in a high vacuum caused by some impurity are greatly impeded by the dissolved gas. A. A. ELDRIDGE.

Thermionic emission from iron–alkali mixtures used as catalysts in the synthesis of ammonia. C. H. KUNSMAN (J. Franklin Inst., 1927, **203**, 635—646).—A convenient source of positive ions of the alkali and alkaline-earth metals is described. Fused artificial magnetite with 1% of aluminium oxide and 1% of the desired alkali or alkaline-earth oxide are placed on a platinum strip, mounted in a vacuum tube, and reduced. The resulting metal mixture forms a plentiful source of positive ions. The emission consists of single positively-charged ions, no joined atoms being detected in any case. In contrast to ions obtained from thin condensed films, the source is free from any marked change in the temperature of the surface. The positive and negative equivalent work functions are determined, and the mechanism of the emission is discussed. Finally, the bearing of the foregoing on the increased catalytic activity of an iron–aluminium–alkali mixture over a plain iron catalyst for the ammonia reaction is discussed. W. E. DOWNEY.

Electrons [as a] gas. T. DE DONDER (Bull. Acad. roy. Belg., 1926, [v], **12**. 854—855).—It is suggested that for purposes of the study of superconductivity, "electron gas" should be considered as a van der Waals gas. Taking T_c as 8°, calculation gives $a=5{\cdot}15\times10^{-4}$ and $b=1{\cdot}25\times10^{-10}$ c.g.s.u.

C. W. GIBBY.

Electron stream and space charge in dense gases. F. SKAUPY and W. DAUDT (Physikal. Z., 1927, **28**, 313—315).

Number of detachable electrons in various elements. M. KIMURA (Japan. J. Phys., 1927, **4**, 71—74).—The number of easily detachable electrons of a number of elements, the enhanced spectra of which have been classified by the author (A., 1925, ii, 726), has been estimated by making use of the Bohr interpretation that arc, spark, and super-spark spectra are to be associated with orbital transitions of neutral, singly-, and doubly-charged atoms, respectively. This number increases with the positive valency of the element, and rises to a maximum in groups IV and V. It is concluded that this number increases with the number of electrons in the highest n_1-orbit, and that the presence of electrons in the n_2-orbit protects the electrons in the former orbit from being detached. R. W. LUNT.

Mechanism of [electron] emission from oxide [coated] cathodes. W. ESPE (Wiss. Veroff. Siemens-Konz., 1927, **5**, 29—45).—The effect of time, temperature, and anode voltage on the electron emission from cathodes coated with oxides of barium, strontium, or calcium is investigated. It is concluded that the oxide layer is electrolysed by the initial small emission current, with the formation of emission centres composed of the free alkaline-earth metal. This also diffuses to the surface. The lack of saturation, characteristic of these cathodes, is attributed to the effect of the anode voltage, which increases the electrolysis and raises the temperature of the cathode. It is not considered that residual gases play an important part. For a constant chemical state, the emission–temperature relation follows Richardson's equation. The constant A in this equation is deter-

mined by the chemical state, but the work function B is unaffected. Any cause which aids the formation of the emission surface increases A and improves the emission. Evaporation and oxidation which destroy the emission centres lower the value of A and decrease the emission. C. J. SMITHELLS.

Work function for cathodes coated with alkaline-earth oxides. W. ESPE (Wiss. Veröff. Siemens-Konz., 1927, **5**, 46—61).—The emission from oxide-coated cathodes is measured at different temperatures and the work function calculated from the results, both for the $\sqrt{T}$- and for the T-- law. The values (in degrees Abs. and volts, respectively), obtained from Richardson's equation are for calcium oxide 22,400±300°, 1·93±0·03; for strontium oxide 16,600±250°, 1·93±0·02; for barium oxide 12,900±250°, 1·11±0·02. The values from Dushman's equation are 20,500±300°, 1·77±0·03; 14,750±300°, 1·27±0·025; and 11·500±300°, 0·99±0·03, respectively. C. J. SMITHELLS.

Influence of the physical and chemical constitution of resistance cellules on the intensity of the radiation which they emit. G. REBOUL, G. DÉCHÈNE, and R. JACQUESSON (J. Phys. Radium, 1927, [vi], **8**, 199—214).—Compressed pastilles of inorganic salts connected to a *P.D.* of a few hundred volts emit short-wave radiations in the region 40—300 Å., the intensity of which can be measured by determining the state of ionisation of the gas in the neighbourhood of one or other of the electrodes. The change in ionisation brought about by changing the chemical constitution or the physical condition of the pastilles has been studied. The emission of short-wave radiation depends on the occurrence of voltage discontinuities near the electrodes. Any physical change likely to influence the cohesion of the particles making up the pastille would be expected to show itself in the intensity of emission. This general idea of the process has been confirmed by detailed investigations of the influence of time, of fatigue in the pastilles, and of the previous history, grain size, moisture content, and degree of compression of the preparation used. The physical factor is of such preponderating importance that no clearly-defined relationship emerges between chemical constitution and intensity of emission. A physical mechanism of the phenomena is suggested which is in accord with the data on the effect of varying the physical conditions (cf. Bodin, this vol., 289). R. A. MORTON.

Chemical activation by collisions. R. C. TOLMAN, D. M. YOST, and R. G. DICKINSON (Proc. Nat. Acad. Sci., 1927, **13**, 188—192).—Since in the great majority of activating collisions the total energy available is only slightly greater than that necessary for activation, the assumption of Fowler and Rideal (this vol., 114) that activation occurs at every collision where the total available energy is sufficient for the purpose, involves the further, apparently improbable, assumption that practically all the energy can flow into one of the two molecules. Another serious difficulty which the theory encounters is that it involves diameters for deactivational collisions which are inconveniently large. J. S. CARTER.

Ionisation by collisions of the second kind in the rare gases. G. P. HARNWELL (Physical Rev., 1927, [ii], **29**, 683—692).—In a mixture of helium and neon (50%) ionised by electron impact the ratio He^+/Ne^+ decreases regularly between 0·03 and 0·15 mm. The probable reaction is $Ne+He^+ \longrightarrow Ne^+ + He$. With a mixture of neon and argon (50%), the regular decrease in the ratio Ne^+/A^+ between 0·05 and 0·15 mm. was less rapid; $A+Ne^+ \longrightarrow A^+ + Ne$. With a mixture of helium and argon (50%), the ratio He^+/A^+ was constant; using 85% of argon, the ratio decreased slightly. Presumably the reaction is $A+He^+ \longrightarrow A^+ + He$. The effects are ascribed to a type of collision of the second kind equivalent to ionisation by positive ions. A. A. ELDRIDGE.

Simultaneous ionisation and excitation by foreign ions in a gaseous mixture. O. S. DUFFENDACK and H. L. SMITH (Nature, 1927, **119**, 743—744).—Experiments with mixtures of carbon monoxide and of nitrogen with argon, neon, and helium indicate that an ion of one kind may, on collision with a molecule of another gas, ionise that molecule and excite the resulting ion to the degree that the energy required to ionise the one exceeds the energy required to ionise the other. The results support Duffendack and Fox's assignment (A., 1926, 777) of the Baldet–Johnson bands. A. A. ELDRIDGE.

Ionisation processes in hydrogen and nitrogen. H. KALLMANN and M. A. BREDIG (Z. Physik, 1927, **43**, 16—27).—H^+ ions originate at the same ionisation potential as H_2^+ ions, and the ratio of intensities is approximately independent of electron energy. The assumption that the H^+ ions arise from thermal dissociation of H_2^+ ions leads to a low value for the heat of ionisation of hydrogen. The discrepancy may possibly be explained by the formation of H^+ ions as a result of chemical change of the H_2^+ ions in the gas space, or else by a greater electrical acceleration of these ions. No primary ionisation into atoms has been detected for nitrogen or hydrogen. Provided the kinetic energy is not considerably in excess of the dissociation energy, the number of atom-ions formed as a result of accelerating the molecular ions is very small. Ions of apparent mass $\frac{1}{2}$H and $\frac{1}{2}$N originate from molecule-ions which have passed through the electric field (cf. A., 1926, 104). R. A. MORTON.

Ionisation by bubbling air through solutions. C. R. PITTS (J. Physical Chem., 1927, **31**, 693—702).—The ratio of the number of positive ions to that of negative ions liberated when air is bubbled through aqueous solutions of many salts has been measured. The ratio may be greater or less than unity for a particular solution, but in every case examined it is greater than the ratio obtained with distilled water. The ratio depends to a small extent on the time of bubbling, and on the concentration of the solution. With an aqueous solution of sodium chloride, the ratio first of all decreases, then increases to a maximum at a mol. fraction of 10%, and finally decreases up to a mol. fraction of 25%. When air is bubbled through distilled water, both positive and negative ions are liberated, the latter in excess. L. S. THEOBALD.

Gaseous explosions. II. Ionisation in detonating and non-detonating mixtures of hydrogen and oxygen. S. W. SAUNDERS (Trans. Faraday Soc., 1927, **23**, 242—248; cf., A., 1926, 689).—The ionisation produced when mixtures of hydrogen and oxygen are exploded in a spherical bomb has been studied by measurements of the currents between parallel electrodes placed at its centre, using an Einthoven galvanometer. The mixtures were sparked at the ends of firing tubes of different lengths which were attached to the bomb. It was found that the currents increased linearly with increasing length of the firing tube, and that the slopes of these lines, and also the magnitude of the current for zero length of firing tube, were greatest for a mixture of the composition $2H_2+O_2$. These results are explained in terms of the changes in temperature of explosion caused by the turbulence set up in the bomb by expulsion of gases from the firing tubes. When the mixtures were sparked near the surface of the bomb, the currents were diminished by the addition of "anti-knocks" and increased by the addition of "knock-inducers." The variation of current with length of firing tube is, however, not affected by "anti-knocks" when the mixtures do not detonate, or by "knock-inducers" when the mixtures are already detonating. G. A. ELLIOTT.

Gaseous explosions. III. Ionisation in explosions of carbon monoxide and oxygen. S. W. SAUNDERS and K. SATO (Trans. Faraday Soc., 1927, **23**, 248—256; cf. preceding abstract).—The electrical conductivity of mixtures of dry carbon monoxide and oxygen exploded in a spherical bomb is greatest for a mixture of composition $2CO+O_2$, and the variation of conductivity with composition confirms the view that ionisation in gaseous explosions is mainly thermal. In presence of hydrogen or water, when the velocity of the explosion wave is increased, there is a corresponding increase in the ionisation produced on explosion, whilst dry mixtures containing no hydrogen, for which the development of pressure during explosion is slow, exhibit a corresponding increased duration of ionisation.

G. A. ELLIOTT.

Gaseous explosions. IV. Ionisation in methane–oxygen and acetylene–oxygen mixtures. S. W. SAUNDERS (Trans. Faraday Soc., 1927, **23**, 256—266; cf. preceding abstracts).—Maximum conductivity is attained when mixtures of methane and oxygen are exploded to form water and carbon dioxide, or when mixtures of acetylene and oxygen are burnt to water and carbon monoxide. The addition of 70% of nitrogen to the acetylene–oxygen mixtures, however, lowers the maximum temperature of explosion so that combustion of carbon monoxide to dioxide occurs in the mixture which gives maximum conductivity. The ionisation is thermal in character and is probably not related to the ignition temperature of the initial mixture.

G. A. ELLIOTT.

Electrodeless discharge and active nitrogen. S (Bull. Acad. roy. Belg., 1926, [v], **12**, 870—880).—The electrical conductivity of nitrogen as been measured during the luminescence produced by an electrodeless discharge. In addition to the usual luminescence, a very brief green glow was observed to continue after the cessation of the discharge at pressures between 2 and 10 mm. It is shown that the ionisation current follows the same variations, as a function of the pressure, as the intensity of the luminescence, and that the latter is not directly connected with the magnitude of the ionisation current (cf. Thomson, A., 1926, 988). Hysteresis is found in the relation between the ionisation current and that in the primary of the exciting coil. The roles of pressure and of the nature and frequency of the discharge are discussed.

C. W. GIBBY.

Continuous spectra obtained by the electrodeless discharge in mercury vapour. G. BALASSE (Compt. rend., 1927, **184**, 1320—1322).—Two continuous spectra have been obtained by electrodeless discharges in mercury vapour at constant temperatures and the results correlated with those of Bloch for the fractionated spark spectra of mercury (A., 1923, ii, 350). The passage from a state of ionisation $(p+1)$ to a state of ionisation p is accompanied by the emission of a continuous spectrum (this vol., 490).

J. GRANT.

General characteristics of electrically exploded wires. J. A. ANDERSON and S. SMITH (Astrophys. J., 1926, **64**, 295—314).—A discussion of experimental procedure and probable mechanism.

CHEMICAL ABSTRACTS.

Diffraction of cathode rays by a thin [celluloid] film. G. P. THOMSON and A. REID (Nature, 1927, **119**, 890).

Velocity selector for atomic rays. J. TYKOCINSKI-TYKOCINER (J. Opt. Soc. Amer., 1927, **14**, 423—430).—Theoretical. The theory of an apparatus for selecting atoms of particular velocities from atomic and molecular rays is given. The characteristics of the expected spectrum-like images are discussed. W. E. DOWNEY.

Radioactivity in the environs of the pitchblende mines of St. Joachimsthal, Czechoslovakia. F. BEHOUNEK (Physikal. Z., 1927, **28**, 333—342).—The radioactivities of spring water, the soil, the air, and the air of mines have been determined at various points near the mines. The effects are found to be extremely local. R. A. MORTON.

Radioactivity of lead exposed for a long period to solar radiation. (MLLE.) S. MARACINEANU (Compt. rend., 1927, **184**, 1322—1324; cf. A., 1926, 6, 879).—Determination by an electrometer of the radiations from the lead roof of the Paris Observatory, at all hours of the day and in all weathers, indicates the existence of radioactivity consisting chiefly of α-particles with probably some penetrating rays of low intensity. This radioactivity is found to be stimulated by sunlight. H. DESLANDRES (Compt. rend., 1927, **184**, 1324—1325) appeals for specimens of lead which have been insolated for long periods to further these experiments. J. GRANT.

Grouping of atoms of radioactive elements in mercury. (MLLE.) C. CHAMIE (Compt. rend., 1927, **184**, 1243—1245).—The effects on a photographic

plate of distilled mercury containing small quantities of platinum and radiothorium have been determined. Well-defined, circular, star-shaped images were obtained similar to those produced directly by a radioactive element. There was evidence of the presence of the radioactive substances in small groups of atoms of diameters of the order of a micron, the photographic effect being due to the emission of α-particles. J. GRANT.

Heat of radiation of radiothorium. A DORABIALSKA and D. K. JOWANOWICZ (Rocz. Chem., 1927, 7, 23—29).—The heat produced by the β-, and γ-radiations from radiothorium enclosed in cylindrical screens of various thicknesses of aluminium, copper, and lead for a quantity of radiothorium the γ-radiation of which is equivalent to that of 289·5 mg. of radium, is (in g.-cal. per hour) 58 for α-, and 8·2 for β-radiation. The average absorption coefficient for the β-radiation of radiothorium in aluminium is 38·3 cm.$^{-1}$ The ratio of the heat of radiation to the intensity of γ-radiation is 60% greater for radiothorium than for radium. R. TRUSZKOWSKI.

Vaporisation of polonium. P. BONET-MAURY (Compt. rend., 1927, **184**, 1376—1378).—When a deposit of polonium is maintained electrically at 400° in a vacuum, the polonium vaporised may be condensed quantitatively on the outside of a thin copper cylinder containing liquid air and placed at a distance from the deposit less than the mean free path of polonium. The polonium atoms travel in straight lines, and are retained by the copper at the points on which they strike it. From measurements of the activity, the distribution of the atoms on the copper was determined, and Lambert's cosine law, that the number of atoms vaporised in an infinitely small solid angle is proportional to the cosine of the angle between the axis of the solid angle and the normal to the surface of emission, was confirmed. J. GRANT.

Effect of the orbital velocity of the electrons in heavy atoms on their stopping power for α-particles. L. H. THOMAS (Proc. Camb. Phil. Soc., 1927, **23**, 713—716).—Theoretical. The stopping powers of neon, argon, krypton, and xenon have been calculated. The electrons are supposed to be moving in orbits; collisions are treated as in Henderson's theory, but, in addition, the speed of the electron in its orbit is taken into account. The values calculated are in fair agreement with those determined experimentally. W. E. DOWNEY.

Stopping power of hydrogen atoms for α-particles according to the new quantum theory. J. A. GAUNT (Proc. Camb. Phil. Soc., 1927, **23**, 732—754).—Mathematical. The α-particle is represented by a point moving with constant velocity in a straight line and forming the centre of a Coulomb field. The effect on the atom is found by perturbation theory. It is deduced on the new quantum theory, as on the classical theory, that there is an average transfer of energy from the α-particle to atoms at all distances, and of nearly the classical amount. The difficulties in the theory of the stopping of α-particles, therefore, are no longer fundamental, as in the old quantum theory. W. E. DOWNEY.

Absolute intensities of the γ-rays of radium-*B* and -*C*. C. D. ELLIS and W. A. WOOSTER (Proc. Camb. Phil. Soc., 1927, **23**, 717—729).—Theoretical. It is shown that the heating effect of the γ-rays, the total number of quanta emitted, and the intensities of the β-ray groups may all be correlated in terms of the absolute intensities of the γ-rays. This correlation depends only on the value and rate of variation with frequency of the internal conversion coefficient of the γ-rays, and once this has been ascertained, the intensities of the γ-rays follow at once from the intensities of the β-ray groups. Determination of this conversion coefficient would settle whether continuous γ-rays are emitted or not. A reasonable value for the conversion coefficient is deduced which accounts for the total energy of the γ-rays, so that the evidence is against the existence of a continuous γ-ray spectrum (A., 1925, ii, 923). W. E. DOWNEY.

Absorptive power of atom-nuclei for γ-rays. W. KUHN (Z. Physik, 1927, **43**, 56—65).—Theoretical. Meitner's ideas (A., 1926, 106) are extended, and it is concluded that marked selective absorption of γ-rays, *e.g.*, from thorium-*C*″ by thorium-Ω, is probable. R. A. MORTON.

Transmutation of elements. L. THOMASSEN (Nature, 1927, **119**, 813).—Smits and Karssen's experiments (this vol., 87) on the spectroscopic behaviour of lead subjected to prolonged arc and spark discharge have been repeated, but the results have not been confirmed; the spectrum of the lead is unchanged. A. A. ELDRIDGE.

Transmutation of hydrogen into helium. F. PANETH (Nature, 1927, **119**, 706—707).—See this vol., 429.

Structure of an atom of nitrogen. III. H. COLLINS (Chem. News, 1927, **134**, 369—374).—Speculative.

Spinning electron and wave mechanics. E. GUTH (Nature, 1927, **119**, 744).—Mathematical. An attempt to derive the assumption that the magnetic moment corresponding with the spinning movement of the electron is exactly twice as great as that of the revolving electric point-charge with the same mechanical angular momentum, from the relativistic Schrödinger wave equation in connexion with the electrodynamic meaning of the wave-function A. A. ELDRIDGE.

Unidirectional quanta in wave mechanics. G. BREIT (J. Opt. Soc. Amer., 1927, **14**, 374—380).—Theoretical. The distribution of charge responsible for the emission is represented by a plane wave having the direction of the emitted quantum for its wave-normal and having the frequency and wavelength of the normal. W. E. DOWNEY.

Wave theory of the electron. W. P. ALLIS and H. MÜLLER (J. Math. Phys. Mass. Inst. Tech., 1927, **6**, 119—132).—The electron is regarded as a wave of frequency $\nu=(mc^2+eV)/h$ and wave number $\mu=c(m^2-m_0^2)^{\frac{1}{2}}/h$, with which electricity is associated as energy is associated with an electromagnetic wave. The velocity of the electron is given by the group velocity $\delta\nu/\delta\mu$. The quantum conditions are studied, with the result that a quantum jump is regarded as a

continuous process, with the charge passing gradually from the wave characteristic of the initial state to that corresponding with the final state. During the process, the waves form groups of velocity $v=\Delta\nu/\Delta\mu$. The electron is thus conceived as a bundle of very slighty differing waves obeying electromagnetic laws. The theory permits the Compton effect to be regarded as a Doppler effect. R. A. MORTON.

Quantum mechanics and direction-degeneration. J. R. OPPENHEIMER (Z. Physik, 1927, **43**, 27—46).—The quantum mechanics of the displacements in degenerate systems are investigated in a simplified manner, and the spontaneous radiation from such disturbed systems is calculated in terms of Dirac's theory. The treatment allows several important rules, such as Heisenberg's polarisation rules for resonance light, Skinner's rules for impact emission, and Hanle's rules for the effect of external fields, to be included as special cases of a wider theory. An explanation of the anomalous polarisation of the mercury resonance line is advanced. R. A. MORTON.

Scattering coefficient for short waves according to Schrodinger's theory. J. A. STRATTON (Physikal. Z., 1927, **28**, 316—323).

Electronic states and band spectrum structure in diatomic molecules. IV. Hund's theory; second positive nitrogen and Swan bands; alternating intensities. R. S. MULLIKEN (Physical Rev., 1927, [ii], **29**, 637—649).—Practically all the available evidence supports Hund's theory of molecular electronic states and band spectra. Hund's interpretation of the second positive nitrogen bands as a $^3P \longrightarrow {}^3P$ transition is extended to the Swan bands. The alternating intensities or alternate missing lines in the He_2, N_2, Swan, and N_2^+ bands are formally accounted for. The NH bands classed by Hulthen and Nakamura (this vol., 185) as $^3P \longrightarrow {}^1S$ are probably $^3P \longrightarrow {}^3S$. A. A. ELDRIDGE.

Bands in the extreme ultra-violet spectrum of a helium discharge. L. A. SOMMER (Proc. Nat. Acad. Sci., 1927, **13**, 213—216).—The helium line $600{\cdot}3\pm0{\cdot}6$ Å. is apparently in reality a band arising from a low-lying term in the spectrum of molecular helium corresponding with the fundamental term ^1S in the spectrum of atomic helium and having almost the same term value. J. S. CARTER.

Structure of the ultra-violet absorption band of ozone. D. CHALONGE and M. LAMBREY (Compt. rend., 1927, **184**, 1165—1167).—The complete structure of the ultra-violet absorption spectrum of ozone has been determined by the use of the continuous spectrum of hydrogen, and the results have been correlated with those obtained in the Shaver and Huggins regions. By means of the microphotometer, a series of undulations on the absorption graph, situated on an ascending curve, has been established, and the positions of their maxima have been determined. J. GRANT.

Absorption spectra of gallium, indium, manganese, chromium, nickel, and cobalt in underwater sparks. A. W. SMITH and M. MUSKAT (Physical Rev., 1927, [ii], **29**, 663—672).—The absorption lines found in the under-water spark spectra of indium and gallium, in agreement with observations in the vapour state, indicate that the normal state of the valency electron is the $2p$ state; for manganese, the normal state of the valency electron is the $1s$ sextet level. The assignment of lines and arrangement of terms with respect to the ground level given by Catalan (A., 1923, ii, 519) and Gieseler (A., 1924, ii, 285) for chromium, Bechert and Sommer (A., 1925, ii, 913, 1014) for nickel, and Catalan (A., 1925, ii, 611) for cobalt are verified. A. A. ELDRIDGE.

Absorption spectra and pleochroism of iodine and herapathite. P. BOVIS (Compt. rend., 1927, **184**, 1237—1239).—The optical densities of layers 1 μ thick of iodine and herapathite have been determined, using natural and polarised light. In natural light, iodine and herapathite prepared according to the Baume and Zimmern–Coutin methods (A., 1926, 706) had almost the same opacities for a wave-length of 0·650 μ. The Baume herapathite had the most accentuated pleochroism, the Zimmern–Coutin preparation behaving like a mixture of iodine and herapathite. Solid iodine gave a large absorption band at a wave-length of about 0·255 μ. J. GRANT.

Bands in the absorption spectrum of mercury. (LORD) RAYLEIGH (Nature, 1927, **119**, 778).—Bands allied to, but not identical with, the emission bands previously observed from 3055 to 2697 Å. (this vol., 496) have been obtained in absorption. Closer examination of the diffuse absorption bands at 2345, 2338, 2334, and 2339 Å. shows that superposed on this structure is a much finer one of the order of 1 Å. The lines 2270 and 2656 Å. were not detected in absorption. A. A. ELDRIDGE.

Intensities of molecular beams. T. H. JOHNSON (Nature, 1927, **119**, 745—746).—When the region between the two slits through which the beam of mercury molecules is passed (Knauer and Stern, this vol., 92) is surrounded by a surface cooled with liquid air, the intensity of the beam increases uniformly with the oven pressure between 0·1 and 30 mm. A. A. ELDRIDGE.

Effect of temperature on the refractive index of rock salt. (SIR) R. ROBERTSON and J. J. FOX (Nature, 1927, **119**, 818).—The acceptance of the 4·4 μ emission band of carbon dioxide or the quartz reflexion bands as bench marks is misleading unless combined with suitable temperature corrections of the prism used. A variation of 5° in the working temperature with rock salt or fluorite results in a difference of 0·075 μ in certain parts of the near infra-red. A. A. ELDRIDGE.

Transformation spectra. E. L. NICHOLS, H. L. HOWES, and D. T. WILBER (J. Opt. Soc. Amer., 1927, **14**, 205—222).—Lenard's observations on the colours of molten beads of salts of the alkali metals (A., 1905, ii, 565) were confirmed and the temperatures at which the effects occur determined. Observations on 37 elements the salts of which cannot readily be obtained in the form of molten beads were made by introducing small quantities of their compounds into sodium phosphate or borax beads. Such beads

when heated in a hydrogen flame underwent transformations characterised by a sudden clouding or clearing at definite temperatures. These transformations were marked by changes of brightness, and frequently by a characteristic colour which was present only during the transformation stage. The effects were reversible, *i.e.*, could be observed either during the heating or the cooling of the beads. The transformation spectra of beads containing the rare earths correspond with those of the cathode fluorescence of the element. L. F. GILBERT.

New infra-red absorption bands of methane. J. W. ELLIS (Proc. Nat. Acad. Sci., 1927, **13**, 202—207).—Five new absorption maxima at 1·15, 1·37, 1·66, 1·72, and 1·80 μ are reported. The combined data of Cooley (A., 1926, 659) and the author are tabulated and the observed bands identified in terms of four fundamental frequencies. Chloroform exhibits bands at 1·15, 1·40, and 1·69 μ. The bands intimately associated with the carbon–hydrogen linking do not appear to constitute a single parabolic series, as was formerly supposed. Wave-length corrections to be applied to all the author's previously published work (A., 1924, ii, 218, 219; 1926, 454, 883) are given. J. S. CARTER.

Spectroscopic researches on aromatic amino-acids and their derivatives. E. ABDERHALDEN and R. HAAS (Z. physiol. Chem., 1927, **166**, 78—83).—Absorption spectra for *o*- and *m*-hydroxyphenylalanines and tyrosine are closely alike, the curve for the *meta*-compound lying between those for the *ortho*- and *para*-compounds. The main absorption band (ν=3580) is independent of the nitrogen, since it also appears in the spectra of glycyl-*l*-tyrosine and tyrosine anhydride (3 : 6-di-*p*-hydroxybenzyl-2 : 5-diketopiperazine). In *O*-carbethoxy-*N*-formyltyrosine, the band shifts to 3740, from which it seems probable that in proteins the phenolic hydroxyl group of tyrosine is free. Absorption spectra for 3 : 5-dibromo- and 3 : 5-di-iodo-tyrosines and 3 : 6-di-(3 : 5-di-iodo-4-hydroxybenzyl)-2 : 5-diketopiperazine are given. Those of thyroxine and tryptophan are quite dissimilar, contrary to the statement of Hicks (A., 1925, ii, 473).

The preparation of 3 : 6-*di*-(3 : 5-*di*-*iodo*-4-*hydroxybenzyl*)-2 : 5-*diketopiperazine*, decomp. about 204°, by the action of iodine on *l*-tyrosine anhydride in alkaline solution is described. C. HOLLINS.

Ultra-violet absorption spectra of *cyclo*hexene, ethyl ether, methyl *n*-amyl ether, and ethylene-chlorohydrin. A. W. SMITH, C. S. ADAMS, and C. S. PEASE (J. Amer. Chem. Soc., 1927, **49**, 1335—1346).—The ultra-violet absorption spectra of *cyclo*hexene, ethyl ether, methyl *n*-amyl ether, and ethylenechlorohydrin all show three series of band spectra, identical with those previously found in benzene. As the only linkings common to the compounds compared are the carbon–hydrogen and carbon–carbon linkings, it appears that one or other of these gives rise to the band systems. On this assumption, the positions of the absorption bands in the near infra-red are found to agree with those calculated from the positions of the observed ultra-violet bands by Henri's formula based on the quantum theory (A., 1922, ii, 679), and it is shown that these positions agree with those reported for a large number of organic liquids. F. G. WILLSON.

Absorption spectra and the constitution of benzene derivatives. IX. N. A. VALASCHKO (J. Russ. Phys. Chem. Soc., 1926, **58**, 779—822).—See this vol., 396. E. ROTHSTEIN.

Ultra-violet absorption spectra of substances containing two benzene rings. A. CASTILLE (Bull. Soc. chim. Belg., 1927, **36**, 292—309).—The absorption spectra of a series of compounds containing two benzene rings have been studied, in hexane solution and in the vapour state, over the range 4000—2000 Å. The coefficients of absorption are considerably greater than the corresponding values for compounds containing a single benzene ring. The spectra of diphenylmethane and of dibenzyl show the seven narrow bands characteristic of benzene, which are, however, broader and displaced towards the visible region by about 90 Å. Compounds in which the two rings are joined by an unsaturated chain exhibit a single wide band resulting from the fusion of the narrow benzene bands, with, in some cases, a second band corresponding with the benzene band in the extreme ultra-violet. An increase in the length of the connecting chain is accompanied by a displacement of these bands towards the region of longer wave-lengths. The coefficients of absorption increase with the number of ethylenic linkings; diphenylamine, however, possesses an abnormally high power of absorption. When the two benzene rings are linked by a group containing a chromophore, as in benzil or azobenzene, the modified benzene bands are displaced, and one or more bands characteristic of the chromophore appear near the visible region. G. A. ELLIOTT.

Resonance, fluorescence, and absorption spectra in group VI of the periodic system. B. ROSEN (Z. Physik, 1927, **43**, 69—130).—The resonance spectra of tellurium, selenium, and sulphur vapours are very similar to the resonance spectra of iodine in respect of fine structure and intensity relations. The resonance spectra of tellurium are given by $\nu=a-250{\cdot}4n+0{\cdot}53n^2$, where a has the values 23,930, 25,451, and 22,411, respectively, for the exciting mercury lines 4359, 4046, and 5461 Å. For selenium, the analogous expression is $\nu-a-397{\cdot}5n+1{\cdot}32n^2$, a being 27,423 for the 4046 series, whilst for sulphur $\nu=a-724{\cdot}0n-2{\cdot}91n^2$, a being 33,359 for 3132 Å. The vapour fluorescence in this group begins to be marked at pressures of the order 10^{-3} mm., and increases up to pressures of 1 mm., beyond which point surface fluorescence occurs. The disappearance of the fluorescence is due largely to re-absorption. With tellurium, the effect of foreign gases is limited to a weakening of the intensity. The absorption and fluorescence spectra of all three elements have been analysed and classified schematically, and formulæ derived. It is shown that the higher the level to which a molecule is raised by the absorption of the exciting line the more numerous will be the "anti-Stokes" lines. The nuclear vibration frequencies in the normal state are approximately inversely proportional to the atomic numbers, a

conclusion valid for groups V, VI, and VII of the periodic system. It follows, therefore, that the binding force is approximately inversely proportional to the atomic numbers or to the atomic weights. The heats of dissociation of diatomic sulphur, selenium, and tellurium are found by the optical method to be 112,000±5000, 84,000, and 65,000 g.-cal., respectively. R. A. MORTON.

Fluorescence and molecular induction by resonance. J. PERRIN (Compt. rend., 1927, **184**, 1097—1100).—Activation occurs when a molecule changes suddenly to a state of higher internal energy as the result of the absorption of a quantum from an exciting source. Fluorescence, which may thus be correlated with deactivation, the reverse of activation, is shown to increase as the concentration of the solution diminishes, since at high concentrations the molecules are closer together and the proportion of non-luminous deactivations is increased. Molecular induction is the non-luminous deactivation, with the expulsion of kinetic energy, resulting from the proximity of an ordinary and an active molecule of the same substance. Selective molecular induction by resonance may be produced between molecules of different substances the absorption bands of which are close or identical. Thus eosin lowers the fluorescence of uranium more than uranium itself. When the absorption bands of the fluorescent substance and the added substance are dissimilar, the mutual induction is less pronounced. The coefficient of mutual induction may be calculated analogously to the method for F. Perrin's expression for the exponential decrease of fluorescence (cf. following abstracts). J. GRANT.

Action of anti-oxygenic compounds on fluorescence. PRIVAULT (Compt. rend., 1927, **184**, 1120—1121; cf. preceding and following abstracts).—The reducing effect of certain anti-oxygenic salts (*e.g.*, iodides, sulphides, etc.) on the luminosity of fluorescence (A., 1926, 223) is due to the physical actions of the ions concerned on the excited molecules of the fluorescent substance, which favour a return to the normal state without emission of light. Such substances should also lower the photochemical activity of fluorescent substances. Thus, quinol inhibits the photochemical oxidation of uranium and also its power of fluorescence, and the latter action has the same physical characteristics as those referred to above. Other anti-oxygenic compounds (phenols, nuclear amines, certain sulphur and nitrogen compounds, and, to a lesser extent, the aliphatic amines and pyridine) behave similarly. The phenomenon is non-chemical. J. GRANT.

Induced deactivation of molecules and the theory of anti-oxygenic compounds. F. PERRIN (Compt. rend., 1927, **184**, 1121—1124).—The phenomenon observed by Privault (cf. preceding abstract) is styled forced induction (in opposition to resonance induction), and is related to the deactivation of an excited molecule by a free electron such as would be found loosely bound in an easily oxidisable substance like an anti-oxygen. An explanation of anti-oxygenic effects is to be found in a chain theory of reaction (such as Bodenstein's), in which the energy liberated by a reacting molecule supplies energy to activate other molecules, which can then also react. The diminution of the mean lives of the activated molecules by the deactivating molecules diminishes the chances of reaction of the former. Thus, anti-oxygens may also inhibit certain photochemical reactions which are not necessarily oxidations. J. GRANT.

Luminescence of cæsium vapour in the silent discharge. G. BALASSE and O. GOCHE (Bull. Acad. roy. Belg., 1926, [v], **12**, 835—839).—A preliminary investigation of the cæsium spectrum produced in the silent discharge shows that all the lines of the arc spectrum are present, together with some of the spark lines. Several faint diffuse lines in the arc series $1s$—md, which have not been observed previously, have been measured. There is some continuous spectrum produced at temperatures above about 200°. The spectra obtained with decreasing intensity of excitation extend less and less into the short wave-length region, an effect which is thought to be independent of the substance studied. The differentiation among rays of the spark spectrum, observed with certain intensities of excitation, is not thought to be due to ionisation with the loss of one and two electrons, as required by Bohr's theory of the structure of the cæsium atom. H. F. GILLBE.

Excitation of phosphorescence by means of slow cathode rays. H. W. ERNST (Ann. Physik, 1927, [iv], **82**, 1051—1076).—With the CaS–Cu phosphor the α- and β-bands are excited both by cathode rays and light, but the α-band is much the stronger of the two with light, whereas the β-band predominates slightly with cathode-ray excitation. The specific light intensity during cathode-ray excitation is over a wide range directly proportional to the electron density, if the voltage is maintained constant. An upper limit to the degree of excitation was not reached. The economy quotient for a defined CaS–Bi phosphor was 0·11, and for other phosphors it was even smaller. Curves expressing the relation between specific light intensity and electron-accelerating potentials are given. For small velocities, the rate of increase of intensity is slow, but as the velocity increases, the intensity gradually approaches a linear rate of increase, which is maintained until the velocity becomes large. For the same band occurring in different preparations with different intensities and voltages (so long as these are not too great), the same economy quotient is obtained, provided the metal content is maintained constant. The momentary light exerts no appreciable effect. The economy quotient for CaS–Cuα and CaS–Cuβ increases with increasing metal content up to a maximum of 0·13 and 0·10 at $0{\cdot}75\times10^{-3}$ and $0{\cdot}9\times10^{-3}$ g. of copper per g., respectively; it falls off somewhat rapidly with further increase of concentration. R. A. MORTON.

Dielectric constants and magnetic susceptibilities in the new quantum mechanics. I. General proof of the Langevin–Debye formula. J. H. VAN VLECK (Physical Rev., 1927, [ii], 29, 727—744).—Mathematical. The proof of the formula $\chi=N\alpha+N\mu^2/3kT$, where χ is the susceptibility,

N the number of atoms or molecules per unit volume, k the gas constant, and α a constant independent of T, is based on the single assumption that the atom or molecule has a "permanent" moment vector of which the precession frequencies are small compared with kT. A. A. ELDRIDGE.

Dielectric constant and the wave-mechanics. R. GANS (Physikal. Z., 1927, **28**, 309—313).

Index of refraction and dielectric constant of water vapour. A. BRAMLEY (J. Franklin Inst., 1927, **203**, 701—711).—By an interferometer method, the variation of the index of refraction of water vapour with the voltage applied to a cylindrical condenser is studied. The effect observed, which was proportional to the square of the electric intensity, agreed well with the predicted effect. A theory of the effect is given. W. E. DOWNEY.

Difference in time lags in the disappearance of the electric double refraction behind that of the electric field in several liquids. J. W. BEAMS and F. ALLISON (Phil. Mag., 1927, [vii], **3**, 1199—1204).—A method has been developed by means of which the difference in time lags of the disappearance of the electric double refraction after the removal of the electric field in various liquids can be measured with a precision of $0{\cdot}4\times10^{-9}$ sec. Of several liquids investigated, carbon disulphide showed the smallest lag. It is therefore probably the best liquid to employ in experiments in which the rate of decay of electric double refraction is used to measure small time intervals. A. E. MITCHELL.

Measurement of the ratio $h:k$ by means of the anomalous dispersion of thallium. E. FERMI and F. RASETTI (Atti R. Accad. Lincei, 1927, [vi], **5**, 566—570).—Investigation of the anomalous dispersion of thallium vapour by Puccianti's interferential method leads to results which give, for the ratio between the universal constants $h:k$ of the form of Boltzmann's statistical law derived from the quantum theory, a value accurate to within 20%.

According to McLennan's results (A., 1921, ii, 665), at 540° the refractivity of thallium vapour should be of the same order of magnitude as that of air at atmospheric pressure. The vapour pressure of thallium at 540° being about 0·001 mm., the atomic refractivity would thus be about 100,000 times that of other metallic vapours. The authors' results indicate that thallium vapour has normal refractivity. T. H. POPE.

Anomalous dispersion and absorption of electric waves. S. MIZUSHIMA (Physikal. Z., 1927, **28**, 418—421).—See A., 1926, 560, 778, 886, 1082.

Calculation of the rotatory power of a system of anisotropic atoms or molecules. R. DE MALLEMANN (Compt. rend., 1927, **184**, 1241—1243).—A general expression for the rotatory power, based on the author's theory, has been deduced for two molecular models (binary molecule and quartz types) in which the symmetrical elements (molecules, radicals, or atoms) are arranged in such a way that two of their principal planes are parallel. The rotation is shown to be proportional to the square of the birefringence. J. GRANT.

General theory of molecular rotation. R. DE MALLEMANN (Compt. rend., 1927, **184**, 1374—1376).—The source of rotatory power resides essentially in the mutual actions of the atoms constituting the system, and these may be related with rotation-vectors in the mechanical sense. An attempt has been made to show that in every asymmetric medium three rectangular directions of propagation exist. The properties of such a medium are completely defined by two symmetrical tensors, viz., the electro-elastic tensor and the rotatory tensor, on which depend the pure refringence and the optical activity, respectively. These tensors are calculable numerically. J. GRANT.

Rotatory power of the tartrate ion. E. DARMOIS (Compt. rend., 1927, **184**, 1239—1241).—The specific rotatory power and rotatory dispersion of sodium tartrate are considerably affected by the presence of neutral salts; thus in solutions of calcium chloride of the concentrations 0, 0·53, 1·41, 2·82, and 4·2M, $[\alpha]^{18}$ of the tartrate ion (yellow mercury line) is +43·3°, +32·9°, +16·2°, +1·0°, and −4·55°, assuming that all the tartaric acid is present as the bivalent ion. Barium and strontium chlorides, and, to a lesser degree, calcium nitrate and sodium, lithium, and magnesium chlorides also have a negative effect (in 3·5M-calcium nitrate, $[\alpha]^{18}=+13°$; in 4·4M-sodium chloride, +37°; in 7·8M-lithium chloride, −4·7°; in 3·2M-magnesium chloride, +30·9°). Salts of the rare earths cause a rapid decrease, followed in some cases by an increase (in 0·3, 0·5, 1·0, 1·5M-lanthanum nitrate $[\alpha]^{18}=-47{\cdot}1°$, −47·1°, −33·5°, −22·8°; in 0·026, 0·092, 0·185, 0·277, 0·415, 0·554M-lanthanum chloride, containing 2·06M-calcium chloride to prevent precipitation of the tartrate, $[\alpha]^{18}=+4{\cdot}0°$, −6·9°, −25·0°, −37·5°, −47·5°, −45·0°). Potassium chloride, on the other hand, causes an increase (in 0·77, 1·54, and 3·08M-solutions $[\alpha]^{18}=+46{\cdot}7°$, +49·0°, and +48·8°); manganous chloride, manganous sulphate, and ferrous chloride have a similar effect. Ferrous sulphate has a pronounced positive effect (in 0·72M-solution $[\alpha]^{18}=+104°$), whilst zinc chloride causes a slight increase, followed by mutarotation, bringing $[\alpha]$ to its original value. In aluminium chloride solution, the initial positive effect is followed by considerable mutarotation. Salts of the quadrivalent metals and those of copper cause a very large increase (in 0·2M-thallium nitrate $[\alpha]^{18}=+165°$). W. J. POWELL.

Dispersion and rotatory power of monoethyl aspartate. M. L. PAGLIARULO (Atti R. Accad. Lincei, 1927, [vi], **5**, 505—510).—The rotation, index of refraction, and temperature differential of the index of refraction in the range 15—20° have been determined for a solution containing 0·748% of monoethyl aspartate in the range 6708—4046 Å. In the range 6300—5300 Å., the curve of the rotation shows two inflexions similar to those characterising the refractive index in the neighbourhood of an absorption maximum; the curve of the temperature differential of the index of refraction shows a corresponding maximum. R. W. LUNT.

Electronic configurations of complex salts. C. D. NENITZESCO (Bul. Soc. Chim. Romania, 1926,

8, 10—17).—Theoretical. A comparison is made between the electronic configurations of inert gases and those of complex salts. It is explained that although it is not absolutely necessary, a complex salt does tend to assume the electronic configuration of an inert gas. Examples of complex salts are quoted to demonstrate the truth of the hypothesis. H. BURTON.

Space configuration of the halogen derivatives of bivalent molybdenum, tungsten, and tantalum. K. LINDNER (Z. anorg. Chem., 1927, **162**, 203—221).—From a combination of tetrahedra and octahedra, representing nuclei with the co-ordination numbers 4 and 6, respectively, figures are derived which represent nuclei containing more than one metal atom and having the co-ordination numbers 6—12. These are applied to explain the structure of the above compounds, and of polymerised halides, such as those of cadmium. R. CUTHILL.

Electric moments of substituted benzene molecules and the structure of the benzene ring. C. P. SMYTH and S. O. MORGAN (J. Amer. Chem. Soc., 1927, **49**, 1030—1038).—The densities and dielectric constants of solutions of the mono- and di-chloro-substitution products of benzene in benzene and hexane have been determined, and by combining the results with the molecular refractions the electric moments of the solute molecules have been calculated. The results agree with those calculated on the assumption that the benzene ring is best represented by a hexagon with all the carbon and hydrogen atoms in the same plane, whereas the figures obtained by assuming Baeyer's or Korner's arrangement deviate widely from the experimental values. It is suggested that substitution in the benzene molecule may cause distortion into a somewhat puckered ring. H. F. GILLBE.

"Florentium" [illinium]. L. ROLLA and L. FERNANDES (Gazzetta, 1927, **57**, 290—292).—Polemical against Noyes; a reassertion of priority in the discovery of element 61 (this vol., 190, 296, 501). E. W. WIGNALL.

Manganese homologues. [Elements of] atomic numbers 43 and 75. W. PRANDTL (Z. angew. Chem., 1927, **40**, 561—564; cf. this vol., 433).—Polemical. A summary of previous criticisms on the work of Noddack, Tacke, and Berg (A., 1925, ii, 939). L. M. CLARK.

Crystalline structure and chemical composition. V. M. GOLDSCHMIDT (Ber., 1927, **60**, [*B*], 1263—1296).—A lecture to the German Chemical Society. H. WREN.

Atomic lattices and atomic dimensions. J. K. MORSE (Proc. Nat. Acad. Sci., 1927, **13**, 227—232).—The Lewis–Langmuir concept of cubic atoms is extended to simple polyhedrons inscribable in spheres. It is shown that such simple models can be built up into various types of observed cubic and hexagonal lattices, and that the lattice constants are geometrically related to the radii of the circumscribing spheres. If atoms are assumed to unite with each other to form lattices by sharing electrons, and centre positions identified with atom centres, and corners with possible electron positions, the possible atomic radii of 34 atoms can be calculated from existing data on the lattice constants. The calculated atomic radius of carbon in diamond, 0·77 Å., is almost identical with the calculated radius in graphite, 0·75 Å. If this agreement is not merely a coincidence, it would appear that a carbon atom in combination can be treated as a cube, that its radius is approximately constant over a wide range of conditions, and that it can unite with other carbon atoms by sharing one electron. J. S. CARTER.

Crystalline structure of tervalent metals. I. Chromic chloride. G. NATTA (Atti R. Accad. Lincei, 1927, [vi], **5**, 592—597).—Chromic chloride crystallises in the rhombohedric system and probably in the holohedral class. Its unit cell contains 1 molecule of $CrCl_3$ and has the side $a=4{\cdot}42$ Å., the axial ratio $c:a$ 1·29—1·30 and $d_{calc.}$ 2·71. T. H. POPE.

Crystalline structure of iodine. I. A. FERRARI (Atti R. Accad. Lincei, 1927, [vi], **5**, 582—586).—*X*-Ray examination shows that iodine exhibits a rhombic lattice with an elementary cell composed of an orthogonal parallelepiped containing 8 atoms; $a=4{\cdot}760$, $b=7{\cdot}164$, and $c=9{\cdot}783$ Å. T. H. POPE.

Lattice constants of rock salt and of pure sodium chloride. T. BARTH and G. LUNDE (Z. physikal. Chem., 1927, **126**, 417—424).—The lattice constant a of a natural rock salt crystal is about 0·002 Å. greater than that of pure sodium chloride. Taking $a=5{\cdot}628$ for rock salt as standard, for pure sodium chloride $a=5{\cdot}626\pm0{\cdot}001$ Å. A systematic error is therefore introduced into powder-diagram measurements in which sodium chloride is employed if a is taken to be 5·628, although such error lies usually within the experimental error. H. F. GILLBE.

Isomorphism of sklodowskite with uranophane. A. SCHOEP (Natuurwet. Tijdschr., 1927, **9**, 30—33).—Sklodowskite, formerly described from optical evidence only as rhombic, is now found to be so by measurement, the constants being $a:b:c=0{\cdot}3114:1:1{\cdot}0554$, $(010):(110)=72—73°\ 45'$. These are very close to the corresponding constants for uranophane, and from this and the similarity in composition the two are believed to be isomorphous. No evidence that they form an isomorphous series, however, is available. S. I. LEVY.

Crystals of kasolite, soddyite, and brochantite. A. SCHOEP (Natuurwet. Tijdschr., 1927, **9**, 25—30).—Measurements of good crystals of the three minerals from Katanga are given. Two varieties of kasolite are described, one translucent, amber-coloured, the other opaque, ochre-coloured; the constants deduced by Buttgenbach (Bull. Acad. roy. Belg., 1922, [v], **10**, 573) are confirmed. The constants for soddyite have been calculated from measurements on a particularly good crystal. New faces and habits for brochantite are described, and the constants calculated. S. I. LEVY.

Identity of the crystalline structures of the compounds Fe_3S_4 and FeS. C. FONTANA (Atti R. Accad. Lincei, 1927, [vi], **5**, 579—581).—The identity in crystalline structure exhibited by ferrous

sulphide (troilite), and by β-pyrrhotites prepared by Allen, Crenshaw, and Johnston (A., 1912, ii, 354), de Jong (A., 1926, 460), and the author shows that the reaction between magnetite and hydrogen sulphide at 1000° and at ordinary pressure is represented by $Fe_2O_3,FeO+4H_2S \longrightarrow 3FeS+S+4H_2O$. The sulphur remaining in the product occupies no fixed, characteristic position in the crystal lattice. The existence of Fe_3S_1 as a chemical individual cannot be regarded as proved (cf. de Jong and Willems, this vol., 502). T. H. POPE.

Nature of the carbon chain in liquid crystal substances. D. VORLANDER (Z. physikal. Chem., 1927, **126**, 449—472).—The first and second m. p. of the phenetoleazophenol and anisoleazophenol esters of the saturated aliphatic monocarboxylic acids have been determined; the two m. p. show the same type of variation with the number of carbon atoms in the chain. The second m. p. falls sharply with increasing number of atoms in the carbon chain up to 5, after which alternation sets in, the general tendency being for the m. p. to increase with increasing number of carbon atoms, so that the curve approaches that of the first m. p. The range of existence of liquid crystals, determined by the distance between the two m.-p. curves, decreases rapidly as the series is ascended. The anisoleazophenol esters have a considerably larger range of existence than the phenetoleazophenol esters. The conclusion is reached that the normal aliphatic carbon chain is of linear or zig-zag form, but not spiral. The same is true of the aliphatic dicarboxylic acids. In the liquid state, all possible forms are capable of existence, but with certain forms, dependent on the nature of the chain, predominating.

Investigation of the unsaturated aliphatic carboxylic acids shows that a double linking in the α-position markedly increases the tendency to liquid crystal formation, whilst in other positions the effect is less noticeable. Two adjacent double linkings have a strong effect, whilst with a third the tendency is still further increased. Copious data are also given for the alkyl esters of azoxycinnamic acid and for aromatic derivatives of the diphenylparaffins.

Whereas all these compounds show alternation of the m. p. with increasing chain length, substances having chains of benzene rings joined in the *para*-position show no alternation, but a steady decrease in the tendency to liquid crystal formation as the number of carbon atoms in the chain increases. The *para*-valency forces of the benzene ring are therefore considered to act in a straight line and in the plane of the ring.

Pentaphenyl forms one liquid crystal phase and probably only one solid crystalline form, whilst hexaphenyl exists in two enantiotropic modifications. H. F. GILLBE.

Distribution of intensity in the *X*-ray spectra of the normal saturated dicarboxylic acids, their diethyl and monoethyl esters. A. R. NORMAND, J. D. ROSS, and E. HENDERSON (Proc. Roy. Soc. Edinburgh, 1926—1927, **47**, 69—80).—The series of normal saturated dicarboxylic acids, their diethyl and monoethyl esters, were investigated by means of *X*-rays, and from the measurement of their principal spacings a definite single-chain structure is assigned to each. Formulæ derived by Shearer for similar compounds are applied, and the intensity distribution among the several orders of reflexion from the principal planes is calculated. Comparison of calculated with observed results showed good agreement in every case, thus confirming the chain structures assigned. W. CLARK.

Molecular space array in liquid primary *n*-alcohols: the cybotactic state. G. W. STEWART and R. M. MORROW [with W. D. CROZIER] (Proc. Nat. Acad. Sci., 1927, **13**, 222—223).—The liquid primary *n*-alcohols from methyl to undecyl have been investigated using the Mo*Ka* *X*-radiation. There are two significant distances determined by diffraction intensity peaks. One of these remains fairly constant, varying from 4·6 Å. with undecyl alcohol to 4·4 Å. with butyl alcohol, and then decreasing more rapidly to 3·8 Å. with methyl alcohol. The other distance varies linearly with the CH_2 content of the molecule, the variation for each such addition being about 1·54 Å. The latter distance appears to be due to the length of the chain, and the former to the distance of separation of molecules perpendicular to the chain. From density measurements and from the polarity of the compounds, it is concluded that two polar hydroxyl groups unite to form a chain two molecules in length, and that the planes containing these groups are not perpendicular to the chains. Addition of each CH_2 group lengthens the molecule by about 1·3 Å., a number in agreement with the results of Müller and Saville (A., 1925, ii, 367) for solid, long-chain hydrocarbons. The present interpretation of separations of chains and relative positions of heads is in agreement with the calculations of Adam (A., 1922, ii, 687; 1923, ii, 539) on the cross-sectional areas of saturated fatty acid chains on water surfaces. The present data indicate a definite space array in these liquids which is not crystalline, but one in which molecular mobility is permitted, the resulting peaks representing the most probable spacings. The name suggested for such an array is cybotaxis (adjective cybotactic). J. S. CARTER.

Crystal structure of benzil. (MISS) N. C. B. ALLEN (Phil. Mag., 1927, [vii], **3**, 1037—1040).—An *X*-ray examination of crystalline benzil has been made with a Bragg ionisation spectrometer. The crystal is built on a hexagonal lattice, and the unit cell contains three molecules disposed spirally about the principal axis. The molecule has a dyad axis, and the space-group is D_3^1 or the enantiomorphous form D_3^2. The axial lengths calculated for this cell are $a=8·42$ and $c=13·75$ Å., which values are in disagreement with those of Becker and Rose (A., 1923, i, 550), who found $a=8·15$ and $c=13·46$ Å. The optical activity, which slightly exceeds that of quartz, is due, as it is in quartz, to the spiral arrangement of the molecules in the cell. A. E. MITCHELL.

Crystal structure of quinol II. W. A. CASPARI (J.C.S., 1927, 1093—1095).—*X*-Ray examination shows that the trigonal-polar crystals of the β-modification of quinol (*d* 1·31, m. p. 166°) which are deposited from methyl-alcoholic solutions at the ordinary temperature have the cell-dimensions $a=$

16·25 and $c=5·53$ Å., and that the space-group is C_3^1. The lattice is hexagonal, and the cell contains 9 molecules. Since the symmetry requires only three lattice units, an asymmetric association of 3 molecules in each unit is indicated. A similar triple crystallographic association was observed with α-quinol (this vol., 10). Similar measurements on the γ-modification (d 1·325, m. p., 169°) obtained by sublimation lead to the values $a=13·24$, $b=5·20$, $c=8·11$ Å. The cell contains 4 molecules. The space-group is C_{2h}, and the crystal is built up on the simple lattice Γm.

J. S. Carter.

Arrangement of micro-crystals in beaten gold foil. S. Tanaka (Mem. Coll. Sci. Kyoto, 1927, **10**, 183—189).—Examination of the micro-crystals in rolled and hammered gold foil by the X-ray method shows that the majority are arranged with their (110) faces nearly parallel to the surface of rolling, and the normals of the (211) faces parallel to the direction of rolling. In foil, prepared by hammering for a long time, the (100) faces of the crystals are arranged parallel to the surface, the orientations in other respects being at random. During the beating process, there is a comparatively persistent stage, during which the crystals assume a fibrous structure with the normals of the (110) faces as their common axis arranged roughly parallel to the surface of the foil.

H. Burton.

Metal single crystals. K. W. Hausser and P. Scholz (Wiss. Veroff. Siemens-Konz., 1927, **5**, 144—164).—Large single crystals can be prepared by cooling the molten metal very slowly. Single crystals of copper weighing 6 kg. have been made. The general properties of single crystals are discussed, with special reference to their hardness and unusually high elongation before fracture. Methods of determining crystal orientation are critically reviewed. Experiments with large single-crystal spheres of copper are described. The orientation is most easily determined by etching, and their appearance is illustrated in coloured plates. The disagreement between calculated and actual values of many properties of metals is ascribed to their polycrystalline structure. Artificial and natural single crystals have not uniform lattices, but are composed of numerous crystallites of similar orientation. The etched surfaces of large single crystals reveal defects which are not observed with wires. The crystals appear to have different chemical properties in different directions, as shown by the forms produced on etching, and by the precipitation of mercury from mercuric nitrate on the rhombododecahedral faces, but not on the corners.

C. J. Smithells.

Thermal and electrical conductivity of a single crystal of aluminium. E. Griffiths (Proc. Roy. Soc., 1927, **A**, **115**, 236—241).—The thermal conductivity of an aluminium crystal (99·6% Al, 0·2% Si, 0·2% Fe), prepared by the method described by arpenter (B., 1926, 792), has been determined by setting up a longitudinal heat flow in the crystal, heat loss from the sides being prevented by the use o a coaxial shield, constituting a guard ring, along m e same temperature gradient is maintained. e value $\kappa=0·55$ was obtained; tests with an extruded bar of aluminium (99·7% aluminium) gave practically the same result. The temperature coefficient of thermal conductivity of the crystal has a small positive value. From measurement of the potential drop when a known current is passed through the crystal, the value $2·89\times10^{-6}$ ohm per c.c. was obtained for the specific resistivity of the crystal at 18°. Calculation of Lorenz's constant, $\kappa/\lambda T$, gives $5·4\times10^{-9}$, which falls within the range of published values, $5·3$—$6·0\times10^{-9}$, previously determined for cast or rolled pure metals.

L. L. Bircumshaw.

Hardness of metals in relation to periodicity. S. A. Korff (Nature, 1927, **119**, 818).—The hardness periodicity determined by Mallock (this vol., 300) accords with the 18-period table given by Russell, Dugan, and Stewart ("Astronomy"). A possible interpretation lies in the completeness or otherwise of the electron shells.

A. A. Eldridge.

Influence of plastic deformation on the thermal expansion coefficient of metals. W. Jubitz (Z. tech. Physik, 1926, **7**, 522—527).—Rolling a cast zinc bar at 150° causes an increase, and further cold treatment a decrease, in the expansion coefficient, in accordance with Polanyi's theory of the directive influence of drawing on micro-crystals. Hammering produces a similar effect. The value for a slowly solidified zinc rod was near the lower limit. Analogous effects were obtained with cadmium and manganese.

Chemical Abstracts.

Change of properties of substances on drying. D. Balarev (J. pr. Chem., 1927, [ii], **116**, 57—58).—Methyl, ethyl, and propyl alcohols, benzene, hexane, and ethyl ether were preserved in highly evacuated vessels with their vapours in contact with phosphoric oxide (cf. Baker, J.C.S., 1922, **121**, 568). The finely crystalline structure, and consequently the dehydrating power, of the oxide disappeared in a few weeks. After 3·5 years, the liquids were fractionated; all left residues which yielded phosphates on hydrolysis. Accordingly, the solvent must in each case have combined with the phosphoric oxide, forming volatile esters, and it is suggested that the presence of these causes the changes in physical properties observed by Baker.

H. E. F. Notton.

Micro-determination of mol. wt. H. Jorg (Ber., 1927, **60**, [B], 1141—1146).—The depression of the temperature is deduced from the potential developed in a thermo-element, one function of which is immersed in the homogeneous, solidifying solvent, whereas the other junction is in the solidifying solution. Copper-constantan–copper and silver-constantan–silver are used below and above 100°, respectively.

H. Wren.

Atomic properties which make an element a metal. K. F. Herzfeld (Physical Rev., 1927, [ii], **29**, 701—705).—The necessary and sufficient condition for metallic conductivity is $R>M/d$, where R is the molar refractivity. This relation is fulfilled for sodium, zinc, and cadmium and the inert gases; results for elements having diatomic molecules also support the relation, but the formula cannot be applied rigorously in that case.

A. A. Eldridge.

Permeability of iron at high frequencies. C. GUTTON and (MLLE.) I. MIHUL (Compt rend., 1927, **184**, 1234—1237).—The permeability of iron at high frequencies has been determined between the wavelengths 8 and 25 metres, using piano wires 7 cm. long and 0·85 and 1·24 mm. in diameter, and having resistivities of 23,300 and 22,900 electromagnetic units, respectively. Stefan's formula was employed for this purpose, the resistances of Blondot resonators composed of similar iron and copper wires being calculated from the self-induction. The differences between the permeabilities corresponding with each of the wires were of the order of experimental error. There was no indication of variations in the permeability of iron analogous with that of the dielectric constant in the neighbourhood of the absorption bands. J. GRANT.

Evolution of the hydrate of cobalt sesquioxide in contact with water. (MLLE.) S. VEIL (Compt. rend., 1927, **184**, 1124—1125).—Analogously with nickel (A., 1925, ii, 183), the hydrate of cobalt prepared by precipitation of a cobalt salt with sodium hypochlorite, and the corresponding calcined oxide, have higher coefficients of magnetisation when the former is prepared in the cold than when it is treated with cold water. In general, re-dissolution and re-precipitation of the hydroxides followed by treatment with warm water increased the magnetisation of the hydroxides, and decreased that of the corresponding oxides, with each cycle of operations.

J. GRANT.

Magnetic behaviour of "modified" hydroxides suspended in hydrogen peroxide. (MLLE.) S. VEIL (Compt. rend., 1927, **184**, 1171—1172).—Immersion in hydrogen peroxide of "modified" nickelous hydroxide (A., 1925, ii, 183) increases the magnetisation slightly, to an almost constant value, less than that of the hydroxide prepared in the cold, that of the corresponding calcined oxide being practically unaltered. Treatment with warm water appears to inhibit the chemical and magnetic activities of nickelous hydroxide. Analogous results were obtained with ferric hydroxide (A., 1926, 567).

J. GRANT.

Hall effect for bismuth in weak magnetic fields. F. KLAIBER (Z. Physik, 1927, **43**, 66—68).—Preliminary. The Hall constant R is not abnormal in weak fields, as found by Craig (Physical Rev., 1926, [ii], **27**, 772). R. A. MORTON.

Optical properties of arsenic. E. GRYSZKIEWICZ-TROCHIMOVSKI and S. F. SIKORSKI (Rocz. Chem., 1927, **7**, 54—66).—The atomic refractions of arsenic in combination with aliphatic radicals are 10·8, 10·9, and 11·3 for the H_α-, D-, and H_β-lines, respectively. The refraction of arylarsines increases with the number of aryl radicals combined with the arsenic atom, similarly as with arylamines. Substitution of chlorine in the benzene nucleus has little influence on the value of the refractive index.

R. TRUSZKOWSKI.

Refractivity of carbon monoxide. R. A. MORTON and R. W. RIDING (J. Physical Chem., 1927, **31**, 723—727).—The refractivity of carbon monoxide for the line 5085·83 Å., after being dried by phosphoric oxide, was found to be $3366{\cdot}60\times10^7$. Further purification by means of liquid air lowered this value to $3366{\cdot}35\times10^7$. Mixtures of carbon monoxide and water vapour obeyed the simple mixture law, indicating that the known changes in chemical reactivity of moist carbon monoxide are not accompanied by changes in refractivity. Activation of the carbon monoxide is not concerned, therefore, with valency electrons.

The refractivity of oxygen for the line 5085·83 Å. was found to be $2717{\cdot}28\times10^7$ with the Jamin refractometer. This value is lower than that of Cuthbertson (A., 1910, ii, 85) owing to a difference in the values for the refractivity of air found by this author and by Meggers and Peters; the value of the latter authors has been used in the present work.

L. S. THEOBALD.

Kamerlingh Onnes. E. COHEN (J.C.S., 1927, 1193—1209).—A memorial lecture, delivered before the Chemical Society on February 10, 1927.

Thermal expansion of graphite. P. HIDNERT and W. T. SWEENEY (U.S. Bur. Stand. Tech. Papers, No. 335, 1927, **21**, 223—230; cf. A., 1926, 231).—Electrodes of artificial graphite (99·2—99·7% C) formed by extrusion of a plastic material containing coke and an organic binding substance with subsequent baking at a very high temperature, possess a higher coefficient of expansion (approximately 45%) in the direction transverse to that of extrusion than in the direction of extrusion. The coefficients of linear expansion were found to increase with increasing temperature over the range 20—600°. The values obtained are low, being $1{\cdot}9\times10^{-6}$ per degree between 20° and 100° along the direction of extrusion. This value is about one sixth of the coefficient of expansion of ordinary steel. G. A. ELLIOTT.

Thermal expansion of metallic compounds. M. DE HEMPTINNE (Bull. Acad. roy. Belg., 1926, [v], **12**, 797—800).—The coefficients of expansion of alloys of silver and antimony have been determined between 0° and 100° by direct measurement of the increase in length with a spherometer. The maximum at 73% silver corresponds with the compound Ag_3Sb, the existence of which has previously been indicated by other physical properties.

H. F. GILLBE.

Thermal conductivity of gases. E. O. HERCUS and T. H. LABY (Phil. Mag., 1927, [vii], **3**, 1061—1064).—The measurements of Gregory and Archer (A., 1926, 231, 340) do not take account of the temperature discontinuity between the gas and the hot wire. When the values for this correction as given by Knudsen (A., 1911, ii, 368) are introduced, Gregory and Archer's method becomes sound, and the results afford a much better verification of Maxwell's law than is claimed by them. Their recalculated values of the thermal conductivities at 0° are for air $5{\cdot}85\times10^{-5}$ and for hydrogen $40{\cdot}6\times10^{-5}$, thus differing from the most probable values, $5{\cdot}33\times10^{-5}$ and $37{\cdot}9\times10^{-5}$, respectively. A. E. MITCHELL.

Heat capacities of liquid metals. A. L. DIXON and W. H. RODEBUSH (J. Amer. Chem. Soc., 1927, **49**, 1162—1174).—A method of measuring the specific heats by reversible adiabatic (isentropic)

expansion is described (cf. Lewis and Randall, "Thermodynamics," 1923, p. 137). Preliminary experiments with molten sodium, potassium, and lead, and also with mercury, yielded satisfactory results. S. K. TWEEDY.

Polymorphism of zinc. G. J. PETRENKO (Z. anorg. Chem., 1927, **162**, 251—252).—Cooling curves indicate that zinc has transition points at 300° and 175°. Microscopical examination confirms the existence of the former only. R. CUTHILL.

Pykno-manometry. New method of determining vapour density, vapour pressure, and liquid density. M. TRAUTZ and E. TRIEBEL (J. pr. Chem., 1927, [ii], **116**, 205—228).—An apparatus is described which can be used for the determination of vapour density, vapour pressure, or liquid density. By assuming values for any two of these quantities, the third can be calculated from the experimental data. A weighed amount of liquid (bromine) is vaporised in an evacuated density bulb kept at a temperature above the b. p. of the liquid. Sealed to this bulb is a long, vertical, narrow, calibrated tube, which is cooled below the b. p. of the liquid. When equilibrium occurs between the cool liquid and hot vapour, the weights of substance in the various parts of the apparatus are calculated and an equation combining vapour pressure, mol. wt., volumes, and temperatures is obtained.

The determination of the vapour pressure of bromine between 35° and 50° gave values agreeing with those obtained by Ramsay and Young (J.C.S., 1886, **49**, 453). Further experiments with a modified apparatus, having the density bulb at temperatures from 300° to 750° and the liquid at 35—51°, gave results indicating that at high temperatures slight dissociation of bromine molecules takes place. Values of the equilibrium constant for the change $Br_2 \longrightarrow Br+Br$ are given, and they agree with the values calculated from the data of Bodenstein and Cramer (A., 1916, ii, 552). During the course of the work, the density of liquid bromine was determined between 25° and 50°. The various sources of error are discussed. H. BURTON.

Fixed point for calibration of pressure gauges. Vapour pressure of carbon dioxide at 0°. O. C. BRIDGEMAN (J. Amer. Chem. Soc., 1927, **49**, 1174—1183).—The vapour pressure of liquid carbon dioxide at 0° is 26144·7±1·0 mm. of mercury (g=980·665 cm./sec.^{2}). The carbon dioxide liquid–vapour system at 0° is suggested as a suitable fixed point for the calibration of piston pressure gauges.

S. K. TWEEDY.

Method of measuring vapour pressure by air bubbling. H. I. DOWNES and E. P. PERMAN (Trans. Faraday Soc., 1927, **23**, 95—106).—See this vol., 194.

Calculation of invariants in the determination of vapour-pressure and m.-p. curves. V. FISCHER (Z. Physik, 1927, **43**, 131—151).—Theoretical. Expressions are deduced for calculating the invariants in vapour-pressure equations, and the results are applied to water vapour and to oxygen–nitrogen mixtures. Baly's experimental results on the dissociation of liquid air (A., 1900, ii, 589) are shown to be in conformity with the theory. Methods for calculating thermodynamic potentials and the invariants in the equations for molten substances are given, and the results are tested by means of data on lead–antimony and zinc–mercury alloys. Heats of mixture may be calculated. R. A. MORTON.

Pressure–volume–temperature relation for gaseous ethyl ether. II. J. A. BEATTIE (J. Amer. Chem. Soc., 1927, **49**, 1123—1130).—With decrease in specific volume, the isometrics of gaseous ethyl ether show increasing curvature (cf. A., 1924, ii, 300): in order to represent the pressure in this region, it is necessary to introduce an extra function of T and v in the Keyes equation of state. On the assumption that the curvature is due to molecular aggregation, the introduction of such a function leads to the equation (p in atm.; v in c.c./g.): $p=1{\cdot}10777T/(v-\delta)(1-\gamma)-\varphi$, where $\gamma=0{\cdot}00145/v\,.\,e^{1596/T}$, $\delta=5{\cdot}7630e^{-5{\cdot}3397/T}$, and $\varphi=5420/v^2\,.\,e^{-13{\cdot}797/v^3}$. The equation holds accurately down to v=10; this improved agreement, however, is attributed mainly to the use of a new form for the φ function, viz., $A/v^2.e^{-l/v^3}$ in place of $A/(v+l)^2$. S. K. TWEEDY.

Equation of state for gaseous carbon dioxide. O. C. BRIDGEMAN (J. Amer. Chem. Soc., 1927, **49** 1130—1138).—On the assumption that the departure from linearity of the isometrics of carbon dioxide are due to molecular aggregation, the equation of state for this gas, based on Amagat's figures between 0° and 100°, is deduced to be: $p=[RT(1-y/2)]/(v-\delta)-\varphi$, where $y=1{\cdot}8764\times10^{-4}/v\,.\,e^{2137{\cdot}8/T}$, $\delta=2{\cdot}6960e^{-1{\cdot}9701/v}$, and $\varphi=3057{\cdot}7/v^2\,.\,e^{-1{\cdot}0617\,v}$. The average deviation between observed and calculated values down to 10 c.c./1 g. is 0·07%. Andrews' low-pressure data agree fairly well with the equation; the data of Maass and Mennie (A., 1926, 233) also fit very well (cf. following abstract). S. K. TWEEDY.

Vapour pressure of liquid carbon dioxide. C. H. MEYERS and M. S. VAN DUSEN (Refrigerating Eng., 1926, **13**, 180—184).—The vapour-pressure measurements of liquid carbon dioxide were made, by the static method, over the whole temperature range from the triple point to the critical point with an accuracy of 1 in 3000, and the triple-point pressure was calculated. The critical temperature was 31·10° and the pressure 72·95 atm.

CHEMICAL ABSTRACTS.

Vapour-pressure curve of benzoic acid. S. KLOSKY, L. P. L. WOO, and R. J. FLANIGAN (J. Amer. Chem. Soc., 1927, **49**, 1280—1284).—The vapour pressure of liquid benzoic acid, measured by the isoteniscope method of Menzies and Smith (A., 1910, ii, 1036) in the range 128·6—247°, is given by $\log_{10} p$ (mm.)=30·172—4714/T—6·720 log T (cf. Kahlbaum, A., 1898, ii, 556). The sublimation pressure of the solid acid in the range 50—121° was measured by a static method; the results are represented by $\log_{10} p$ (mm.)=11·956—4409/T, with a maximum deviation of 2·5%. The calculated latent heat of fusion is 32·8 g.-cal./g. S. K. TWEEDY.

Specific volume of cotton cellulose. G. F. DAVIDSON (J. Text. Inst., 1927, **18**, T175—186).—There is evidence that the value observed when helium is the immersion medium may be regarded as

the true specific volume of cellulose. This has been determined for soda-boiled cotton (the purest form of cotton cellulose) of three types (American Upland, Sea Island, and Sakellarides), the same after mercerisation, and for viscose, nitro-, and cuprammonium-silks. Small differences were established between the different cottons, the average value being 0·640 at 20°. The mercerised cottons had the average value 0·646, viscose 0·646, nitro-silk 0·648, and cuprammonium-silk 0·653. Values obtained at 20° for American Upland cotton in liquid media were: water 0·621, acetone 0·642, chloroform 0·644, benzene 0·644, carbon tetrachloride 0·644, nitrobenzene 0·644, and toluene 0·645. The temperature coefficients for water and toluene were according to the equations $V_t=0{\cdot}6190(1+0{\cdot}000198t)$ and $0{\cdot}6449(1+0{\cdot}000085t)$, respectively. The low value in water indicates the existence of a compressed layer of water molecules on the surface, and the minimum compressive force in kg./cm.^{2} has been calculated as follows: cotton (average) 2260, the same mercerised 1980, viscose 1480, nitro- and cuprammonium-silks 1890. On the other hand, the high value in toluene suggests that cellulose is not completely penetrated by toluene molecules. J. C. Withers.

Viscosity of a gas composed of Sutherland molecules of a particular type. H. R. Hasse and W. R. Cook (Phil. Mag., 1927, [vii], **3**, 977—990).—Theoretical values for the viscosity of gases have been calculated on the assumption that the molecules are composed of rigid spheres in which the attractive force varies as the inverse fifth power of the distance from the centre of the molecule. For argon, the calculated values are in good agreement with the experimental. For nitrogen, carbon dioxide, and air, the agreement between the theoretical and observed values is fair. For helium there is no agreement. A. E. Mitchell.

Viscosity of liquids above their b. p. I. T. Titani (Bull. Chem. Soc. Japan, 1927, **2**, 95—105).—The absolute viscosities of methyl acetate and fluorobenzene, at temperatures considerably above the b. p., have been determined by Heydweiller's method (Ann. Physik, 1895, **55**, 561; 1896, **59**, 198). A modification of this method, involving the use of a glass-sealed viscosimeter, is described and employed in the measurement of the viscosities of carbon tetrachloride, chlorobenzene, and ethyl alcohol. The method of calculation of the value of the viscosity from the experimental data is discussed. At the lower temperatures, the results are in good agreement with the work of other investigators. M. S. Burr.

Viscosity and geometrical isomerism. (Mlle.) G. Cauquil (Compt rend., 1927, **184**, 1248—1250).—The *cis*- and *trans*-isomerides of certain hydrocyclic compounds are distinguishable by their different viscosities. The internal friction is least in the former case (cf. Vavon, A., 1926, 837). For the ethylenic isomerides and homologues of maleic and fumaric acids, the differences in viscosity are of the order of experimental error. J. Grant.

Permeability of nickel to hydrogen. Influence of the thickness of the metal. V. Lombard (Compt. rend., 1927, **184**, 1327—1329).—The author has applied his method (A., 1926, 349) to the determination of the permeability to hydrogen of nickel plates 0·16—1·99 mm. thick. The formula $d=K/h$ (where d is the number of c.c. of gas at N.T.P. passing through a surface of 1 cm.^{2} per hour, h the thickness of the metal, K a constant) expresses the results over a wider range than that previously suggested. K is a function of temperature and pressure. J. Grant.

Equilibrium pressures of a gas in a mixture, especially of ammonia mixed with nitrogen. E. Lurie and L. J. Gillespie (J. Amer. Chem. Soc., 1927, **49**, 1146—1157).—If the equilibrium pressure of any gas in a mixture equals the product of its mol. fraction and the total pressure, then the laws of Boyle and Avogadro must hold for the pure gases in that mixture. The composition and total pressure of various mixtures of ammonia and nitrogen in equilibrium with a mixture of barium chloride and the compound $BaCl_2,8NH_3$ at 45° have been determined over a pressure range of 7—60 atm. Dalton's law of partial pressures and Gibbs' modification of the law fail to account for the observations. The equilibrium pressure of ammonia may be approximately calculated by Lewis and Randall's fugacity rule over that pressure range to which the rule can be applied. The equilibrium pressure calculated by the equation of state for mixtures agrees remarkably well over the entire pressure range with the observed pressures. The results of Pollitzer and Strebel (A., 1925, ii, 104) were also fairly well represented by an equation of state for mixtures. The dissociation pressure of the system $BaCl_2$–$BaCl_2,8NH_3$–NH_3 is represented between 38° and 50° by $\log_{10} p$ (mm.) $=-2031{\cdot}39/T+10{\cdot}1191$. S. K. Tweedy.

Comparison of the behaviour in thermal diffusion of nitrogen and carbon monoxide and of nitrous oxide and carbon dioxide. T. L. Ibbs and L. Underwood (Proc. Physical Soc., 1927, **39**, 227—237).—The thermal separation obtained in gas mixtures containing nitrogen is compared with that in mixtures containing carbon monoxide. A similar comparison is made of mixtures containing carbon dioxide or nitrous oxide. The gas analysis was made by means of the Shakespear katharometer. The behaviour of nitrogen is similar to that of carbon monoxide. The effect shown by carbon dioxide is generally a little different from that shown by nitrous oxide. The pairs of gases examined provide a special case for the application of the Enskog–Chapman theory, as in each pair the mol. wt. and mean collision areas are the same. It is inferred that the molecular field of nitrogen is similar to that of carbon monoxide, and that the field of carbon dioxide differs little from that of nitrous oxide. C. J. Smithells.

Density and refractive index of solutions. G. de Lattre (J. Chim. phys., 1927, **24**, 289—308).—The refractive index n_v of a binary mixture is given by $n_v=(m_1+m_2)/(m$), where and μ_v are the respective densities of the constituents. The ratio of the "contraction of density, to the contraction of the refractive index, dn/n, assuming pure additivity of properties (*i.e.*, no chemical combination) and using the Lorenz–Lorentz

relationship, is given by $6n^2/(n^2-1)(n^2+2)$; thus the ratio varies with any factor which affects the refractive index, such as composition of the mixture or wave-length of the light used, and is not constant, as previously supposed. This formula is verified by reference to data for binary mixtures of various alcohols, fatty acids, etc. with water, and the concordance between observed and calculated values of the ratio indicates the absence of chemical combination. Only for the system pyridine–water is the formula unsatisfactory; the formation of a hydrate, $C_5H_5N,2H_2O$, has been suggested by Timmermans, according to which a mixture of this composition should give maximum deviation between observed and calculated values of the contraction ratio, whereas actually it gives a minimum one. Thus the hydrate theory is unsatisfactory as an explanation of critical solution phenomena. S. J. Gregg.

Binary azeotropes. V. M. Lecat (Rec. trav. chim., 1927, **46**, 240—247; cf. A., 1926, 1199; Ann. Soc. scient. Bruxelles, **45**, I, 284; **47**, I, 21).—An examination of 255 binary mixtures of organic liquids has shown the existence of 128 new positive (first type) azeotropes, 27 new negative (second type) azeotropes, and 13 eutectic mixtures (incompletely miscible at the b. p.). The remaining 87 systems were non-azeotropic. The b. p. of each constituent, the composition and b. p. of the azeotropic and eutectic mixtures, and the temperature changes produced on mixing the constituents in azeotropic or other proportions are tabulated. The experimental numbers are briefly discussed. J. S. Carter.

Existence of some azeotropic mixtures. O. Fuchs (Chem.-Ztg., 1927, **51**, 402).—Hannotte's statement (A., 1926, 671) that methyl acetate can be separated from its mixtures with water by fractional distillation is incorrect, since an azeotropic mixture containing 3·2—3·7% of water distils at a temperature 0·6—0·7° below the b. p. of the ester. In the case of *iso*amyl alcohol–*iso*amyl acetate mixtures, there is some evidence for the existence of an azeotropic mixture containing about 2·5% of the ester. The composition of the binary azeotropic mixture, methyl alcohol–ethyl acetate, given by Lecat ("L'Azéotropisme," 1918, 95) is clearly erroneous, since available data indicate that this mixture contains 43—47% of methyl alcohol. The ternary azeotropic mixture, methyl alcohol–acetone–methyl acetate (Lecat, *ibid.*, 184), is shown to be non-existent. J. S. Carter.

Adsorption phenomena of silver iodide. A. Frumkin and A. Obrutscheva (Biochem. Z., 1927, **182**, 220—232).—The capacity of silver iodide to adsorb octoic acid reaches a maximum at a given silver-ion concentration. At this concentration, the *P.D.* of a silver electrode measured against a normal calomel electrode is 0·16 volt. A theoretical treatment of this observation is given. J. Pryde.

Adsorption of basic colouring matters by filter paper. S. Mokruschin and O. Esin (J. Russ. Phys. Chem. Soc., 1926, **58**, 882—887).—See s vol., 305. E. Rothstein.

Area of the internal surface of charcoal as rmined by the adsorption of the normal aliphatic alcohols from aqueous solution. W. E. Garner, D. McKie, and B. C. J. G. Knight (J. Physical Chem., 1927, **31**, 641—648).—The adsorption isotherms of *n*-propyl, *n*-butyl, and *sec.*-amyl alcohols on the charcoal used in a former investigation (Garner and Blench, A., 1924, ii, 537) have been determined by measurements of surface tension (cf. Donnan and Barker, Proc. Roy. Soc., 1911, **85**, **A**, 557). The results support the view that the change of slope of the isotherm corresponds with the completion of a unimolecular layer on the surface of the charcoal. The internal area of unit weight of charcoal is 66 m.², and evidence is afforded for the view that a small fraction of the atoms composing the surface of the charcoal are in a highly activated state, confirming the view of Rideal and Wright (A., 1925, ii, 806). L. S. Theobald.

Adsorption by metallic hydroxides. III. Adsorption by precipitated aluminium hydroxide. K. C. Sen (J. Physical Chem., 1927, **31**, 686—692; cf. Yoe, A., 1925, ii, 107; this vol., 509).—The adsorption of various acids by aluminium hydroxide, precipitated at the ordinary temperature from 2*N*-aluminium chloride by ammonia and allowed to "age" for 25 days, has been studied. Arsenious acid is adsorbed, equilibrium being reached in 20 hrs. Heating the aluminium hydroxide in boiling water for 15 min. reduces its adsorptive power at the ordinary temperature. The presence of potassium chloride is without effect on the equilibrium, which is reversible. With acid of the same normality, adsorption increases with increase in volume of the solution and decreases when the amount of solute is constant. Adsorption is unaffected by the addition of sucrose or alcohol. The iodine values for adsorption of sodium arsenite and arsenious acid are the same. Adsorption of oxalic, citric, racemic, malic, and sulphuric acids by aluminium hydroxide is considerable, as is also the case with sodium hydroxide.
L. S. Theobald.

Adsorption. XVIII. Coagulation of sols by a mixture of electrolytes and the phenomena of positive and negative acclimatisation. S. Ghosh and N. R. Dhar (J. Physical Chem., 1927, **31**, 649—680; cf. A., 1925, ii, 778).—Marked ionic antagonism occurs when sols of ferric, aluminium, and chromic hydroxides are coagulated by mixtures of hydrochloric acid with potassium chloride, potassium sulphate, or potassium ferrocyanide. These sols are stabilised by the preferential adsorption of the similarly charged hydrogen ions. Aluminium hydroxide sol shows ionic antagonism when coagulated by a mixture of potassium chloride and aluminium nitrate, due to the adsorption of aluminium ions, but not when coagulated by mixtures of potassium chloride and sulphate, or potassium chloride and oxalate. Hydrochloric acid has a greater stabilising influence on this sol, prepared in the cold, than on ferric hydroxide sol prepared from a boiling solution of the chloride. Negative manganese dioxide sol behaves normally when coagulated by mixtures of potassium chloride and bromide, barium and magnesium chlorides, potassium bromide, and barium chloride, but shows ionic antagonism with a mixture of potassium chloride

and hydroxide, the hydroxyl ions being adsorbed. A positive sol is normal towards a mixture of potassium nitrate and sulphate, but shows antagonism with potassium and silver nitrates and with potassium nitrate and cupric chloride, the silver and cupric ions being adsorbed. No ionic antagonism is shown between positive thorium hydroxide sol, negative vanadium pentoxide sol, and positive stannic hydroxide, and mixtures of potassium bromate and sulphate, potassium and barium chlorides, and potassium chloride and sulphate, respectively. Negative uranium ferrocyanide sol is slightly abnormal when coagulated by a mixture of potassium and barium chlorides, but develops marked antagonism towards potassium chloride and ferrocyanide, due to preferential adsorption of the ferrocyanide ion. Antagonism is greatest in dilute sols. Sols of gamboge, gum dammar, gold, and silver have also been investigated in this connexion.

Acclimatisation has been observed in the following cases of coagulation: gold sol by potassium hydroxide or oxalate; antimony sulphide and gum dammar sols by potassium chloride or nitrate, and by barium or strontium chloride; and positive manganese dioxide sol by silver nitrate and cupric chloride. Antimony sulphide sol shows negative acclimatisation when coagulated by strychnine hydrochloride and methylene-blue, as does negative manganese dioxide sol coagulated by silver nitrate or cupric chloride. The adsorption of the oppositely charged ion in these cases is high in comparison with that of the ion of the same charge. Sols of aluminium hydroxide, vanadium pentoxide, and gold show no acclimatisation when coagulated by potassium chloride, oxalate, or ferrocyanide or by barium chloride.

The views of Weiser on acclimatisation are considered to be inadequate, and a reply is made to his criticisms (A., 1926, 242) of the authors' views.

Various other effects attributable to the adsorption of ions carrying the same charge as the sol are considered. L. S. THEOBALD.

Surface phenomena and adsorption at the contact of two liquid phases. R. DUBRISAY (Rev. gen. Colloid., 1927, **5**, 485—489).—A review of the author's previous work on the lowering of surface tension at the interface between water and a benzene solution of a fatty acid (cf. A., 1924, ii, 154, 731; 1926, 119). L. L. BIRCUMSHAW.

Surface tension of mercury and the action of aqueous solutions on a mercury surface. R. S. BURDON and M. L. OLIPHANT (Trans. Faraday Soc., 1927, **23**, 205—213; cf. Burdon, A., 1926, 348).—Pure water spreads very slowly when placed on a clean mercury surface in air. Drops of very dilute solutions of inorganic or organic acids spread rapidly until they attain a definite area such that, assuming complete dissociation of the acids employed, 1 cm.^{2} contains 10^{14} hydrogen ions. The spreading of pure water may be induced by means of an electric current passing from mercury to water, when the velocity is equivalent to 1 cm.^{2} for a flow of 10^{14} electrons. The velocity of normal spreading increases with the diameter of the drop, and it is most rapid for surfaces prepared in oxygen. The phenomena of spreading cannot be predicted from Antonov's rule or from the spreading coefficient of Hardy and Harkins. A critical discussion of the methods employed previously to determine the surface tension of mercury, and of the changes in surface tension indicated by the spreading and by other phenomena, is included. G. A. ELLIOTT.

Relation between the surface tension of very viscous liquids and the temperature. G. TAMMANN and H. RABE (Z. anorg. Chem., 1927, **162**, 17—21).—The surface tensions of salicin and piperine have been determined at a series of temperatures by various methods. Within the viscosity region 10^4—10^9 g./cm. sec., the surface tension decreases linearly with rising temperature. The presence of water vapour causes the surface tension to increase with rise in temperature. R. CUTHILL.

Ductility, surface tension, and specific heat of glassy substances. G. TAMMANN and R. TAMPKE (Z. anorg. Chem., 1927, **162**, 1—16).—Determinations have been made of the length of the threads which can be drawn, under specified conditions, from piperine, narcotine, dextrose, "betol," and "alphol" at temperatures above their softening points. In all cases, the maximum length of thread rapidly decreases with rising temperature, and, for "betol," is inversely proportional to the length of time for which the drawing is carried out. If one point in a thread of a glassy substance is heated, the thread first lengthens, then contracts, and again commences to elongate when the load is greater than the surface tension at the heated point. The surface tension of glass and salicin has been measured by utilising this phenomenon. Surface-tension determinations by the method of maximum bubble pressure have also been made with salicin, "betol," "alphol," piperine, and dextrose at temperatures for which the viscosity does not exceed 20 g./cm. sec., the temperature coefficient being found to be negative and dependent on the temperature. From heating and cooling curves, it has been possible to calculate the variation in the specific heat with the temperature of several of the above substances. It appears that in the temperature range corresponding with viscosities of 10^{13}—10^{14} g./cm. sec. the specific heat and probably also the coefficient of expansion increase rapidly. R. CUTHILL.

Forces operating in thin layers. Dielectric constants of thin layers. H. KALLMANN and K. E. DORSCH (Z. physikal. Chem., 1927, **126**, 305—322).—In accordance with Haber's theory it is shown that although the charges concentrated in the surface of a liquid exert the greatest influence on the properties of the surface, yet even at macroscopic distances below the outer layer, forces of considerable magnitude are called into play. The question of the change of structure of a liquid in the neighbourhood of the surface layer is discussed and the dielectric constants of very thin layers (about 1·2 μ thick) of ether, benzene, toluene, xylene, ethyl alcohol, water, amyl acetate, and triolein have been measured. The results obtained do not deviate more than 0·5% from the normal values. The greatest deviation of the dielectric constant occurs in the ultimate surface layer

of molecules, whilst molecular layers not far removed from the surface show normal values. This result is true for all the substances investigated, but especially for those in which the electric polarisation is due to dipoles, as with ethyl alcohol and water. Further, Palmer's conclusion that the dielectric constant of the surface layer of water is very nearly the same as that of ice, can be true only for layers of the order of 1 molecule thick. Change of structure in the liquid occurs chiefly, if not entirely, in the surface layer of molecules. H. F. GILLBE.

Passivity of metals. I. Isolation of the protective film. U. R. EVANS (J.C.S., 1927, 1020—1040).—The passivity of iron is shown to be due to the existence of a protective film which is too thin to give interference tints. This film, which consists of ferric oxide or hydroxide, has been obtained as a transparent envelope by dissolving the metal beneath by anodic treatment in sodium chloride solutions. The transparent skin can also be removed by treatment with iodine. Chlorides favour the activation, since the film is permeable to chloride ions, and under anodic conditions the metal is dissolved away beneath the skin; mere immersion in a chloride solution, under conditions precluding the flow of local currents, does not cause activation. The attack on passive iron is often localised at the water surface, the protective film tending to cling to the gas–liquid interface rather than to the metal–liquid interface, thus initiating a breakdown. Nitric acid is a rather untrustworthy reagent for producing passivity. Transparent films have also been isolated from the surface of passive copper and aluminium.

J. S. CARTER.

Viscosity of saturated solutions of certain sodium and potassium salts. K. HRYNAKOWSKI (Rocz. Chem., 1927, 7, 34—41).—An Ostwald viscosimeter gives good results only when the viscosity of the saturated solution lies between 0·025 and 0·070. When the viscosity is greater, the results obtained have only an approximate value. It would appear that the ratio of the diameter of the capillary tube to that of the molecules of the liquid should always be of the same order of magnitude. For saturated solutions of potassium chloride, bromide, sulphate, chlorate, iodide, and nitrate, the values of η vary from 0·00720 to 0·00900 g./cm. sec., the differences between the first four salts lying within the limits of experimental error. In the absence of hydration and association, it would appear that saturated solutions of salts with a common cation have the same viscosity. The high values of η found for sodium salts are due to hydration. R. TRUSZKOWSKI.

F. p. of concentrated solutions. I. Experimental methods and the f. p. of potassium solutions. E. R. JONES and C. R. BURY (Phil. Mag., 1927, [vii], **3**, 1032—1037).—With a carefully controlled f.-p. apparatus, measurements have been made of the f. p. of solutions of potassium chloride over the range 0·0988—1·818*M*. The results obtained are used to evaluate the activity coefficients of the solutions over the concentration range 0·778—0·[illegible]. These values are in agreement with those obtained by Noyes and MacInnes from *E.M.F.* measurements at 25° of cells containing potassium chloride solutions. A. E. MITCHELL.

Assumptions in the measurement of hydration of substances in aqueous solutions. J. N. RAKSHIT (Chem. News, 1927, **134**, 289—291).—A critical review of the different methods employed for determining the hydration of solutes in aqueous solutions. All the methods involve the introduction of a second solute, and no account is taken of the interaction of the two dissolved substances.

M. S. BURR.

Mol. wt. of optically active polyhydroxy-compounds in ammoniacal copper solution (Schweizer's reagent). E. MESSMER (Z. physikal. Chem., 1927, **126**, 369—416).—The polarimetric method described (A., 1884, 577; 1921, i, 401) for studying the formation of complexes in copper hydroxide–ammonia solutions of cellulose and *iso*propylideneglucose has been tested by the investigation of water-soluble carbohydrates of known mol. wt. Normal mol. wts. are obtained for compounds of the methylcelluloses, hydrocellobiose, dextrose, and trehalose. Methylcellulose combines with 2 atoms of copper, hydrocellobiose with 1 atom, and trehalose with 1½ atoms. Under the same conditions as those employed for cellulose, dextrose yields two different complexes, of which the one of higher copper content is stable to sodium hydroxide of high concentration and is of similar composition to the trehalose compound.

Further results for cellulose and *iso*propylidineglucose confirm the earlier measurements. From the temperature coefficient of the rotation of the cellulose solutions, it is found that the tendency to the formation of copper complexes diminishes with fall of temperature.

Investigation of the "strong dextrin" of Schardinger and Pringsheim shows that this substance also forms complexes, although measurement of the rotation was not possible. The similarities between the various dextrins are exhibited also in their copper compounds. H. F. GILLBE.

Amphoteric hydroxides, their aqueous solutions, and crystalline salts. V. Variation of diffusion coefficient and optical absorption of tungstate solutions with hydrogen-ion concentration. H. SCHULZ and G. JANDER (Z. anorg. Chem., 1927, **162**, 141—148; cf. this vol., 122).—The diffusion coefficient of the tungstate ion in aqueous solutions of sodium tungstate decreases considerably with increasing acidity of the solution, which is probably due to an increase in complexity of the ions according to some such scheme as $7WO_4'' + 8H^{\cdot} \rightleftharpoons W(WO_4)_6'''''' + 4H_2O$. In solutions 0·1*N* in respect of a mineral acid and containing neutral salts, the degree of aggregation of the tungstate ion is 5—7 times that of the ion in alkaline solutions. In solutions which contain no neutral salts, but are 0·1*N* in respect of a mineral acid and have been boiled, the degree of aggregation is 9—11. With increasing acidity, the optical absorption limit of the solutions moves towards the region of longer wavelengths, which points to aggregation of the anions.

R. CUTHILL.

Survey of the main principles of colloid science. J. W. McBain (Fourth Colloid Symposium Monograph, 1926, 7—10). Chemical Abstracts.

Colloid particle as revealed by catalytic studies. H. S. Taylor.—See this vol., 632.

Colloid syntheses with the aid of titanium trichloride. A. Gutbier, B. Ottenstein, E. Leutheusser, K. Lossen, and F. Allam. **I. Products of hydrolysis and oxidation of titanium trichloride.** F. Allam (Z. anorg. Chem., 1927, **162**, 87—100).—The colour of titanium trichloride solutions changes from red to blue and ultimately disappears when these are diluted and exposed to air or boiled; this is accompanied by an increase in acidity and a decrease in the concentration of tervalent titanium (cf. Heydweiller, A., 1915, ii, 266). The change is much slower if oxygen is excluded, probably because such reactions as $2TiCl_3+H_2O+O=2TiOCl_2+2HCl$, $TiOCl_2+H_2O=TiO(OH)Cl+HCl$, and $TiO(OH)Cl+H_2O=TiO(OH)_2+HCl$ cannot then occur. It appears, however, that the hydrolysis $TiCl_3+3H_2O\rightleftharpoons Ti(OH)_3+3HCl$ plays an important part, the trihydroxide being later oxidised to the tetrahydroxide, which remains in colloidal solution, but may be precipitated by sulphate ions. By following with the aid of the tensi-eudiometer the desiccation of titanic acids prepared by various methods, no indication of the existence of definite compounds has been obtained, the water in all the preparations being simply held osmotically. With progressive loss of water, *i.e.*, with increasing temperature, the curves given by all the specimens tend to coincide. A specimen prepared by hydrolysis and oxidation with air of a titanium trichloride solution with subsequent desiccation up to 490° has the crystal lattice of anatase, whereas ignition of the product obtained by addition of ammonia to a titanium tetrachloride solution gives a substance with the rutile lattice. Fresh preparations give no *X*-ray interference effects. R. Cuthill.

Colloid syntheses with the aid of titanium trichloride. II. Colloidal gold and colloidal selenium. A. Gutbier, B. Ottenstein, and K. Lossen (Z. anorg. Chem., 1927, **162**, 101—109; cf. preceding abstract).—Titanium trichloride is a suitable reducing agent for the production of gold sols, the titanic hydroxide formed by oxidation and hydrolysis exerting a protective action. To obtain stable sols, the molecular ratio of titanic hydroxide to gold should not be less than 1·7 : 1. Excessive acidity must also be avoided. Selenium sols may be obtained by adding 20 c.c. of a 0·2% selenium dioxide solution to 16 c.c. of a 1·5% titanium trichloride solution, which has previously been boiled to produce sufficient quadrivalent titanium to reduce the selenium.

R. Cuthill.

Preparation of metal oxide–silicic acid sols from the ignited oxide and silicic acid hydrosol. A. Fodor and A. Reifenberg (Kolloid-Z., 1927, **42**, 18—35).—Ignited ferric oxide, chromic oxide, and aluminium oxide, although attacked very slowly by strong acids, are brought into solution by dialysed silicic acid, the action being one of peptisation. Since electrodialysed silicic acid cannot thus peptise the ignited oxides, the formation of the sol appears to be connected with the replacement of alkali still present in the micelle of the silicic acid submitted to ordinary dialysis. Ferric oxide gives a red sol, chromic oxide a green sol, and aluminium oxide a milk-white sol, the particles of all these sols being visible in the ultramicroscope and exhibiting the Brownian movement. The silicic acid and metal oxide wander together to the anode. The sols are flocculated by electrolytes, and the process has several points in common with the flocculation of clay suspensions. On coagulation by neutral salts, the feebly alkaline reaction of the ferric oxide–silicic acid sol changes to an acid reaction, suggesting that on removal of iron the free alkali enters the silicic acid micelle again. A ferric oxide–silicic acid sol has considerable alkali-fixing power. The significance of these observations in regard to the buffering effects of naturally occurring silicates is briefly considered. E. S. Hedges.

Approximate determination of the size of particles in hydrosols. R. Zsigmondy and C. Carius (Ber., 1927, **60**, [*B*], 1047—1049).—The method depends on the use of membrane filters with pores of different sizes, calibration being effected by gold hydrosol containing particles of measured dimensions. Certain hydrosols, regarded hitherto as consisting of very fine particles because of their homogeneous appearance and absence of sedimentation, have been found to be very coarsely disperse. H. Wren.

Stability of coarse particles in solutions. I. H. Werner (Ber., 1927, **60**, [*B*], 1040—1045).—Magnesium chloride exerts its optimal clarifying action on aqueous suspensions of *Bolus alba* at 0·01—0·1*M*-concentration. Increase in concentration of the electrolyte beyond this point is accompanied by progressive decrease in the rate of sedimentation, which, however, is more rapid in the saturated solution than in electrolyte-free water. Sodium nitrate does not accelerate the sedimentation in concentrated magnesium chloride solution. Starch in 0·007% concentration causes *Bolus* particles suspended in magnesium chloride solution to aggregate within a few minutes and rapidly subside. More dilute solutions of starch cause incomplete aggregation. More concentrated solutions have a stabilising action, which becomes more marked as the concentration increases; the aggregating action decreases simultaneously. The optimal concentrations of magnesium chloride and starch acting together is the same as when they are acting singly. *Bolus* particles which have been aggregated by starch can be dispersed by simple agitation. After shaking for a short time, the dispersed particles are again aggregated by the original starch, but the latter becomes inactivated after prolonged agitation. H. Wren.

Production of fog in the neutralisation of alkali with hydrogen halides. H. O. Askew (J.C.S., 1927, 966—983).—When air carrying hydrogen chloride or bromide is passed into aqueous alkaline media, the acid is incompletely absorbed and fogs are produced. The lower limiting hydroxyl-ion concentration for the production of fog is greater than $10^{-5}N$. The amount of fog produced depends on the width of the jet, the depth of liquid, and the rate of bubbling. The partial pressure of the water vapour

in contact with the fog particles and, under comparable conditions, the concentration of acid in the particles are remarkably constant, and independent of the amount of fog formed. The logarithm of the amount of fog produced increases linearly with the logarithm of the alkali concentration. The presence of organic substances (alcohols, ether, etc.) in the alkaline solution causes the production of dense fogs. Addition of capillary-active substances (gelatin, methylene-blue, "aquadag," etc.) likewise causes an increase in the amount of fog obtained. The concentration of acid in the fog particles decreases somewhat as that of the capillary-active substance decreases. For a given concentration of capillary-active substance, the concentration of acid in the droplets is independent of the concentration of alkali. The partial pressure of the water vapour remains constant. Under comparable conditions, the amount of fog F produced varies with the concentration of the capillary-active substance C according to the equation $\log F=m \log C+K$, where m and K are constants characteristic of the capillary-active substance. With solutions containing alcohol the concentration of acid in the droplets decreases with increasing concentration of alcohol. Pyridine solutions give very dense fogs. The fog particles are smaller the denser the fog produced. No electrical charges have been found on the particles. The alkaline film around the gas bubbles slows down the rate of absorption of the acid vapour. The film, however, is readily permeable to water vapour.

J. S. CARTER.

Electricity in dust clouds. I. G. B. DEODHAR (Proc. Physical Soc., 1927, **39**, 243—249).—Fine dusts of a large number of materials were blown by means of a rapid stream of air into an insulated metal box and the nature of the charge developed on the box was measured. No obvious generalisation can be made, but simple salts usually gave a positive charge, whilst metallic and organic dusts showed both positive and negative charges in different cases. The charges due to sodium and potassium chlorides were of the same order of magnitude, but that of sodium nitrate gave more than four times the charge due to potassium nitrate. It was also found that the charge increases rapidly as the particle size decreases.

C. J. SMITHELLS.

Light-scattering capacity (Tyndall effect) and colloidal behaviour of gelatin sols and gels. E. O. KRAEMER and S. T. DEXTER (J. Physical Chem., 1927, **31**, 764—782; cf. A., 1925, ii, 1057).—The relation between light-scattering capacity and p_H has been quantitatively studied for gelatins from various sources. The maximum Tyndall effect corresponds with the p_H of the isoelectric point, which may vary according to the sample of gelatin used from p_H 4·8 to 5·5, and even to p_H 8. Blended gelatins containing components with different isoelectric points behave as a single gelatin with an intermediate isoelectric point. The fluctuations in these points may indicate inherent differences in the gelatin precursors.

The influence of acid, alkali, and of temperature on the Tyndall effect in de-ashed gelatin was also studied. Above 30°, a high and approximately constant degree of dispersion is found at all values of p_H from 2·7 to 12·2, but below this temperature a sharp fall in dispersion quickly develops near the isoelectric point. Traces of acid or alkali repress the change. The bearing of these results on the condition of gelatin sols is discussed in detail.

L. S. THEOBALD.

Colloidal behaviour of aqueous gelatin systems. E. O. KRAEMER (Fourth Colloid Symposium Monograph, 1926, 102—121).—1% Solutions of de-ashed gelatin show slightly increased Tyndall light-scattering at p_H 5, but at 17° the effect increases at least 400% for a change from p_H 4·87 to 4·90. Even 0·001N-hydrochloric acid causes the formation of "solution units" of low light-scattering capacity; this property is not simply related to combination of gelatin with acid or base, or the dependence of cataphoretic mobility on p_H. Five hide gelatins showed maximal effect (isoelectric point) at p_H 4·95—5·01, but an ossein gelatin at p_H 5·5. Calf skin gelatins showed a maximal effect at p_H 4·9—5·0; bone stock gave p_H 5·5, decreasing for successive extractions, and a pigskin gelatin p_H 8. Mixtures of the gelatins gave average values, but the component having an isoelectric point near p_H 5 usually has a predominating influence. Specific rotation of 0·47% gelatin solutions does not vary greatly with p_H, but temperature has an important influence. Maximal gel strength appears near the isoelectric point (p_H 4·95) at which gel formation is small over a sharp minimum. On addition of hydrochloric acid, and at low temperatures, another region of high specific rotation and great gel strength appears at p_H 1—1·5. The general relations are the same with other acids. Pig skin gelatin exhibits anomalous behaviour.

CHEMICAL ABSTRACTS.

Stability of colloidal solutions towards electrolytes. M. A. BOUTARIC (Rev. gen. Colloid., 1927, **5**, 450—460).—Methods for the determination of the stability of colloidal solutions towards electrolytes are discussed, and the use of the Fery spectrophotometer for the exact determination of the coagulation point is described. The effects of temperature, stirring, concentration of electrolyte, and of luminous radiations are considered. Data for the coagulation of gamboge by sulphuric acid are in agreement with the formula $\log C=\log a+m/t$, where C is the concentration of the electrolyte, t the time, and m and a are constants. Certain sols when flocculated by certain multivalent ions show two zones of flocculation. With gamboge and sulphuric acid and with arsenious sulphide and lithium chloride, the previous addition of small quantities of electrolyte to the sol alters the time required for coagulation. In the case of arsenious sulphide, the protective effect of lithium chloride added 11 hours before the coagulation experiments at first increases rapidly with the amount of lithium chloride added, passes through a maximum, and then decreases rapidly. With a constant amount of lithium chloride, this effect increases with the length of time from which it is added, passes through a maximum, then decreases. Investigations have also been made by the same method on the protective effect of a number of other hydrophilic colloids on the stability of gamboge and mastic and of arsenious

sulphide and ferric hydroxide. Zsigmondy's results are in general confirmed, but the phenomena are considered to be somewhat complex. In most cases, the addition of a very small quantity of colloid renders the sol more sensitive to the action of electrolytes. L. L. Bircumshaw.

Colloidal solutions of ferric ferrocyanide. G. Rossi and M. Marzari (Zymologica, Chim. Coll. Zucc., 1927, 2, 25—38).—Previous experiments on colloidal sulphur and the colloidal acetate of tetramercuriacetanilide (cf. A., 1924, ii, 459) have shown that the stabilising action of electrolytes on colloids may be due to selective adsorption of ions. Further observations show that potassium ferrocyanide is necessary for the continued existence of Prussian-blue in colloidal solution and that stabilisation is favoured by a definite ratio of ferric ferrocyanide to excess of potassium ferrocyanide, the value of which depends on the concentration of the ferric ferrocyanide.

It has been shown also that the stabilising electrolytes conduct an electric current better in absence of the colloid than in its presence; this is in agreement with previous experiments with sulphur etc., and confirms the view that stabilisation is due to the adsorption of ions of the stabilising electrolyte. As a first approximation, this adsorption is proportional to the ratio of ferric chloride to potassium ferrocyanide and increases with increasing concentration of potassium ferrocyanide. M. Carlton.

Mass-action effects in the interaction of gelatin and acids. W. K. Lewis and C. F. Daniel (Fourth Colloid Symposium Monograph, 1926, 122—131).—The disagreement between Procter's mass-action equation for the reaction of gelatin in acid solution and Loeb's data is explained by the assumption of an internal interaction of amino- and hydroxyl groups of the gelatin. A general mass-action equation is derived. With increasing hydrogen-ion concentration, increasing amounts of the anions are held electrostatically, increasing the effective molecular size and the viscosity. With high acid concentration, the strongly solvated solute competes with the gelatin for the solvent. To explain the anomalous behaviour of sulphuric acid, it is supposed that one of the hydrogen ions combines with an amino-group, the other being held nearby electrostatically.

Chemical Abstracts.

Emulsification. I. Oil-soluble emulsifying agents. B. Mead and J. T. McCoy (Fourth Colloid Symposium Monograph. 1926, 44—57).—The efficiency of a product containing sodium oleate 83, sodium resinate 5·5, sodium silicate 5, phenol 4, paraffin 1·5, water 1% is ascribed to the oleate and phenol. The interfacial tension curves of kerosene and "nujol" containing oleic and stearic acids against water indicate an adsorption. Heating oil to cause heavy metal soaps to dissolve in it produces erratic changes in the oil/water surface tension. Sodium oleate solutions "age" rapidly, probably owing to interaction with some atmospheric constituent, and may then give a water-in-oil emulsion instead of the usual oil-in-water emulsion. Chemical Abstracts.

Making and breaking of emulsions. W. P. Davey (Fourth Colloid Symposium Monograph, 1926, 38—43).—Water-in-oil emulsions may be made by using (1) an emulsifying agent the molecules of which cannot disentangle themselves at the ordinary temperature, (2) an emulsifier having weak adsorptive power for water, *e.g.*, oleic acid, (3) an emulsifier, *e.g.*, soap with a multivalent metal, where the area covered by the methyl groups considerably exceeds that covered by the carboxyl groups united to the univalent metal, (4) so low a water : oil ratio that the coalescence of the oil is forced. Spontaneous emulsification may be effected by dispersing the emulsifier in the oily phase; soap is dissolved in oil at 250°, boiling water is added slowly, with mixing, and the mixture diluted to a non-gelling point. Emulsions may be broken by mechanical action, concentration, electro-deposition, or by plunging a piece of metal or porcelain at 250° into an oil-in-water emulsion.

Chemical Abstracts.

Mechanics of adsorption and swelling of gels. C. Terzaghi (Fourth Colloid Symposium Monograph, 1926, 58—78).—An attempt to explain the relationship between the elastic expansion of coarse-grained soils and the swelling of elastic gels. The formulæ of Katz and of Freundlich and Posnjak for the swelling pressure give discordant values. Harkins' pressure hypothesis is not in accord with the facts. If the adsorbed layer is considered as a zone of forced vibrations, the effect of the solid phase is similar to undercooling, and it extends much beyond molecular range. This mechanical tension can account for increased density and viscosity in the liquid, and for vapour-pressure changes. Lowering of vapour pressure is regarded as due to (*a*) tension in the liquid, representing the capillary part of the swelling process, and (*b*) a change in the molecular energy of the liquid, representing the molecular mechanical part of the adsorption process. With increasing concentration of the gel (*a*) is dominant. Chemical Abstracts.

Desiccation and rehydration of precipitates with large surfaces. O. Hahn and M. Biltz (Z. physikal. Chem., 1927, 126, 323—355).—The evolution of thorium emanation from a gel in the pores of which radiothorium has been deposited has been studied under widely differing conditions of hydration of the gel. The "emanation ratio" is the ratio of the quantity of emanation evolved from the gel to the total quantity formed.

Ferric hydroxide gels, unlike those of most other metallic hydroxides, show an emanation ratio of more than 0·8, illustrating the large surface of the colloid. The dependence of the emanation ratio on the water content of the gel has been studied quantitatively; drying the gel causes a decrease in the ratio, but on rehydration, the original value is obtained in the case of ferric hydroxide. If thorium, zirconium, or aluminium hydroxide gels be employed, a more or less irreversible change takes place on drying. The mode of preparation of the gel has a large influence on the effect of drying. Ferric hydroxide gels precipitated, *e.g.*, from ferric salt solutions exhibit a totally different form of drying curve from that given by gels prepared directly from the sol.

Ferric hydroxide gel adsorbs considerable quantities of radium and thorium emanations, but only when

containing comparatively little water. The adsorbed thorium emanation is easily displaced by other gases, although not completely, whilst radium emanation is unaffected. The reversible decrease of the emanation ratio of gels containing radiothorium may thus involve adsorption of the emanation on the internal walls of the colloid, thereby delaying its evolution. Since the adsorption of radium emanation, which has a much slower rate of decay, is not affected by the presence of other gases, the decrease of the emanation ratio is in this case ascribed to the structure of the gel.

The velocity with which the emanation ratio approaches its initial value on re-hydrating a dried gel has been studied quantitatively. Two processes occur, the first being complete in about 10—15 min., whilst the second has a half period of about 12—15 hrs. This slow change is ascribed to the slow swelling of the colloid, the shrinkage of which on drying is the cause of the incomplete displacement of thorium emanation by inert gases. H. F. GILLBE.

Orthokinetic and perikinetic coagulation. Theory of streaming coagulation and the coagulation theory of Smoluchowski and Müller. Coagulation of colloidal and coarsely-dispersed systems and analysis by elutriation. P. TUORILA (Koll.-Chem. Beihefte, 1927, 24, 1—122; cf. A., 1926, 1005; Wiegner and Tuorila, A., 1926, 242).—In systems containing both submicrons and microns, the particles may be brought into contact by the Brownian movement, by stirring, or by the streaming of the particles in one direction, as in sedimentation or centrifuging. Coagulation caused by the Brownian movement is designated "perikinetic," whilst that due to the movement of the particles in one direction only is termed "orthokinetic." In an exhaustive discussion of perikinetic coagulation, it is shown that if the initial number of particles in a system is small (10^7 or fewer per cm.) it will remain practically unchanged over the usual coagulation period, so that the perikinetic coagulation in such a case may be disregarded. Smoluchowski's coagulation equation holds for the rapid coagulation of paraffin and gold sols, and of dilute, finely-dispersed quartz, clay, and graphite suspensions. For these dispersoids, the attraction radius is approximately twice the particle radius.

In the case of orthokinetic coagulation, from a consideration of the number of small particles per second which come within the sphere of action of a large particle, and from the dependence of this value on the ratio of the radii of the particles and on the number of particles, it is shown *a priori* that orthokinetic coagulation can occur only in polydisperse, not in monodisperse, systems. Formulæ are derived to express the course of orthokinetic coagulation in systems (*a*) with a small initial number of particles in which coagulation due to the Brownian movement may be disregarded, and (*b*) with a greater initial number of particles, where perikinetic coagulation must also be considered. The validity of the equations is proved by experiments with quartz and clay suspensions and gold sols. Particles of quartz or clay radii greater than 20 or 50 μ, respectively, possess no nuclear action. For completely coagulated quartz and soil suspensions, the same distribution curves are obtained, and these are unchanged by the addition of electrolytes. In the case of coarse, sedimenting systems (*e.g.*, soil suspensions), the only type of coagulation that need be considered is often the orthokinetic type, but under ordinary conditions gold sols show only perikinetic coagulation. The orthokinetic type may, however, be caused by centrifuging coarsely-dispersed sols.

A number of coagulation and sedimentation phenomena, such as the formation of layers in coagulating suspensions and the existence of S-shaped coagulation curves, are discussed and explained on the basis of the new coagulation theory. Problems connected with soil analysis are considered. Analysis by elutriation gives trustworthy results only if the potential of the particles is greater than the critical potential, but even when this is not the case, the disturbing influence of coagulation may be very greatly diminished by using very dilute suspensions and an experimental arrangement giving the least possible height of fall. A mathematical criterion is derived for determining the accuracy of the results of elutriation analysis and for calculating the order of magnitude of the deviation from the sedimentation curve due to coagulation. The results of investigations with a modified form of Wiegner's elutriation apparatus are in agreement with the orthokinetic coagulation theory. L. L. BIRCUMSHAW.

Instability and the charge of colloidal particles. N. P. PESKOV and V. I. SOKOLOV (J. Russ. Phys. Chem. Soc., 1926, 58, 823—839).—When a ferric hydroxide sol is treated with just sufficient magnesium sulphate to initiate coagulation, and hydrochloric acid is added, it is found that low concentrations of the latter increase the stability of the colloid, whilst high concentrations decrease it, although coagulation is never complete. Neither gelatin nor acidified gelatin has any action on the sol, but in presence of the above quantity of magnesium sulphate small quantities of gelatin render the sol unstable, whilst large quantities increase the stability. If the sol is mixed with the amount of gelatin which gives the optimum amount of coagulation and the concentration of magnesium sulphate is increased, the instability of the sol is increased. When sulphuric acid is used as a coagulant, the presence of hydrochloric acid increases the instability to a greater extent than in the case of magnesium sulphate.

Sodium carbonate solution has no action on arsenious sulphide sol, but if magnesium sulphate is added, more of the latter is needed in presence of sodium carbonate than without it. At low concentrations, gelatin renders pure arsenious sulphide sol unstable; in large quantities it stabilises it. Magnesium sulphate, in presence of gelatin and sodium carbonate, has practically no action on the sol. Sodium carbonate in presence of gelatin renders the sol unstable. The author concludes that the mechanism ascribed by Zsigmondy (A., 1925, ii, 35) is not entirely correct, and that the electrical conditions of the lyophobe and lyophile colloids are the most important factors concerned. E. ROTHSTEIN.

Coagulation of colloids by electrolytes. Arsenic trisulphide sol and barium chloride. A. I. RABINOVITSCH (J. Russ. Phys. Chem. Soc., 1926, **58**, 849—855; cf. A., 1925, ii, 778).—The increase of hydrogen-ion concentration which occurs when arsenic trisulphide sol is coagulated with barium chloride affords a new method for following the course of coagulation. When the sol is titrated with barium chloride, the conductivity increases, the increase being due partly to the presence of the added electrolyte, and partly to the formation of the more mobile hydrogen ions. When the conductivity of the solution is plotted against the hydrogen-ion concentration, a curve is obtained which has a maximum at the same point as the minimum obtained when an acid solution is titrated with sodium hydroxide.

E. ROTHSTEIN.

Coagulation of hæmoglobin in presence of alcohols. II. B. JIRGENSONS (Kolloid-Z., 1927, **42**, 59—65; cf. this vol., 512).—A study was made of the effect of methyl, ethyl, and propyl alcohols on the coagulation of hæmoglobin by calcium chloride and by magnesium chloride, the concentration of the hæmoglobin being kept constant and that of the electrolyte and of the alcohol being varied between wide limits. The following results were obtained. Methyl alcohol has a sensitising effect in all cases. Ethyl alcohol has generally a sensitising effect, but has a stabilising influence when present in large quantities at relatively high concentrations of electrolyte. Propyl alcohol sensitises hæmoglobin in presence of small amounts of the electrolyte, but has a stabilising effect with greater concentrations of electrolyte and alcohol. E. S. HEDGES.

Flocculation of hydrophobic sols by mixtures of electrolytes. A. RABINERSON (Kolloid-Z., 1927, **42**, 50—58).—Experiments on the flocculation of the positive ferric oxide sol and the negative sols of Prussian-blue, wax, and mastic by various mixtures of electrolyte show an antagonistic effect which is ascribed to a competition between cations and anions. The stabilising effect of ions of the same charge as the colloid is greater the weaker the coagulative effect of the ions of opposite sign. The antagonistic effect appears more strongly in colloids of somewhat hydrophilic character than in strictly electrocratic sols, where the ions of the same sign as the colloid have an almost negligible effect: the flocculating effect of the components of a mixture of electrolytes is in the latter case additive. E. S. HEDGES.

Dispersion of cellulose by salt solutions. P. P. VON WEIMARN (Kolloid-Z., 1927, **42**, 43—50).—Cellulose commences to be dispersed by solutions of sodium chloride or barium chloride when boiled with the saturated solution at 170° and 8 atm. pressure. At higher temperatures, some hydrolysis occurs simultaneously, forming a yellow or brown colloidal solution, which reduces solutions of gold or silver salts and can be used for the preparation of stable sols of these metals. By similar treatment with saturated lithium chloride solution at 160°, a maximum concentration of 10—12 g. of cellulose per 100 c.c. can be obtained. On cooling, the viscous, dark brown sol becomes covered with a thin crust of lithium chloride crystals, often in the form of Liesegang rings, and then sets to a stiff gel. With calcium thiocyanate, dispersion takes place even more readily. Intermediate concentrations of salts do not affect cellulose unless it is contaminated with decomposition products. With pure cellulose, however, dispersion is also possible when extremely dilute solutions of salts are used, the optimum concentration lying between 0·1 and 0·01 millimol. per litre. E. S. HEDGES.

Peptisation of ferric and chromic hydroxides in presence of arsenious acid and other substances. M. R. MEHROTRA and K. C. SEN (Kolloid-Z., 1927, **42**, 35—42).—A quantitative study was made of the peptisation of ferric and chromic hydroxides containing excess of alkali by arsenious acid, sucrose, and glycerol. A simple relation between the amount of hydroxide peptised and the amount of peptising substance could not be obtained, for the ratio varied with the concentration of the chloride solution used in the preparation of the hydroxide, with the final volume of the system, and in particular with the degree of excess of alkali. It is therefore improbable that a definite compound is formed between the metal hydroxide and the peptising agent. Arsenious acid differs from sucrose and glycerol in that it peptises ferric hydroxide in absence of alkali.

E. S. HEDGES.

Physical chemistry of colouring matters. II. Development of Fürth's method of determining the electrical charge of colouring matters, and some experimental results. J. GICKLHORN (Kolloid-Z., 1927, **42**, 9—18).—Further experiments have been carried out on Fürth's method of determining the charge on colloid particles of colouring matters by electrolysis with electrodes of "semi-conducting" material (cf. A., 1925, ii, 1057). The electrode material should be a substance possessing a fine structure, so as to be wetted easily by the liquid; it should be pure white and chemically indifferent. These conditions are best fulfilled by fireclay, paper, and especially filter-glass. The preparation of these materials in a suitable form is described and their relative advantages are discussed. Gypsum, chalk, and magnesia were found to be quite unsuitable for electrodes, and a study was also made of many organic substances, including several kinds of wood and some colloidal membranes; some of these were useful for special cases. Improvements in the apparatus and in the method of working are described, and experimental results are given for a number of colloids.

E. S. HODGES.

Structure of metallic hydroxide gels. M. BILTZ (Z. physikal. Chem., 1927, **126**, 356—368).—The emanation ratios (cf. this vol., 622) of ferric hydroxide hydrogels containing radiothorium and radium have been determined for gels in the form of large pieces and of powder. From the results, the conditions governing the emanation from dry and moist gels have been derived. It is shown that two kinds of capillary exist in the gel, viz., primary and secondary canals. The absorption of water by a dry hydrogel is due, not to adsorption followed by condensation in the capillaries, but to the filling first of the primary canals, and then, at a higher water-vapour pressure, of the

secondary canals. Measurements have been made of the average size of the passages. H. F. GILLBE.

Capillarity. VIII. K. SCHULTZE (Kolloid-Z., 1927, **42**, 3—9).—A description is given of the preparation of capillaries of agar and of gelatin, and of the examination of the effect of immersing the capillaries in solutions of colouring matters. Both organic and inorganic colouring matters are unevenly distributed in the walls of the capillaries, there being a deficiency in the region of the meniscus. This is compared with the well-known water-line corrosion of metals in aqueous solution, but an explanation based on the displacement of the surface-water of the gel is preferred. Further experiments were carried out with paraffin oil–agar emulsions. E. S. HEDGES.

Colloid chemistry of "viscose" solutions. III. Synæresis of "viscose" gels. T. MUKOYAMA (Kolloid-Z., 1927, **42**, 79—86; cf. this vol., 201).—The synæresis of viscose gels was followed by immersing the gel contained in a tube in a thermostat at 17° and measuring the volume of the liquid phase at regular time intervals. Synæresis sets in suddenly after a definite time, and the volume of the liquid phase increases at first rapidly and then slowly to a constant value. The effects of concentration, alkali content, and age were studied. With the more dilute gels, synæresis occurred earlier and the maximum was reached more rapidly, and between the values 0·25% and 8% the volume of liquid produced is a linear function of the concentration. Increasing alkali content has the effect of delaying and reducing the synæresis. E. S. HEDGES.

Zone pattern formed by silver dichromate in solid gelatin gel. E. R. RIEGEL and M. C. REINHARD (J. Physikal Chem., 1927, **31**, 713—718; cf. Riegel and Widgoff, A., 1925, ii, 863).—Silver dichromate in washed gelatin forms an unbroken deposit exhibiting a pattern similar to that formed by copper ferrocyanide in a gelatin cake (*loc. cit.*). No lines appear in the silver dichromate pattern. Addition of 0·1% of sodium chloride or less to the solution of washed gelatin causes the red bands to reappear. The red bands do not form unless the substructure due to the chloride impurity is provided. The chloride present in commercial gelatin forms a zone pattern when the gelatin cake is immersed in 1% silver nitrate solution. L. S. THEOBALD.

Cataphoresis in colloids. M. VINCENT (Rev. gen. Colloïd., 1927, **5**, 481—485).—A device is described for the rectification of alternating current for experiments on the cataphoresis of colloids. Four three-electrode valves, or kenotron valves, are employed, and from alternating current at 200 volts direct current at 60 volts can be obtained. L. L. BIRCUMSHAW.

Ideal solutions. Perisphere constant, *C*. N. MARINESCU (Bul. Soc. chim. Romania, 1926, **8**, 92—100).—Some properties of the "perisphere constant" are described (cf. A., 1926, 673); the application of this constant in the theory of concentrated solutions, in biochemistry, and in the calculation of hydration of ions is indicated. S. K. TWEEDY.

Law of "particle projection" and its experimental verification. A. SOÓS (Koll.-Chem. Beihefte, 1927, **24**, 123—156).—A solution may be regarded as homogeneous if a cube (termed the elementary cube) can be taken in it in which the perpendicular projection of the included molecules, or colloid particles (termed the elementary number), is just sufficient to cover the six faces of the cube as this is displaced or rotated. The law previously deduced (cf. A., 1926, 575), by means of which the edge of the elementary cube, h, which is identical with the thickness of a complete elementary layer, may be measured by various experimental methods, is now considered quantitatively. If the molecules or colloid particles in a solution are assumed to be spherical, then the elementary number, S_0, is given by $h^2/r^2\pi$, where r is the particle radius. If the particles are cubic, then $S_1 = h^2/a^2$, a being the length of the edge of the particle cube. From the formulæ $S_0 = 16s^2/9c^2$, and $S_1 = d^2/c^2$, where c is the concentration of the solution and d the density of the dissolved or dispersed phase, it follows that the elementary number remains unchanged at constant concentration, being independent of the value of h and of the degree of dispersion of the dissolved phase. Values are calculated for the elementary numbers of all the elements, assuming the particles to be spherical, and using the highest known values for the specific gravity, d. The "particle projection law" is tested by measurements with a polarisation spectrophotometer, and values of h are obtained for blue and violet gold hydrosols, silver hydrosol, and manganese dioxide sol. The experimental error is estimated as being about $20/n$%, where n is the number of elementary layers in the thickness of solution investigated. Values are given for the elementary number and particle size of gold sols prepared at 10°, 25°, and 40°, calculations being made for both spherical and cubical particles. The volume of the particles found by this method in violet gold sol is almost a million times smaller than that found by Zsigmondy's method. Reasons for this large discrepancy are discussed. L. L. BIRCUMSHAW.

Electrolytic dissociation of hydrogen chloride, bromide, and iodide in anhydrous methyl alcohol. M. HLASKO and E. KAMIENSKI (Rocz. Chem., 1927, **7**, 6—22).—Dry hydrogen chloride, bromide, or iodide is dissolved at −70° in anhydrous methyl alcohol and the conductivity of the solutions measured at 0° and 25°. The temperature coefficient of conductivity is 0·0120 for all three substances, whilst the values of are 202·5, 212·3, and 221·8, respectively. Ostwald's dilution law does not apply to the above halogen acids, which behave in the same way as in aqueous solution. At 25°, the degree of dissociation of 0·1*N*-hydrogen chloride is 0·577, of 0·1*N*-hydrogen bromide 0·605, and of 0·1*N*-hydrogen iodide 0·618, although in aqueous solution these substances dissociate to the same extent. It hence follows that, in acids of the above type, the degree of dissociation increases with the atomic weight of the anion. R. TRUSZKOWSKI.

Effect of ionisation on optical rotation. II. Amino-acids, polypeptides, and ketopiperazines. P. A. LEVENE, L. W. BASS, R. E. STEIGER, and I. BENCOWITZ (J. Biol. Chem., 1927, **72**, 815—826).—

d-Alanyl-*d*-alanine anhydride exhibits a marked change in optical rotation with varying p_H which must be regarded as due to enolisation; the point at which the change is most rapid corresponds with a dissociation constant of $10^{-13\cdot5}$. The dissociation constants of glycyl-*l*-alanyl-*l*-alanylglycine were found by titration to be pG_1 3·30 and pG_2 7·96; values in close agreement with these were calculated from the observed changes in optical rotation with changes in the p_H. C. R. HARINGTON.

Correction for the new series of buffer solutions. I. M. KOLTHOFF and J. J. VLEESCHHOUWER (Biochem. Z., 1927, **183**, 444—445; cf. this vol., 329).—Tables show the revised proportions required for the preparation of solutions of p_H 2·2—3·6 using monopotassium citrate (0·1*M*) and hydrochloric acid (0·1*N*) of p_H 3·8—6·2 using the citrate with sodium hydroxide (0·1*N*), of p_H 2·2—3·8 using the citrate with citric acid (0·1*M*), and of p_H 3·8—6·0 using the citrate with borax (0·05*M*). P. W. CLUTTERBUCK.

Activity coefficients of small ions. H. MULLER (Physikal. Z., 1927, **28**, 324—333).—The Debye–Hückel theory of strong electrolytes has hitherto been inapplicable to small ions, owing to the failure of the approximation sinh $(\phi=\varepsilon\psi/kT)$. A solution of the equation $\Delta\phi=\sin\phi$ is advanced. The relation $kT\log f_i=\partial W/\partial n_i$ fixes the activity coefficient f, if $-kT\log f$ is the difference in the work to charge one ion in pure water, and to charge it in an electrolyte of concentration c in which the other ions have full charges. The mathematical treatment leads to curves connecting $\log_{10}f$ and c which are different from Debye's limiting curves, but very near to those obtained by Bjerrum on the assumption of association of ions. It is therefore held that the mathematical extension of Debye's theory to small ions corresponds with observations without the necessity for association arising. R. A. MORTON.

Equilibrium in solutions of alkali carbonates. A. C. WALKER, U. B. BRAY, and J. JOHNSTON (J. Amer. Chem. Soc., 1927, **49**, 1235—1256).—The carbonate–hydrogencarbonate equilibrium for sodium, potassium, and lithium between 0·01 and 2·5*M* was investigated at 25° and in part at 37°. For sodium and potassium, carbonate solutions containing the chlorides of the metals were also investigated. The equation $[MHCO_3]^2/[M_2CO_3]p=\phi-\gamma\lambda c\times K_1/K_2\times\beta/\alpha^2$ is derived, where p is the partial pressure of carbon dioxide in the gas phase and c its total concentration in solution when $p=1$; K_1, K_2 are the first and second dissociation constants of carbonic acid, and γ, λ, β, α are the activity coefficients of carbonic acid, water, CO_3'', and HCO_3' in the solution. The graph of ϕ, determined experimentally against the concentration of alkali metal, is shown to yield information about β/α^2 when extrapolated to zero concentration. Assuming Kendall's value for K_1 (cf. A., 1916, ii, 512), the value of K_2 is calculated to be (in terms of activities) $3\cdot85\times10^{-11}$ at 25° and $5\cdot46\times10^{-11}$ at 37°. Independent values of α and β are obtained from potential measurements on a hydrogen electrode and on a silver-silver carbonate electrode immersed in a mixed potassium carbonate–hydrogen carbonate solution of ionic strength between 0·01 and 0·02. These values are shown to conform to the requirements of the Debye–Hückel theory. The solubility product of crystalline silver carbonate (in terms of activities) is $8\cdot2\times10^{-12}$ at 25°. S. K. TWEEDY.

Apparent diameters of ions in the Debye–Hückel theory of strong electrolytes. T. H. GRONWALL (Proc. Nat. Acad. Sci., 1927, **13**, 198—202).—It has been pointed out (Scharer, A., 1924, ii, 455; LaMer, King, and Mason; LaMer and Mason; Bjerrum, this vol., 314) that the theory of Debye and Hückel (A., 1923, ii, 459) leads to values of apparent ion diameters which, in certain instances, are either unreasonably small or negative. In the present mathematical paper, it is shown that by starting out from Debye and Huckel's unabridged fundamental equation, satisfactory values of the apparent diameters are obtained without having recourse to Bjerrum's (*loc. cit.*) hypothesis of ion association. J. S. CARTER.

Free energy of a mixture of ions. H. A. KRAMERS (Proc. K. Akad. Wetensch. Amsterdam, 1927, **30**, 145—158).—Mathematical. Employing the methods of statistical mechanics, an attempt has been made to determine the influence of electrostatic forces acting between the ions in a solution of an electrolyte in so far as this influence is independent of ionic radii. For dilute solutions, the formulæ reduce to that of Debye and Hückel (A., 1923, ii, 459). The maximum concentrations for which the present formulæ are valid are extremely low and depend on the nature of the electrolyte concerned. For electrolytes such as potassium chloride and magnesium sulphate, the maximum concentrations are 0·03 and 0·0005*M*, respectively. The importance of considering the influence of ionic radii in calculations of this type is emphasised. J. S. CARTER.

Free energy change in adsorption at a solid–vapour interface. S. LENHER and I. R. MCHAFFIE (J. Physical Chem., 1927, **31**, 719—722; cf. Lenher, this vol., 198).—The relation between the change of free energy, $-\Delta F$, and the amount of vapour adsorbed per unit area of solid–vapour interface is expressed under certain limits by $-\Delta F-k_1\ c^{-a\theta}$ and $\Delta F=k_2/\theta^n$, where θ is the number of molecular layers. Empirical equations of these types are given for the adsorption of water on glass, silica, and platinum, and for benzene on platinum. L. S. THEOBALD.

Corresponding states for the entropy of elements. B. BRUZS (J. Physical Chem., 1926, **31**, 681—685).—For a large number of elements, the entropy at the m. p., S_m, calculated from the equation $S_m=S_{298}+2\cdot303c_v\ .\ \log T_m/298$, is 22 entropy units for the liquid pnase. The m. p. and, possibly, the critical temperature are corresponding states for the entropies of the elements. L. S. THEOBALD.

Cohesion. I and II. V. A. KIREJEV (J. Russ. Phys. Chem. Soc., 1926, **58**, 856—876).—See A., 1926, 1088; this vol., 404.

Sorel effect. I. C. C. TANNER (Trans. Faraday Soc., 1927, **23**, 75—95).—See this vol., 204.

Ionic equilibria. P. M. VÈZES (Compt. rend., 1927, **184**, 1246—1248; cf. this vol., 515).—The equilibrium state concerned in the precipitation of

calcium oxalate (CaC_2O_4,H_2O) by calcium chloride and oxalic acid has been examined. At 15°, calcium oxalate is less than 87% precipitated, and the hydrochloric acid formed is 99·3% dissociated.

J. GRANT.

Vapour pressure of aqueous hydrocyanic acid at 18°. M. SHIRADO (Bull. Chem. Soc. Japan, 1927, **2**, 85—95).—The vapour pressures of solutions of hydrocyanic acid of concentrations varying from 5% to 100% have been determined by a dynamical method at 18°. The results are not in agreement with Duhem's formula for the connexion between partial pressure and molecular composition, except for solutions which contain from 30 to 60 mols.-% of hydrocyanic acid. This may be attributable to the association of hydrocyanic acid or water. The value 566·2 mm. obtained for anhydrous hydrocyanic acid is in accord with previous measurements.

M. S. BURR.

Measurement of evaporation of sea-water. W. SHOULEJKIN (Nature, 1927, **119**, 891—892).—The method is based on observation of the cooling effect of evaporation. A. A. ELDRIDGE.

Magnetic transformation of iron. F. WEVER (Z. anorg. Chem., 1927, **162**, 193—202).—From direct observation, there is no doubt that the A3- and A4-transformations of iron are polymorphic changes. There is, however, no evidence whatever that the magnetic transformation is accompanied by structural change, even within the crystallites. Attempts to detect changes in physical properties at this point, *e.g.*, by cooling curves, must be regarded as unsuccessful. The experimental data is therefore insufficient to decide whether the A2-transformation is a phase-change or not. R. CUTHILL.

Volume change in cast iron during solidification. Criticism of the double diagram of the iron–carbon system. K. HONDA and H. ENDÔ (Sci. Rep. Tohoku Imp. Univ., 1927, **16**, 9—25).—See A., 1926, 897.

System manganese-zinc. C. L. ACKERMANN (Z. Metallk., 1927, **19**, 200—204).—A re-examination of the system manganese–zinc has confirmed the existence of the eutectic (0·4—0·5% Mn, m. p. 414°) and of the compound $MnZn_9$, but the compound previously formulated as $MnZn_7$ is now found to be $MnZn_6$. $MnZn_9$ melts at 560° and $MnZn_6$ at 620°; they are totally immiscible with each other in the solid state, but below about 290° alloys containing both compounds undergo some sort of transformation, possibly associated with a reaction between the two compounds or with their decomposition into $MnZn_3$ and zinc. Manganese increases the hardness of zinc considerably, the alloy with 5% Mn having a Brinell number of 122; at the same time, the tensile strength is appreciably increased, whereas the compression strength is much reduced. Small quantities of manganese improve the resistance of zinc to repeated impacts, but more than 3% Mn has the reverse effect. Alloys with up to 8·5% Mn have a negative potential against zinc in *N*-zinc sulphate solution; those containing the compound $MnZn_9$ have a small positive potential and those containing $MnZn_6$ a much smaller positive potential under the same conditions, whereas the potential of $MnZn_9$ itself is equal to that of pure zinc. A. R. POWELL.

Miscibility-gap in molten iron–copper alloys. A. MÜLLER (Z. anorg. Chem., 1927, **162**, 231—236; cf. Ostermann, A., 1925, ii, 1050).—When an alloy of equal parts of iron and copper is heated at various temperatures, the structure of the product examined when cold shows that the lower critical point for the miscibility is about 1520°. Carbon reduces the miscibility probably because it is soluble in the iron only.

R. CUTHILL.

Binary systems of halides of the quadrivalent elements. Systems with quadrivalent tin. M. G. RAEDER (Z. anorg. Chem., 1927, **162**, 222—230; cf. A., 1923, ii, 867).—M. p. and crystallisation curves for the system stannic chloride–stannic iodide show the existence of a *compound*, $SnCl_4,SnI_4$, with an upper limit of stability of about −47°. The action of iodine on stannous chloride yields this compound, thus: $2SnCl_2+2I_2=SnCl_4+SnI_4$. Examination of the system stannic chloride–stannic bromide yields no indication of compound formation. Compounds which have been reported from time to time are apparently mixtures. This view is supported by the b.-p. curve of the system. R. CUTHILL.

Systematic doctrine of affinity. XXXVII. Halogen–halide systems. II. W. BILTZ and K. JEEP (Z. anorg. Chem., 1927, **162**, 32—48; cf. A., 1924, ii, 165).—The behaviour of various chlorides and bromides with chlorine, bromine, and iodine has been studied by thermal analysis. With phosphorus trichloride and chlorine, there seems to be a possibility of the existence of chlorides higher than the pentachloride, and in the case of antimony trichloride a *compound*, $SbCl_5,2Cl_2$, has been isolated. Bromine forms no compounds with the tetrabromides of silicon, titanium, and tin. The system phosphorus tribromide–bromine manifests a somewhat complicated behaviour, but the existence of *polybromides*, probably $PbBr_3,2Br_2$ and $PBr_5,6Br_2$, is indicated. No compounds of bromine with arsenic tribromide, antimony tribromide, carbon tetrachloride, or stannic chloride have been observed.

R. CUTHILL.

Systematic doctrine of affinity. XXXVIII. Thiohydrates of carbon disulphide. W. BILTZ and M. BRÄUTIGAM (Z. anorg. Chem., 1927, **162**, 49—56; cf. preceding abstract).—The freezing curve for the system carbon disulphide–hydrogen sulphide shows the existence of the *compounds* $CS_2,6H_2S$ and CS_2,H_2S, the latter being isomeric with thiocarbonic acid. Examination of the systems sulphur dioxide–hydrogen sulphide and carbon tetrachloride–hydrogen sulphide gives no evidence of compound formation. R. CUTHILL.

System lithium chlorate–water. C. A. KRAUS and W. M. BURGESS (J. Amer. Chem. Soc., 1927, **49**, 1226—1235).—The solubility curve indicates the existence of a trihydrate and a monohydrate; there is no indication of a lower hydrate (cf. Berg, A., 1926, 1014). The trihydrate has a congruent m. p. at 8° and the monohydrate–(γ) anhydrous salt transition occurs at 21·0°. The anhydrous salt exists in three modifications; the m. p. of the α-form is 127·6°;

the transition β occurs at 99°, and γ⟶β at 41·5°. The transition β⟶γ could not be effected. Lithium chlorate in concentrated solution (88%) decomposes at about 100°. S. K. TWEEDY.

System water–phenol. J. B. FERGUSON (J. Physical Chem., 1927, **31**, 757—763).—The specific heats of solutions of water and phenol have been measured at 70—74°. A slight positive deviation from a linear relationship appears, the point of maximum deviation occurring at the consolute composition. The heats of formation of these solutions at 71° and the vapour pressures of certain solutions at 75° have also been measured. A thermodynamical study of the data is made. L. S. THEOBALD.

Three-phase lines of the systems: water–*o*-cresol, water–*m*-cresol, and water–*p*-cresol. A. MICHELS and E. C. F. TEN HAAF (Proc. K. Akad. Wetensch. Amsterdam, 1927, **30**, 52—54).—The solubility curves for the above binary systems have been determined by the turbidity method. The three curves are all of the same parabolic type. As indication of the orders of magnitude encountered, the following numbers represent the cresol contents of mixtures homogeneous at higher temperatures which become heterogeneous at the temperatures indicated: *o*-cresol: 2·9%, 46·2°; 6·9%, 121·0°; 16·4%, 157·9°; *about 41%, 168·9°*; 64·7%, 160·1°; 82·9%, 92·8°; 86·2%, 50·5°; *m*-cresol: 2·7%, 50·8°; 10·8%, 121·7°; 23·2%, 147·5°; *about 38%, 148·8°*; 62·2%, 137·7°; 80·0%, 85·2°; 85·9%, 36·2°; *p*-cresol: 3·74%, 82·1°; 9·2%, 127·9°; 16·4%, 138·0°; *about 36%, 142·6°*; 66·6%, 124·4°; 79·5%, 71·0°; 83·7%, 37·1°. The italicised numbers are the respective critical concentrations and critical solution temperatures. All three systems exhibit barotropy, the cresol-rich phase, heavier at low temperatures, and the aqueous phase interchanging places at a definite temperature. The approximate barotropic temperatures for *o*-, *m*-, and *p*-cresol are 145°, 148°, and 138°, respectively. The decomposition of cresols with production of a dark colour is accompanied by a change in the miscibility with water.

J. S. CARTER.

Equilibria in binary systems containing cresol as one component. N. A. PUSCHIN and D. BASARA (Monatsh., 1927, **48**, 51—60).—The binary systems formed by *o*-, *m*-, and *p*-cresols with α- and β-naphthylamines and diphenylamine have been examined by the method of thermal analysis. With each cresol the two naphthylamines form 1 : 1 *compounds*. Diphenylamine yields only mechanical mixtures. The m. p. of the compounds, the eutectic points, and composition of the eutectic mixtures in mol. percentages are, respectively, as follows (B=1 mol. of naphthylamine): *o* cresol–α-naphthylamine, m. p. 33·3°, 15·3° (18 % B), and 27·5° (70% B); *o*-cresol–β-naphthylamine, m. p. 70° (decomp. into its components), 25·3° (5% B) and a point of inflexion at 70·2°; *m*-cresol–α-naphthylamine, m. p. 170°, −16° (14% B) and 14·5° (58% B); *m*-cresol–β-naphthylamine, a eutectic at −3·3° (6% B) and a point of inflexion at 50°; *p*-cresol–α-naphthylamine, m. p. 28·8°, 14° (24% B) and 25·1° (67% B); *p*-cresol–β-naphthylamine, m. p. 76°, one eutectic only at 29° (7% B). With diphenylamine, the eutectic points (25% B in each case) with *o*- and *p*-cresols are 8° and 17·3°, respectively. J. W. BAKER.

Ternary system: silver–tin–copper. W. GUERTLER and W. BONSACK (Z. anorg. Chem., 1927, **162**, 22—30).—The above system has been investigated by the "Klärkreuz" method, and the results are expressed diagrammatically. When copper is melted with the compound Ag_3Sn, the reactions $4Cu+Ag_3Sn=3Ag+Cu_4Sn$, and $3Cu+Ag_3Sn=3Ag+Cu_3Sn$ occur. In the silver mixed-crystal region, the hardness of the alloys increases as the compound Ag_3Sn_2 is approached. R. CUTHILL.

Tula alloy. (Ternary system: cuprous sulphide–silver sulphide–lead sulphide.) R. SCHWARZ and A. ROMERO (Z. anorg. Chem., 1927, **162**, 149—160).—A commercial sample of "tula alloy" consisted of 12% of silver sulphide, 52% of cuprous sulphide, and 36% of lead sulphide. The ternary system consisting of the three sulphides has been examined, and the results have been found to agree with Sahmen and Vegesack's theory of the crystallisation of binary mixed crystals in ternary systems (A., 1907, ii, 532). No evidence of compound formation in the system cuprous sulphide–silver sulphide has been obtained. R. CUTHILL.

System $AlCl_3$–KCl–H_2O at 25°. G. MALQUORI (Atti R. Accad. Lincei, 1927, [vi], **5**, 510—511).—Observations at 25° show that there is no double salt formation and that the solid phases in equilibrium with the solution are KCl and $AlCl_3,6H_2O$.

R. W. LUNT.

Systems $AlCl_3$–HCl–H_2O, KCl–HCl–H_2O, and KNO_3–HNO_3–H_2O at 25°. III. G. MALQUORI (Atti R. Accad. Lincei, 1927, [vi], **5**, 576—578).—The solubility of aluminium and potassium chlorides in water is diminished by the presence of hydrochloric acid, whereas that of potassium nitrate is increased by the presence of nitric acid. Aluminium nitrate follows the general rule (cf. Inamura, A., 1920, ii, 625; 1921, ii, 114, also preceding abstract).

T. H. POPE.

System calcium ferrocyanide–sodium ferrocyanide–water. II. (MISS) M. FARROW (J.C.S., 1927, 1153—1158; cf. A., 1926, 236).—Previous work on the system calcium ferrocyanide–water has been extended and the complete solubility curve from −10·1° to 90° determined. The hydrated calcium salt undergoes transition to a less hydrated form at 59·7°. Above this temperature, the solubility is almost independent of temperature (44·4 g. of anhydrous salt/100 g. of solution). An investigation of the system calcium ferrocyanide–sodium ferrocyanide–water shows the existence of a double salt, $Ca_2Fe(CN)_6,Na_4Fe(CN)_6$, stable at all three temperatures, the range of stability increasing with rise of temperature. The solubility of the double salt decreases with increasing temperature.

J. S. CARTER.

Equilibrium between benzene, hydrogen, and *cyclo*hexane. G. H. BURROWS and C. LUCARINI (J. Amer. Chem. Soc., 1927, **49**, 1157—1161).—The equilibrium was studied at 266° and 280° in presence of a platinum catalyst. The mean heat of the re-

action (in the vapour phase) is 51,400 g.-cal. (evolved). The results agree with those calculated from Nernst's approximation formula (benzene and *cyclo*hexane in the liquid state). The anomalous results of Dougherty and Taylor (A., 1923, ii, 549) are attributed to the disturbing influence of side-products attending the use of nickel catalysts. S. K. TWEEDY.

Reactions between solids. J. A. HEDVALL (Z. anorg. Chem., 1927, **162**, 110—114).—Polemical against Balarev (this vol., 314). R. CUTHILL.

Thermobalance analysis of the change in various compounds heated in different gases. H. SAITÔ (Sci. Rep. Tohoku Imp. Univ., 1927, **16**, 37—200; cf. A., 1926, 1101).—A modified form of thermobalance (Honda, *ibid.*, 1915, **4**, 97, 215) has been employed to follow continuously the changes in weight of compounds when heated in a stream of gas passing through the furnace at a definite velocity. The temperature may also be raised at a constant rate, or alternatively in steps. By plotting temperature against weight, more accurate and extensive knowledge relating to the different reactions, chiefly metallurgical, may be obtained than by using alone the methods ordinarily employed. Among the reactions studied are: the effect of heating manganese dioxide in air, sulphates, such as ferric and ferrous sulphate, and copper and zinc sulphates, in air or air and sulphur dioxide, and calcium and magnesium carbonates in air or a mixture of air and carbon dioxide; the dehydration of clay; the roasting of a large number of sulphide ores in air or a mixture of air and sulphur dioxide, these ores including several pyrites, zinc blende, galena, realgar, cinnabar, stibnite, and so on, the rate of evolution of sulphur dioxide when heated in air being also determined and lixiviation tests made on the resulting product; the dissociation of iron pyrites and reduction by hydrogen; the reduction of manganese dioxide, ferric oxide, and nickel oxide by hydrogen or carbon monoxide: the oxidation of metallic copper; the roasting in air and sulphur dioxide of a siliceous nickel ore containing garnierite; the volatilisation of silver chloride and of arsenious oxide; and the dry distillation of shale. M. S. BURR.

Reconciliation of thermochemical data and correction coefficients relating to these data. W. SWIENTOSLAWSKI (Bull. Acad. Polonaise, 1927, A. No. 2, 3—63).—See this vol., 194.

Heat of formation of calcium ferrates. N. M. YASUIRKIN (Ann. ecole super. agr. amelior. Don [Russia], 1925, **6**, 57—60).—The following values for the heat of formation are recorded: $2CaO,Fe_2O_3$ 32·03 $4CaO,Fe_2O_3$ 2·9 g.-cal.; CaO,Fe_2O_3 1·5 g.-cal.; $3CaO,Fe_2O_3$ 6·9 g.-cal. CHEMICAL ABSTRACTS.

Calorimetric researches on nucleic acids, their fission products and their compound with protamine. J. ELLINGHAUS (Z. physiol. Chem., —318).—The following heats of combustion are recorded: guanine (587·8 kg.-cal. per mg.-mol.), guanine sulphate (589·5), synthetic (655·7), adenine sulphate (652·5), xanthine (660·4), synthetic hypoxanthine (559·1), anhydrous cytosine (477·3), synthetic uracil (409·4), inosine (1115·0), vernine (=guanosine, 1179·5), barium inosate, $C_{10}H_{11}O_8N_4PBa,7·5H_2O$ (1164·4), guanylic acid (1130·0), and adenylic acid (1220·0). The value, 4970, obtained for thymonucleic acid on Steudel's formula, $C_{43}H_{59}O_{33}N_{15}P_4$, agrees with the constitution 4 dextrose+1 guanine+1 adenine+1 cytosine+1 thymine (total 4984). Yeast-nucleic acid gives a value more in accordance with Levene's formula, $C_{38}H_{49}O_{29}N_{15}P_4$ (4470 against a calculated 4370), than with Kowalewski's formula, $C_{29}H_{42}O_{23}N_{13}P_3$ (3873 against 3401), or with $C_{38}H_{59}O_{28}N_{16}P_4$ (4767 against 4438 for guanine+adenine+2 cytosine+4 ribose). Calorimetric determinations on preparations of herring sperm heads and clupeine show that the former consist entirely of a neutral salt of clupeine and nucleic acid. C. HOLLINS.

Calorimetry by compensation using the Joule and Peltier effects. Heat of dissolution and heat of slow reactions. (MME.) BERENGER-CALVET (J. Chim. phys., 1927, **24**, 325—345).—The heat evolved or absorbed in the calorimeter is as nearly as possible compensated by means of the Peltier or Joule effects, respectively, so that the usual correction for heat interchange between calorimeter and surroundings is eliminated. The reaction cell is immersed in a large bath at constant temperature, and the small temperature difference between the two is measured by an accurate thermopile, the experiment being carried out in a room of constant temperature to avoid adventitious thermo-electric effects. Of the heat to be measured, 95% is easily compensated, the remainder being readily calculated from the curve showing the variation of thermopile readings with time. The heat of dissolution of potassium nitrate was determined for a range of concentrations from 0·089*N* to 1·68*N*, and in the case of the weaker solutions the heat of dilution was determined directly. The heat of dissolution per gram of salt becomes constant at 8·67 kg.-cal. for solutions weaker than 1 g. of potassium nitrate per 80 g. of water, this constant value being termed the "initial heat of dissolution." The heat of hydrolysis of ethyl acetate was found to be 1·07 kg.-cal. and the heat of esterification 0·94, excess of alcohol being added to dissolve the ethyl acetate. S. J. GREGG.

Change in electrical conductivity of electrolytes and sols with increasing age. N. R. DHAR (Z. anorg. Chem., 1927, **162**, 237—242).—The gradual increase in conductivity of solutions of sparingly soluble acids or bases is probably due to slow hydrolysis with the formation of colloidal particles, which release adsorbed substances on ageing. With salts which give no insoluble products, hydrolysis is practically instantaneous. In the case of hydrophilic colloids, stability, degree of hydration, viscosity, and adsorptive power increase with age, whilst the conductivity and surface tension decrease; with hydrophobic colloids the reverse is true. R. CUTHILL.

Attempt to prepare aurous oxide, and the potential of the gold-aurous oxide electrode. T. F. BUEHRER, F. S. WARTMAN, and R. L. NUGENT (J. Amer. Chem. Soc., 1927, **49**, 1271—1272).—The product obtained by reducing dilute potassium bromoaurate solution with sulphur dioxide solution at 0°

and then precipitating with dilute potassium hydroxide solution is reproducible, but cannot be proved to be aurous oxide. Assuming the product to be this oxide, the *E.M.F.* of cells of the type $H_2(g)|H_2SO_4(xM)|Au_2O(s)+Au$ were measured at 25°. The *E.M.F.* rises from 1·1 volts to a limiting value of 1·363 volts, which corresponds with the potential of the analogous cell involving auric oxide. The reactions $3Au_2O=Au_2O_3+4Au$ and Au (colloidal)⟶Au (crystalline) are supposed to occur.

S. K. TWEEDY.

Electro-affinity potential of molybdic anhydride. L. ROLLA and G. PICCARDI (Atti R. Accad. Lincei, 1927, [vi], **5**, 546—547).—By the method previously described (A., 1925, ii, 1018, 1105), the electronic affinity potential of molybdic anhydride, completely freed from bases by sublimation, is found to be 2·73 volts; this value is calculated on the assumption that, at the flame temperature used, viz. about 1970° Abs., the anhydride does not undergo appreciable dissociation. T. H. POPE.

Photo-voltaic elements containing glycerol. A. GRUMBACH (Compt. rend., 1927, **184**, 1169—1171).—The Becquerel effect and the *E.M.F.* of adsorption (A., 1925, ii, 549) of the cells Pt|glycerol|water|Pt have been determined for varying concentrations of glycerol, one electrode being illuminated by a mercury arc. Two maximum values of the former were obtained and one of the latter. An aqueous solution of sodium fluoresceinate gave one maximum in each case, no Becquerel effect being obtained at high concentrations. In all cases, both effects disappeared at low concentrations. Certain inactive solutions of glycerol and of fluorescein gave a positive adsorption-*E.M.F.* when mixed, and a small negative Becquerel effect, which increased when the solution contained less glycerol. J. GRANT.

Overvoltage. I. T. ONODA (Z. anorg. Chem., 1927, **162**, 57—81).—See this vol., 24.

Anodic behaviour of metals in non-aqueous solutions. U. SBORGI (Atti R. Accad. Lincei, 1927, [vi], **5**, 571—575).—When ethyl-alcoholic solutions of sodium or ammonium chloride or ammonium nitrate are electrolysed with a cadmium anode, the latter is dissolved in amount exceeding that calculated for the bivalent metal, especially with ammonium nitrate (cf. A., 1923, ii, 213). In ethyl-alcoholic, as in aqueous, ammonium nitrate solution, cadmium is attacked without passage of a current. The results confirm the view that, in general, the anodic behaviour of metals is similar in aqueous and in non-aqueous solutions. T. H. POPE.

Influence of pressure on the electrolysis of water. A. COHEN (Ber., 1927, **60**, [*B*], 1078—1081).—If the *E.M.F.* is maintained constant during the electrolysis of aqueous potassium hydroxide between nickel electrodes, the current increases with increasing pressure on the gas. A possible improved process for the technical preparation of hydrogen and oxygen is thus indicated, provided the gases are collected without intermediate release of the pressure.

H. WREN.

Periodic electro-deposition of metals through secondary reaction. E. S. HEDGES (J.C.S., 1927, 1077—1087).—When solutions containing a mixture of mercuric chloride or mercurous nitrate with salts of the alkali metals, alkaline-earths, or aluminium, or solutions of mercuric or cadmium cyanide in potassium cyanide, are electrolysed, alternate deposition of the two metals occurs and periodic changes in the cathode potential and current strength are observed. This behaviour is observed only when one of the metals is deposited as a result of secondary reactions. The values of the limiting current densities, between which periodicity is observed, depend on the relative amounts of the components of the mixed solution. Periodicity has been realised where the thickness of metal deposited in each period is of molecular magnitude. J. S. CARTER.

Velocity of chemical reaction in the silent electric discharge. G. A. ELLIOTT, S. S. JOSHI, and R. W. LUNT (Trans. Faraday Soc., 1927, **23**, 57—60).—See this vol., 212.

Law of flame speeds. W. PAYMAN and R. V. WHEELER (Nature, 1927, **119**, 779—780).—Bone's experiments (this vol., 26, 424), whereby the invalidity of the law of flame speeds is deduced, are criticised.

A. A. ELDRIDGE.

Supposed law of flame speeds. W. A. BONE (Nature, 1927, **119**, 922—923).—Polemical against Payman and Wheeler (preceding abstract). The evidence against the general validity of the "law" is summarised. A. A. ELDRIDGE.

Vibrational movements which occur during the inflammation of combustible gases. J. D. MORGAN (Phil. Mag., 1927, [vii], **3**, 1161—1166).—It is suggested that the audible explosions (pinking or knocking) in internal-combustion engines are due to vibrational movements sometimes developed in the gases in the later stages of inflammation. Experiments are described in which gaseous combustible mixtures were ignited in tubes of different lengths, and it is shown that a mixture which exploded without audible effect in one tube could develop pinking in a longer tube. It is also shown that the phenomenon of pinking can occur only if the flame velocity is sufficiently high. These and associated experiments indicate that pinking is due to vibrational movement in the gas; it depends on a suitable correlation of the rate of heat generation and the vibration frequency of the gas in the direction of motion of the flame. A. E. MITCHELL.

Homogeneous reactions involving complex molecules. Kinetics of the decomposition of gaseous dimethyl ether. C. N. HINSHELWOOD and P. J. ASKEY (Proc. Roy. Soc., 1927, **A**, **115**, 215—226).—At about 500°, dimethyl ether decomposes thus: $CH_3{\cdot}O{\cdot}CH_3 \longrightarrow [CH_4+H{\cdot}CHO] \longrightarrow CH_4+H_2+CO$. The formation of formaldehyde is only transitory. The reaction is homogeneous, and is empirically unimolecular at pressures above 300—400 mm., but at lower pressures, the time taken for any given fraction of the ether to decompose increases, and the reaction assumes more and more a bimolecular character. In presence of a sufficient quantity of hydrogen, the reaction preserves its unimolecular character down to low pressures. The hydrogen

probably acts only by maintaining the Maxwell distribution among the dimethyl ether molecules when this would otherwise begin to be disturbed by the chemical transformation of activated molecules. It cannot do more than restore the rate of reaction to its normal limiting value, and cannot increase it beyond this. Helium, nitrogen, carbon monoxide, carbon dioxide, and methane have no effect similar to that of hydrogen. Carbon monoxide and dioxide have a slight retarding action.

The limiting rate of reaction is expressed by the equation $\log_e k = 30{\cdot}36 - 58{,}500/RT$. To account for the observed rate of reaction, the energy of activation must be supposed to be distributed among about 11 energy terms. L. L. Bircumshaw.

Gaseous combustion at high pressures. VII. Spectrographic investigation of the ultra-violet radiation from carbonic oxide–oxygen (or -air) explosions. W. A. Bone and D. M. Newitt (Proc. Roy. Soc., 1927, **A**, **115**, 41—58; cf. A., 1926, 480).—Using an explosion chamber with quartz windows specially adapted for the spectrographic examination of explosion flames, a study has been made of explosions of the type $2CO+O_2+xR_2$ (where $R_2=O_2$, CO, or N_2, and $x=4$, 5, or 5·5) at initial pressures between 10 and 25 atm. Photometric measurements of the comparative densities on the same plate of the spectrograms from the explosions showed that the resultant ultra-violet radiations were much less when R was carbon monoxide or nitrogen than when it was oxygen. This indicates that carbon monoxide or nitrogen strongly absorbs the ultra-violet radiation emitted by the burning carbon monoxide under such conditions. The absorption is general, although not uniform, over the ultra-violet range 4400—3200 Å., and although there are no absorption bands or lines, the absorption is relatively stronger at lower than at higher frequencies. The marked nitric oxide formation which always occurs in a carbon monoxide–excess of air explosion at an initial pressure of 25 atm. does not take place during the actual combustion, or while radiation of wave-length shorter than 4400 Å. is being emitted. When nitric oxide is present during the actual combustion period in a carbon monoxide explosion, a definite absorption band spectrum is superposed on the continuous carbon monoxide flame spectrum. The results support the view that either carbon monoxide or nitrogen is "activated" by the radiation emitted by the burning carbon monoxide, but in the case of nitrogen, such "activation" is of a lesser degree than that involving the formation of Rayleigh's active nitrogen. A study of the effects of monatomic diluents showed that the resultant ultra-violet radiation from a carbon monoxide (2)–oxygen (1)–argon (4) explosion at an initial pressure of 14 atm. is much greater than that from a carbon monoxide (2)–oxygen (1)–helium (4) explosion at the same pressure, although the maximum temperatures attained differ by only 130°.

L. L. Bircumshaw.

Study of flame movement. O. C. de C. Ellis.—See B., 1927, 354.

Kinetics of catalysed gas reactions in flow systems. A. F. Benton.—See B., 1927, 399.

Thermal decomposition of ozone. I. Homogeneity, order, specific rate, and dependence of rate on total pressure. II. Effect of oxygen and accidental catalysts on the rate. O. R. Wulf and R. C. Tolman (J. Amer. Chem. Soc., 1927, **49**, 1183—1202, 1202—1218).—I. The conditions are described under which the thermal decomposition of ozone can be made to proceed at 100° and 127° as a homogeneous reaction of the second order with respect to ozone. The velocity coefficient (which is very small) varies with the sample of gas and is inversely proportional to the total pressure in the case of the second order decomposition of ozonised oxygen.

II. The relation between the total pressure and the second order velocity coefficient for the thermal decomposition of ozone in mixtures with oxygen is attributed to the inhibiting effect of oxygen itself; the absence of this effect noted by Chapman and Jones (J.C.S., 1910, **97**, 2463) is attributed to the accidental presence of a positive catalyst in the oxygen. Such catalysts (? alkali spray; hydrogen) are present in oxygen prepared by the electrolysis of sodium hydroxide solution, and they are greatly reduced in quantity on passing the oxygen through a Siemens ozoniser. The ease of ozonisation of oxygen varies with the sample; it appears to be related with the lowness of the second order velocity coefficient. Ozonised oxygen free from catalyst (or containing a practically constant amount of catalyst) may be prepared by the electrolysis of sulphuric acid. S. K. Tweedy.

Raffinase. V. I. Isajev (Chem. Listy, 1927, **5**, 191—202; cf. this vol., 591).—The velocity of hydrolysis of raffinose in presence of raffinase is of the order of a unimolecular equation; in those cases where lævulose, dextrose, and melibiose are added separately or together, the velocity is better expressed by a linear equation. This shows that the enzyme is distributed between the substrate and the decomposition products. Michaelis' formula (Euler, "Chemie der Enzyme," 141—149) for the velocity of hydrolysis of sucrose cannot be applied to the above reaction. Raffinose is much more slowly hydrolysed by raffinase than is sucrose. The "affinity" of this enzyme for raffinose is less than for sucrose or melibiose, but greater than for lævulose or dextrose. Top yeast extracts decompose raffinose to lævulose and melibiose, which is further decomposed by bottom yeasts to galactose and dextrose.

R. Truszkowski.

Mutarotation. I. Velocity of mutarotation of α-glucose in methyl alcohol and water. F. P. Worley and J. C. Andrews (J. Physical Chem., 1927, **31**, 742—746; cf. Baker, Ingold, and Thorpe, A., 1924, i, 262).—The velocity of mutarotation of α-glucose in methyl alcohol at 25° varied in different determinations under conditions which were apparently the same. The values of k^{25} vary from 0·00003 to 0·00087, and, in all cases, are lower than those found by previous investigators (cf. Lowry and Richards, A., 1925, i, 886). Lower or even zero values may be possible under ideal conditions. For α-glucose in water, the values of k^{25} are 0·00957, 0·00956, and 0·00950, in close agreement with those

obtained by Osaka (A., 1901, i, 127) and by Hudson (A., 1907, ii, 942). With mixtures of methyl alcohol and water, the velocity constants lie on a smooth curve. Addition of small amounts of the alcohol to water has a greater effect in reducing the rate of mutarotation than has the addition of water to alcohol in increasing the rate. A discussion of the mechanism is reserved. L. S. THEOBALD.

Detonation wave from solid explosives. W. C. HOLMES.—See B., 1927, 429.

Inflammation of coal dusts. Effect of chemical composition of the dust. T. N. MASON and R. V. WHEELER.—See B., 1927, 434.

Principles of electrolytic studies on corrosion. W. BLUM and H. S. RAWDON.—See B., 1927, 447.

Acid and salt effects in catalysed reactions. VIII. Determination of hydrolytic velocity coefficients from isocatalytic data. Reaction velocities in buffer solutions and compound catalytic catenaries. H. M. DAWSON (J.C.S., 1927, 1146—1153).—The catalytic coefficients k_H and k_{OH} of the hydrogen and hydroxyl ions, respectively, may be derived from the minimum velocity of a hydrolytic reaction (*i.e.*, any reaction catalysed by both the hydrogen and hydroxyl ion) and the corresponding hydrogen-ion concentration. The value of k_{OH}/k_H varies enormously with the hydrolyte (*e.g.*, 12×10^6 for ethyl aminoacetate and 1·6 for benzamide). Approximate velocity and hydrogen-ion concentration data may be obtained by the use of buffer solutions, provided a correction is made for the catalytic effects of constituents other than the hydrogen and hydroxyl ions. The curves obtained on plotting reaction velocity against the p_H value of a series of acid–salt buffer solutions characterised by constant concentration of acid are catenary in type, but are compound in character, since the anionic catalytic effect is also shared by the anion of the acid in the buffer mixture. The compound catenaries form a continuous series limited on the one side by the H^+—OH^- catenary and on the other by the simple H^+—A^- catenaries corresponding with the mixtures cHA+xMA. The compound catenaries conform to the requirements of the general catalytic catenary, the applicability of which is further extended to include anionic catalytic effects shared by the hydroxyl ion with other acid anions.

J. S. CARTER.

Catalysis in the reaction between persulphate and iodide ions. A. VON KISS and L. VON ZOMBORY (Rec. trav. chim., 1927, **46**, 225—239).—An examination of the kinetics of the stoicheiometrically termolecular reaction between persulphate and iodide in dilute aqueous solution shows that, when allowance is made for the amount of iodide ion involved in the tri-iodide equilibrium, the experimental numbers conform to the requirements of a reaction of the second order. The reaction scheme is therefore: (i) $S_2O_8''+I'=S_2O_8I'''$ (measurable rate); (ii) $S_2O_8I'''+I'=2SO_4''+I_2$ (rapid). As predicted from considerations of Bronsted's theory of reactions (A., 1922, ii, 699), the rate of reaction is increased in presence of neutral salts. In presence of ferrous or copper salts, an actual catalytic effect is observed, which is due to the opening of new reaction paths. In the case of ferrous salts, the effect is satisfactorily represented by the additional reaction scheme: (iii) $Fe^{\cdot\cdot}+S_2O_8''=FeS_2O_8$ (measurable rate); (iv) $FeS_2O_8+Fe^{\cdot\cdot}=2Fe^{\cdot\cdot\cdot}+2SO_4''$ (rapid); (v) $2Fe^{\cdot\cdot\cdot}+2I'=2Fe^{\cdot\cdot}+I_2$ (rapid). A similar scheme involving cuprous and cupric ions explains the catalytic activity of copper salts. The rate of the catalytic process is determined by reaction (iii), and, as predicted by Bronsted's theory, the neutral salt effect is negative. In presence of acid, the rate of reaction is slightly lowered. The velocity of the uncatalysed reaction is increased somewhat on illumination.

J. S. CARTER.

Negative catalysis in a homogeneous system. A. C. ROBERTSON (Proc. Nat. Acad. Sci., 1927, **13**, 192—197).—Vanadic acid greatly reduces the rate of the catalytic decomposition of hydrogen peroxide by potassium dichromate. This negative catalytic effect is explained on the assumption of a change in the catalytic path (A., 1926, 917). The catalytic decomposition by potassium dichromate is due to the reactions: (i) $K_2Cr_2O_7+H_2O_2=2KCrO_4+H_2O$; (ii) $2KCrO_4+H_2O_2=K_2Cr_2O_7+H_2O+O_2$. Corresponding reactions occur with vanadic acid, the reactivity of pervanadic acid being, however, much smaller than that of potassium dichromate. In the present case, reaction (ii) is largely replaced by the reaction: (iii) $2KCrO_4+HVO_3=K_2Cr_2O_7+HVO_4$. As a result, the concentration of the more reactive dichromate decreases with consequent retardation of the peroxide decomposition. J. S. CARTER.

Colloid particle as revealed by catalytic studies. H. S. TAYLOR (Fourth Colloid Symposium Monograph, 1926, 19—28).—Catalytic action is regarded as a branch of colloid chemistry. An oxide catalyst surface is composed of two catalysts, metal ions and oxide ions, and the nature of the changes induced is determined by the charge on the ion on which the reactant molecule is adsorbed. The extent of the two alternative changes depends on the relative extent of adsorption of the reactant on the two ions, on the relative frequency of occurrence of the ions, and on their specific catalytic activities. These factors depend on the degree of saturation of the lattice ions, and the extent to which the ions are already covered by poisons.

CHEMICAL ABSTRACTS.

Contact catalysis and the activation of gases by adsorption. G. M. SCHWAB and E. PIETSCH (Z. physikal. Chem., 1927, **126**, 473—474).—Polemical (cf. this vol., 426). H. F. GILLBE.

Influence of temperature on the catalytic decomposition of hydrogen peroxide. A. GALECKI and G. JERKE (Rocz. Chem., 1927, **7**, 1—6).—The temperature coefficient of the uncatalysed decomposition of hydrogen peroxide has a maximum value at about 50°. The temperature coefficients of the same reaction catalysed by gold hydrosols vary inversely as the temperature in those cases where the catalyst is very active; with less active catalysts, a maximum value is obtained at 35—45°. With still weaker preparations, the temperature coefficient

increases with rise in temperature, and finally, with such gold hydrosols as possess no appreciable catalytic action, the temperature coefficient at first falls to a minimum at 35—45°, after which it rises. In all cases, the value of the temperature coefficient between 35° and 45° is lower than for the uncatalysed reaction; between 25° and 35° it is, on the other hand, slightly higher. With silver hydrosols, the value of the temperature coefficient diminishes with rise of temperature. R. TRUSZKOWSKI.

Kinetics of chemical reactions. I. Interpretation of conjugated autocatalysis in the isomerisation of alkyl phosphites. W. STARONKA (Rocz. Chem., 1927, 7, 42—53).—The velocity coefficient for the reaction of isomerisation of alkyl phosphites (Zawidzki and Staronka, Bull. Acad. Sci. Cracovie, 1915, 310—386) with ethyl iodide as catalyst is only an apparent case of conjugated autocatalysis; in reality, the changes in velocity are due to changes in the reaction medium which at first is triethyl phosphite and ethyl iodide, whilst at the end it is diethyl ethylphosphite, $PEtO(OEt)_2$, and ethyl iodide. As a result, the physical properties of the medium change, and with them the velocity of reaction. Hence it is concluded that Doroszewski's law is applicable also to the velocity coefficients of reactions. R. TRUSZKOWSKI.

Preparation of formaldehyde by catalytic dehydrogenation of methyl alcohol. I. J. C. GHOSH and J. B. BAKSI.—See B., 1927, 426.

Deterioration of mineral oils. I. Mechanism of oxidation and action of negative catalysts as determined by a dynamic method. R. T. HASLAM and P. K. FROLICH.—See B., 1927, 355.

Electro-deposition of iron–nickel alloys. I. S. GLASSTONE and T. E. SYMES (Trans. Faraday Soc., 1927, 23, 213—226).—An investigation has been made of the compositions of alloys deposited from well-buffered solutions of definite hydrogen-ion concentration containing mixtures of ferrous and nickel sulphates. At very low current densities, the deposit from solutions containing more than about 20% of the total metal as iron contains a greater proportion of nickel than does the electrolyte; for solutions containing a smaller proportion of iron, the results are not definite. The proportion of iron in the alloy increases rapidly with increasing current density, reaches a maximum, and then either remains constant or slowly diminishes. The maximum corresponds in all cases with the deposition of an alloy containing a greater proportion of iron than the solution, the excess being greatest in the more concentrated solutions or in solutions containing a greater relative amount of iron. Diminution of the iron content of the alloy beyond the maximum point is most marked for dilute solutions or solutions of low hydrogen-ion concentration, and disappears almost completely when the electrolyte is stirred so as to facilitate diffusion of the ferrous ions. The process of stirring also brings about an increase in the iron content at the maximum. G. A. ELLIOTT.

—ectro-deposition of tin. W. FRAINE.—See B., 1927, 447.

Study of the electrolytic deposition of the radio-elements. JOLIOT (Compt. rend., 1927, **184**, 1325—1327).—An apparatus is described for the continuous study of the deposits produced in a given time on a gold electrode immersed in solutions (10^{-8} to $10^{-16}N$) of polonium in nitric acid. The deposition electrode forms part of the electrolysing vessel, and is thin enough to allow the passage of the radiation from the active deposit into an ionisation chamber. The corresponding saturation-current is proportional to the amount of the deposit. The deposition potential has been determined and the rate of deposition for the electrode-potential of +0·43 volt (Hg) shown to fall from a large value almost to zero in a few hours. Below this potential, the rate remains constant for a particular potential, but increases as the potential falls. J. GRANT.

Flat luminous flames. D. S. CHAMBERLIN and W. E. THRUN (Ind. Eng. Chem., 1927, **19**, 752—754).—The size and shape of flat luminous flames burning at a slit are investigated by photographic methods and the Poiseuille formula for the flow of gases through a circular orifice is modified for narrow slits. There is no simple relation between the size of the flame and the width of the slit; wide slits do not conform to the same principles as narrow slits. A comparison was also made of the gas jet in the form of a flame and in the unignited state. S. K. TWEEDY.

Chemiluminescence of phosphorus vapour. E. J. BOWEN and E. G. PELLS (J.C.S., 1927, 1096—1099).—Assuming that the final product of oxidation, phosphoric oxide, is produced as a result of a series of consecutive reactions, of which only one, involving one molecule only of oxygen, emits light, experiments in which the ratio of the number of quanta of visible light emitted to the number of molecules reacting in the glow of phosphorus vapour and oxygen was determined photographically, show that at least 1 in 2000 molecules of phosphorus undergoing oxidation emits a quantum of visible light. The glow of phosphorus appears to be a chemiluminescence of the type described by Kautsky (A., 1926, 558), oxidation at the surface of solid particles of an oxide exciting to luminescence adsorbed molecules of some other oxide. J. S. CARTER.

Nature of phosphorus ionisation. W. BUSSE (Ann. Physik, 1927, [iv], 82, 873—911).—Luminous white phosphorus is undergoing slow oxidation with concomitant formation of ozone and the appearance of positively and negatively charged ions in the surrounding gas. Bloch (A., 1903, ii, 206; 1904, ii, 117; 1905, ii, 72; 1908, ii, 1032) and Harms (A., 1904, ii, 331) have investigated the mobilities of the large ions. Repetition of the measurements with improved methods shows that the ions do actually arise at the oxidising phosphorus. The two kinds of ions do not at first show different mobilities, but the results are difficult to reproduce owing to the influence of temperature and moisture; the method used nevertheless allows the ageing of ions to be followed, although an exact upper limit to the increase in ionic size cannot be fixed. A continuous range of sizes has been demonstrated, and it is therefore

concluded that the phosphorus cannot be the only place at which ions originate. The rate of growth of the large ions indicates that ionisation must occur also in the air stream away from the phosphorus. Small temperature differences play an important part in the gradual disappearance of ions. The evidence of the rate of growth of positive and negative ions indicates that the latter must be multiply charged. On the assumption of single positive charges, the positive ions increase in size from 5×10^{-8} cm. to about $2—4\times10^{-6}$ cm. in 8 sec.

Downey (A., 1924, ii, 250) found that the light emitted from phosphorus could ionise air through a plate of fluorite. It has not been possible to repeat this experiment, and all the evidence considered is against the view that rays between 120 and 200 μμ are generated. It is also concluded that photo-electric action plays no part.

The oxidation of phosphorus is greatly influenced by the presence of water vapour, and reaches a maximum when the moisture content is regulated by means of concentrated sulphuric acid (10^{14} to 10^{15} molecules of water per c.c. of vapour). It is confirmed that extreme drying retards the oxidation of phosphorus, but does not effect complete inhibition, so that, whilst water is a catalyst for the process, it is not essential.

Dry phosphorus becomes coated with a film of oxide in the dark so that a store of phosphorus trioxide accumulates. This undergoes sudden oxidation to the pentoxide accompanied by luminescence when local temperature changes occur. The high mobilities of the negative ions are ascribed to multiple charges, four to six times as great as those carried by the positive ions. The latter appear to be predominantly singly charged, and in any case four charges is regarded as the maximum for a positive carrier (cf. A., 1905, ii, 244; 1906, ii, 326; 1924, ii, 255).

R. A. MORTON.

Light-sensitiveness of zinc and silver salts. F. G. BRICKWEDDE (J. Opt. Soc. Amer., 1927, **14**, 312—322).—Lithopone, a white pigment containing about 26% of zinc sulphide, darkens on exposure to ultra-violet light. The sensitivity of several commercial brands was determined for light of different wave-lengths between 2536 and 3650 Å. Whilst the rate of darkening varied with different samples, the ratio of the sensitivities remained constant for all wave-lengths. The sensitivity of lithopone showed a maximum at about 3126 Å., and similar measurements on precipitated silver chloride showed an increase in sensitivity at 3650 Å. Indirect evidence was obtained that the darkening of lithopone is due to the formation of metallic zinc and liberation of hydrogen sulphide. If impurities capable of forming dark sulphides are present, the sensitivity of lithopone is increased. A comparison of the therapeutic value of several arcs, based on their effect on lithopone, is given.

C. J. SMITHELLS.

Law of blackening of the photographic plate at low densities. E. A. BAKER.—See B., 1927, 461.

Activation of hydrogen in the electric discharge. G. A. ELLIOTT (Trans. Faraday Soc., 1927, **23**, 60—75).—See this vol., 187.

Cuprammonium salts. VII. A complex thiosulphate. D. W. HORN and R. E. CRAWFORD (Amer. J. Pharm., 1927, **99**, 274—279; cf. Horn and others, A., 1904, ii, 662; 1906, ii, 231; 1907, i, 595, ii, 871; 1908, i, 121, 392).—A new, complex *cuprammonium thiosulphate*, $Cu_{10}S_{15}O_{18},9NH_3$, was prepared by mixing a solution, d^{-1} 1·26, of sodium thiosulphate in concentrated ammonia solution with cupric chloride solution. The substance forms stable, deep blue crystals.

M. CARLTON.

Action of salts on metals. T. PECZALSKI (Compt. rend., 1927, **184**, 1159—1161).—Copper and iron, when heated in presence of salts, increase in volume and electrical resistance if no reaction occurs. Cementation of the metal by the salt is the result of decomposition of the latter, and is facilitated by volatile salts. Copper heated at 800° in chromic chloride vapour absorbs the latter with a rise in temperature. The copper then fuses and sublimes, and its vapour combines with that of the salt to form a volatile chemical compound with liberation of heat. These phenomena explain the increased fragility and powers of electronic emission in such cases.

J. GRANT.

Treatment of pollucite and preparation of cæsium chloride. A. KASTLER.—See B., 1927, 439.

Surface film of aluminium. W. H. WITHEY (Nature, 1927, **119**, 923—924).—A claim for priority against Sutton and Willstrop (this vol., 530).

A. A. ELDRIDGE.

[Surface film of aluminium.] H. SUTTON and J. W. W. WILLSTROP (Nature, 1927, **119**, 924).—A reply to Withey (preceding abstract).

A. A. ELDRIDGE.

Silicic acids. III. R. SCHWARZ and H. RICHTER (Ber., 1927, **60**, [*B*], 1111—1116; cf. A., 1925, ii, 222).—The conception of the existence of definite hydrates of silica is strengthened by the observation that whereas the *meta* acid is found by Röntgen spectrographic analysis to be amorphous, the acid $H_2Si_2O_5$ is crystalline. At 150°, the latter acid becomes amorphous and subsequently does not yield a crystalline, less hydrated system, but passes gradually into stable, crystalline quartz. The dehydration isotherm of the acid $H_2Si_2O_5$ at 12° exhibits a definite break corresponding with the presence of about 17% of water; the divergence from the theoretical value (13%) is ascribed to the extensive development of the surface and consequent great adsorptive power, as shown by its behaviour towards methylene-blue and its marked hygroscopicity. The water content corresponding with the break in the curve increases if the surface of the acid is increased by grinding, and it must therefore be expected that silicic acid gels will not give characteristic dehydration isotherms even if distinct hydrates are present. Metasilicic acid at 17° gives a continuous dehydration isotherm, whereas the curve of the acid at 2° exhibits two breaks at points immediately before and after that corresponding with the theoretical water content. At the first break, about 4% of adsorbed water is present, which can be removed only by decreasing the vapour tension to a value at which the metasilicic acid is itself unstable. The dehydration isobar

at 10 mm. does not give evidence of the existence of a hydrate of the acid $H_2Si_2O_5$. The conclusion is therefore reached that the isothermic is to be preferred to the isobaric method in the investigation of systems of this type. H. WREN.

Ionic exchange of zeolitic silicates with hydrolysable salts. I. Permutite. H. KAPPEN and F. RUNG.—See B., 1927, 364.

Occurrence of indium in tin. J. R. GREEN (Nature, 1927, **119**, 893).—Garrett's observation (this vol., 393) is confirmed. A. A. ELDRIDGE.

"Active" nitrogen. E. J. B. WILLEY (Nature, 1927, **119**, 924—925).—Experiments indicate that glowing and chemically active forms of nitrogen are distinct. The luminous variety is due to the recombination of atoms with a heat of formation of about 250,000 g.-cal./g.-mol.; the other variety, which possesses an energy of about 45,000 g.-cal./g.-mol., may be metastable molecular nitrogen or a more complex substance such as N_3. A. A. ELDRIDGE.

Decomposition of nitrous oxide in the silent electric discharge. S. S. JOSHI (Trans. Faraday Soc., 1927, **23**, 227—238).—When nitrous oxide is subjected to the silent electric discharge in a Siemens ozoniser at 6000—12,500 volts (r.m.s.) and 150 cycles per sec., the gas is completely decomposed, with intermediate formation of nitrogen peroxide, to nitrogen and oxygen. The amounts of nitrous oxide decomposed and of nitrogen and oxygen formed increase steadily for decreasing values of the initial pressure and a constant time of exposure to the discharge, or during the course of a single decomposition. The amount of nitrogen peroxide, however, rises to a maximum and then decreases to zero. The pressure–time curves show an initial rapid pressure increase, an intermediate stage for which the gradient is much smaller, and finally a sudden increase to a constant value corresponding with complete decomposition. The current–time curves are similar, with the exception that during the initial stage of increasing pressure the current diminishes. A mechanism for the decomposition is proposed from a consideration of these results. G. A. ELLIOTT.

Oxidation reactions. I. P. ASKENASY and E. ELOD. **Production of nitrates and arsenic acid.** H. ZIELER (Z. anorg. Chem., 1927, **162**, 161—192).—The oxidising action of nitric acid usually ceases when reduction to nitric oxide has occurred. Since the reaction $4NO+3O_2+2H_2O=4HNO_3$ involves a diminution in volume, attempts have been made to carry out oxidations with oxygen under pressure in presence of nitric acid, the latter to act merely as the oxygen carrier. With oxygen under a pressure of 20 atm., sodium nitrite in solutions acidified with nitric acid is quantitatively oxidised to nitrate, the oxidation occurring in slightly acid solutions entirely in the liquid phase. The rate of oxidation increases with increase in the acidity, dilution of the salt, temperature, and, to a less extent, with the oxygen pressure. With neutral nitrite solutions, no oxidation occurs. Arsenious oxide, when sufficiently finely divided, can be oxidised practically quantitatively at 90° with oxygen under 20 atm., and twice its weight of 40—60% nitric acid in about 1 hr., the nitric acid being nearly completely regenerated. The rate both of re-formation of the nitric acid and of the oxidation increases with increase in oxygen pressure and in the temperature. Increase in the acid concentration accelerates the oxidation, but retards the regeneration of the acid. The nitric acid can be removed from the reaction mixture nearly quantitatively by distillation under 15 mm. pressure. With neutral solutions, no oxidation occurs. Arsenic sulphides are oxidised by nitric acid and oxygen under pressure to arsenic acid and sulphuric acid. With oxygen at 20 atm. and at 120°, realgar is completely oxidised with twice its weight of 10% acid in 30 min., whilst orpiment requires 40% acid for 15 min. In the case of arsenical pyrites, about 16% of the arsenic is not attacked, and some oxygen is used in oxidising the iron. The amount of nitric acid required is in every case less than the amount that would theoretically be needed if no oxygen were used, and the losses are very small. Treatment of aqueous suspensions of the sulphides with oxygen alone oxidises some of the sulphur to sulphuric acid, but no arsenic acid is formed. Sulphuric acid may be removed as calcium sulphate from the arsenic acid solutions by addition of calcium carbonate or hydroxide, and subsequent concentration of the filtrate. The solubility of calcium sulphate in arsenic acid solutions at 25° is maximal for a 32% solution of the acid. R. CUTHILL.

Decomposition of nitrogen pentoxide in presence of foreign gases. W. F. BUSSE and F. DANIELS (J. Amer. Chem. Soc., 1927, **49**, 1257—1269).—Hydrogen, carbon monoxide, bromine, and chlorine are without influence on the thermal decomposition of nitrogen pentoxide, but certain organic vapours bring about rapid, almost explosive, reaction. Nitric oxide is oxidised immediately. Hydrogen and air have no effect on the photochemical decomposition, but bromine retards it, possibly because of optical screening (cf. Hirst, A., 1925, ii, 554). The mechanism of the decomposition is considered to be $N_2O_5 \longrightarrow NO+NO_2+O_2$ (slow); $NO+N_2O_5 \longrightarrow 3NO_2$ (rapid) (cf. Norrish, this vol., 119). In presence of organic vapours, intermediate compounds are probably formed. Thus, on addition of ethyl ether, the pressure falls (formation of compound) and then rises (decomposition of compound). In the case of carbon disulphide, the initial pressure decrease is lacking either because direct oxidation can occur without intermediate compound formation or because the measurements were not adequate for detecting the decrease. S. K. TWEEDY.

Formation of ozone by silent electric discharge in presence of other gases. A. JULIARD (Bull. Acad. roy. Belg., 1926, [v], **12**, 914—920).—The influence of the presence of hydrogen, nitrogen, silicon tetrafluoride, and nitric oxide on the formation of ozone by a silent electric discharge has been studied up to concentrations of 20%, 40%, 10%, and 2%, respectively. The gas was drawn through a train consisting of a flow meter, drying tubes, and an ozoniser immersed in an oil thermostat. Concordant results could be obtained only if the total pressure lay between 300 and 600 mm., and if the partial

pressure and rate of flow of the oxygen were kept constant. Hydrogen and silicon tetrafluoride reduce the yield of ozone, and 2% of nitric oxide reduces it to zero. Nitrogen affects the yield to an extent depending on the rate of flow and the energy of the discharge. For small rates of flow, the yield passes through a maximum, which shifts towards smaller concentrations of nitrogen as the energy of the discharge is increased. C. W. GIBBY.

Sulpho-salts. II. Sulphoxypolymolybdates of ammonium and of guanidine. L. FERNANDES and F. PALAZZO (Atti R. Accad. Lincei, 1927, [vi], **5**, 339—343).—The action of even a relatively weak acid, such as acetic or formic acid, on a solution of a normal sulphomolybdate results in decomposition of the salt with evolution of hydrogen sulphide and precipitation of molybdenum sulphide. On the contrary, the sulphoxymolybdates, although decomposed by strong mineral acids, undergo polymerisation similar to that occurring with the oxygenated salts when treated with a weak acid in low concentration. When the compound $(NH_4)_2MoO_2S_2$ is dissolved in the least possible amount of water and treated with different amounts of *N*-acetic acid, the *compound* $[H_2(MoS_2O_2)_6](NH_4)_4H_6,5H_2O$ is always obtained. With both the ammonium and the guanidine salts, experiments have been made in which increasing quantities of the normal sulpho-salt were added. With the guanidine salts, it is impossible to obtain highly sulphured compounds, but in the case of the ammonium salts it is possible to obtain *compounds* such as $[H_2(MoS_3O)_6](NH_4)_5H_5$, which contain only 6 oxygen atoms and may be regarded as corresponding with the hypothetical aquo-acid $(H_2O)_6H_{10}$. The other *compounds* described are:
$[H_2(MoS_2O_2)_3(MoS_3O)_3](NH_4)_5H_5,16H_2O$;
$[H_2(MoS_2O_2)_6]Gu_4H_6,8H_2O$;
$[H_2(MoS_2O_2)_6]Gu_5H_5,9H_2O$;
$[H_2(MoS_2O_2)_2(MoS_3O)_3]Gu_4H_6,10H_2O$;
$[H_2(MoS_3O)_2(MoS_2O_2)_3]Gu_5H_5,9H_2O$;
$[H_2(MoS_2O_2)_2(MoS_3O)_4]Gu_5H_5,7H_2O$. T. H. POPE.

Molybdenyl salts and the co-ordination number of oxygen. W. WARDLAW and R. L. WORMELL (J.C.S., 1927, 1087—1092; cf. this vol., 296, 327).—The *hydrate*, $MoCl_3,3H_2O$, has been obtained from an electrolytically reduced solution containing tervalent molybdenum. The following molybdenyl salts have been prepared: *fluoride*, $MoOF,3{\cdot}5H_2O$; *phosphate*, $(MoO)_3PO_4,12H_2O$; *benzoate*, $PhCO_2{\cdot}MoO,2{\cdot}5H_2O$; *tartrate*, $(MoO)_2C_4H_4O_6,6H_2O$. The *oxalate* and *citrate* have also been prepared. The facts so far available furnish strong evidence in favour of the presence of the molybdenyl radical in all solutions of tervalent molybdenum. The water content of molybdenyl salts is often less than would be anticipated from a co-ordination number of 6 for molybdenum, and it is suggested that oxygen may in certain circumstances occupy two positions in the co-ordination sphere. J. S. CARTER.

Properties of tungsten carbide, W_2C. K. BECKER.—See B., 1927, 439.

Entrainment of manganous hydrate by alumina in an ammoniacal medium. PARISELLE and LAUDE (Compt. rend., 1927, **184**, 1176—1177; cf. A., 1925, ii, 903).—From solutions containing equimolecular quantities of manganese and aluminium sulphates, the former is precipitated by ammonia, in the complete absence of oxygen, when at least 4 mols. of ammonium chloride are present for each mol. of sulphate. In the absence of ammonium chloride, an excess of ammonia precipitates alumina and manganese hydroxide almost integrally, and independently of the amount of oxygen present. Manganous hydroxide is entrained to decreasing extents as the amount of ammonium chloride is increased, and this phenomenon is almost independent of the degree of dilution. Experiments on the entrainment of the respective hydroxides by alumina in presence of increasing amounts of magnesium or manganese salts indicate that this is due to adsorption, the alumina hydrogel adsorbing the manganous hydroxide to a greater extent than the magnesia in an ammoniacal medium. There is also evidence of the formation of meta-aluminates, in the case of manganese. J. GRANT.

Occurrence of dvi-manganese in manganese compounds. V. DOLEJSEK and J. HEYROVSKY (Rec. trav. chim., 1927, **46**, 248—255).—A defence of the authors' previously published work (A., 1926, 37, 258) against the criticisms of W. Noddack and I. Noddack (Z. angew. Chem., 1927, **40**, 250, 254) and of Prandtl (this vol., 433). J. S. CARTER.

Inertness towards commercial iron, copper, and zinc [?] of liquid hydrogen sulphide. J. B. FOURNIER and FRITSCH-LANG (Compt. rend., 1927, **184**, 1174—1175).—Clean commercial samples of iron, copper, and aluminium [?] showed no apparent alteration in appearance or properties after immersion in liquid hydrogen sulphide for 11 years at the ordinary temperature, or 15 days at temperatures varying up to 60°. J. GRANT.

Green cobalt compounds. A. BERNARDI (Gazzetta, 1927, **57**, 232—234).—When dilute solutions of cobalt salts are treated in the cold with sodium hydroxide in the presence of air, the blue basic salt at first formed rapidly changes to a green, stable *compound*. E. W. WIGNALL.

Ruthenium tetrachloride. S. AOYAMA (Sci. Rep. Tohoku Imp. Univ., 1927, **16**, 27—35).—See A., 1926, 698.

Preparation and analysis of pure auric oxide. W. E. ROSEVEARE with T. F. BUEHRER (J. Amer. Chem. Soc., 1927, **49**, 1221—1226).—The following modification of Fremy's method yields pure auric oxide (Ann. Chim. phys., 1851, [iii], **31**, 481). Potassium hydroxide solution is added slowly to a boiling aqua regia solution of gold until the initial precipitate just redissolves. The solution is slightly acidified with 3*N*-sulphuric acid and boiled. The oxide is separated, redissolved in boiling potassium hydroxide, and reprecipitated with sulphuric acid. The precipitate is then shaken violently with 0·01*N*-sulphuric acid and the resulting suspension centrifuged, this process being repeated until chlorides and sulphates are entirely removed. The accurate volumetric determination of the oxide in hydrochloric acid solution may be carried out by adding excess of titanous

chloride in an atmosphere of carbon dioxide and back titrating with ferric chloride, using potassium thiocyanate as indicator. French's method (the analogous titration of solid oxide with ferrous sulphate and potassium permanganate solutions) yields erratic results (cf. Min. Eng. World, 1913, **37**, 853).

S. K. TWEEDY.

Pure zinc. H. M. CYR.—See B., 1927, 390.

Mechanism of the production of zinc. M. BODENSTEIN.—See B., 1927, 447.

Preparation of phosphorus pentafluoride. H. J. LUCAS and F. J. EWING (J. Amer. Chem. Soc., 1927, **49**, 1270).—A mixture of 25 g. of phosphorus pentoxide and 55 g. of dry calcium (not potassium) fluoride is heated in an iron tube: $5CaF_2+6P_2O_5=2PF_5+5Ca(PO_3)_2$. Moisture is excluded as much as possible by rapid working. The rate of gas evolution is controlled by the temperature; the product is probably about 94% pure. No *iso*amyl fluoride is produced on passing phosphorus pentafluoride into boiling, anhydrous *iso*amyl alcohol for 1·5 hrs.

S. K. TWEEDY.

Preparation of compact and colloidal molybdenum. E. WEDEKIND and O. JOCHEM.—See B., 1927, 390.

[Preparation of] pure oxides and salts of tungsten and molybdenum. E. K. JENCKES.—See B., 1927, 439.

Recommended specifications for analytical reagent chemicals. W. D. COLLINS, H. V. FARR, J. ROSIN, G. C. SPENCER, and E. WICHERS (Ind. Eng. Chem., 1927, **19**, 645—649).—Detailed methods of analysis and specifications ensuring a degree of purity sufficient for analytical work are given for ammonium nitrate, diammonium hydrogen phosphate, barium carbonate, barium hydroxide (octahydrate), cupric sulphate, lead dioxide, potassium bromate, potassium bromide, potassium chlorate, potassium iodate, potassium iodide, sodium acetate, and sodium bismuthate.

W. J. POWELL.

Polarised platinum electrode in neutralisation reactions. A. H. WRIGHT and F. H. GIBSON (Ind. Eng. Chem., 1927, **19**, 749—750).—The polarised platinum electrode system described by Willard and Fenwick (A., 1923, ii, 33) may be used in electrometric titrations involving neutralisation. S. K. TWEEDY.

Protection of iron wire used for standardisation. M. HOLLINGSWORTH (Ind. Eng. Chem., 1927, **19**, 738).—The spool of wire is mounted on a perpendicular axle attached to the cork of a wide-necked bottle, the latter containing a layer of lime covered by cotton wool and a piece of gauze. The wire is withdrawn through a hole in the cork.

S. K. TWEEDY.

Use of filtering-rods in Pregl's micro-analysis. K. HELLER and K. MEYER (Z. anal. Chem., 1927, **71**, 117—122).—Emich's filtering-rods ("Mikrochemische Praktikum," München, 1924, p. 63) can be used satisfactorily in conjunction with Pregl's micro-methods for the determination of arsenic, phosphorus, methoxy-groups, the halogens, and sulphur ("Die quantitative organische Mikroanalyse," Berlin, 1923).

R. CUTHILL.

Apparatus for the electrometric determination of hydrogen-ion concentration. F. EMSLANDER (Biochem. Z., 1927, **184**, 234—236).—A claim of priority against Lüers (A., 1926, 813).

P. W. CLUTTERBUCK.

Reversing p_H indicator. E. W. TODD (Facts about Sugar, 1927, 22, 14—15, 17).—The p_H of moving liquids, *e.g.*, beet-sugar thick juice, is recorded by means of the current produced between two electrodes, one of iron and the other of an antimony–cadmium (50 to 2—3 parts) alloy. Compensation for variations in temperature is automatic.

CHEMICAL ABSTRACTS.

Potentiometric titrations with hydrazine sulphate. M. G. MELLON and V. N. MORRIS (Proc. Indiana Acad. Sci., 1925, **35**, 165—167).—Potentiometric titration of hydrazine sulphate with 0·18*N*-sodium hydroxide, barium hydroxide, or sodium carbonate indicates that the titrations are accurate with methyl-orange as indicator. Methyl-red is suitable for the hydroxides. Hydrazine sulphate solutions are stable.

CHEMICAL ABSTRACTS.

Some sources of error in the colorimetric determination of p_H values. J. W. SCHLEGEL and A. H. STUEBER (Ind. Eng. Chem., 1927, **19**, 631—633).—Various sources of error, due to manipulative details and to the method of preparation of the indicator solution, are discussed. Since indicator solutions which are standardised against standard buffer solutions give erroneous results when used with slightly buffered solutions, a method is given for the preparation of indicator solutions which will give correct results with both buffered and unbuffered solutions such as are encountered in sugar-refinery practice.

W. J. POWELL.

Methoxytriphenylcarbinols as one-colour indicators. I. M. KOLTHOFF (J. Amer. Chem. Soc., 1927, **49**, 1218—1221).—The indicator properties of some of the above carbinols are described; the use of these compounds as indicators is illustrated. They are colourless in alkaline and coloured in acid solutions. 2 : 4 : 2′ : 4′ : 2″ : 4″-Hexamethoxytriphenylcarbinol ("hexamethoxy-red") has a p_H range of 4·6—2·6, whilst the corresponding "pentamethoxy-red" has a range of 3·2—1·2.

S. K. TWEEDY.

Water analysis. D. BURTON and J. K. HASLAM.—See B., 1927, 382.

[Detection of] chlorine ions in complex mixtures of ions (CN', SCN', $Fe(CN)_6''''$, $Fe(CN)_6'''$, Br', I'). (MLLE.) E. SPIRESCU (Bul. Soc. chim. Romania, 1926, **8**, 115—117).—Strongly alkaline hydrogen peroxide (20%) completely oxidises cyanides and thiocyanates, as well as sulphides, sulphites, and thiosulphates, after boiling for a few minutes. If ferro- and ferri-cyanides are also present, the solution is further treated with *N*-sulphuric acid and a few drops of 20% hydrogen peroxide. The whole is warmed, chlorine being detected in the vapours with the aid of starch and potassium iodide, or, if bromine and iodine are also present, the starch–iodide is replaced by water containing a little magnesium dust, the resulting magnesium halides being identified by Ludwig's method (A., 1921, ii, 273). S. K. TWEEDY.

Determination of soluble iodides. J. F. SPENCER and M. L. SMITH (Analyst, 1927, **52**, 270—271).—Dietz and Margosches' method for the determination of soluble iodides is modified by adding a measured excess of a standard potassium iodate solution to the solution of soluble iodide which contains about 20 c.c. of an approximately 2*N*-solution of phosphoric acid. The mixture is boiled until colourless, cooled, treated with 1—2 g. of potassium iodide, and the liberated iodine titrated with standard thiosulphate solution. Decomposition of some of the excess of iodate is thus avoided, and addition of calcite to aid expulsion of iodine is rendered unnecessary. D. G. HEWER.

Determination of sulphur in steel. W. HERWIG.—See B., 1927, 413.

Determination of sulphate in presence of other sulphur compounds. A. KURTENACKER and R. WOLLAK (Z. anal. Chem., 1927, **71**, 37—42).—The solution is treated with 0·05 vol. of glycerol and stirred with freshly-precipitated zinc carbonate to remove sulphide. The filtrate is treated with sufficient formaldehyde to combine with any sulphite present and acidified with 10 c.c. of 20% acetic acid. Thiosulphate is then removed by addition of the requisite quantity of 0·1*N*-iodine and the sulphate precipitated by the addition of 0·1*N*-barium chloride drop by drop to the cold solution with vigorous stirring. The precipitate so obtained is coarsely crystalline and filters readily. Methods involving destruction of the lower sulphur acids by boiling with hydrochloric acid in an inert atmosphere invariably yield high results for sulphate. A. R. POWELL.

Determination of sulphuric acid by precipitation with benzidine. L. W. HAASE (Z. angew. Chem., 1927, **40**, 595—599).—Precipitation of sulphuric acid with benzidine followed by alkalimetric titration of the precipitate, using phenolphthalein as indicator, gives results which are within 1% of the theoretical when the concentration of the sulphuric acid exceeds 80 mg. per litre; for concentrations between 30 and 70 mg. per litre, the error is 5—10%, and for lower concentrations quite low and erratic results are obtained. Ferric salts in amounts exceeding 1 mg. per litre, magnesium salts in concentrations exceeding 50 mg. per litre, and calcium chloride exceeding 3·5% of the weight of solution cause low results to be obtained, but ferrous and manganous salts are without action. The solution before precipitation must react acid towards phenolphthalein. If only a small quantity of a ferric salt is present, it may be reduced to the ferrous state by boiling with 1% hydroxylamine hydrochloride solution before precipitation of the sulphuric acid. A. R. POWELL.

Analysis of concentrated and fuming sulphuric acid by thermometric titration. T. SOMIYA.—See B., 1927, 439.

Occlusion of barium chloride by barium sulphate. F. G. GERMUTH (Amer. J. Pharm., 1927, **99**, 271—274).—Certain conditions tend to increase the occlusive properties of barium sulphate towards barium chloride. By addition of a calculated amount of a 10% barium chloride solution to different concentrations of sodium sulphate under similar conditions as regards dilution etc., the amount of barium chloride occluded by the precipitate of barium sulphate was determined when precipitation was carried out in cold and boiling solutions, respectively. The results indicate that from the point of view of accuracy, precipitation from cold solution is preferable to that from hot solution, even for concentrations of sulphur lower than 25%. M. CARLTON.

Determination of thiocyanates in the presence of chlorides, sulphides, and cyanides. Z. CHARATZ.—See B., 1927, 408.

Colorimetric determination of nitrogen in foods. W. GOLUB.—See B., 1927, 397.

Significance of nitrogen determinations in sanitary analysis. S. L. NEAVE and A. M. BUSWELL.—See B., 1927, 382.

Test for nitrates applicable in presence of nitrites. A. H. WARE (Analyst, 1927, **52**, 332—334).—From 0·01 to 1 g. of the substance to be tested is roughly mixed with 0·2 g. of sodium nitrite and added to a cold solution of 0·05 g. of *o*-cresol in 10 c.c. of concentrated hydrochloric acid, and stirred. In about 1 min. a dichroic solution results, deep green to reflected, and crimson or purplish-red by transmitted light, in presence of nitrate. Much less than 0·001 g. of nitrate may be thus detected, but for minute quantities after elimination of interfering constituents, particularly of bromides or ethyl alcohol, the material may be mixed in a mortar with the *o*-cresol and nitrite, the acid added, the mixture triturated for 2 min., and kept for not more than 15 min. D. G. HEWER.

Detection and determination of nitrite and **nitrate.** J. EISENBRAND (Pharm. Ztg., 1927, **72**, 672—673).—The characteristic absorption bands of nitrite and nitrate ions in the ultra-violet serve for the detection of these ions in admixture with other common anions. Nitrates show a wide band between 260 and 320 mμ, with a maximum at 302 mμ, having an extinction coefficient ε of 6·93; the nitrite band between 300 and 380 mμ has a maximum at 366 mμ, ε = 19·1. For the detection of the weaker nitrate band in presence of nitrites, the latter are first decomposed by addition of carbamide. By the determination of the extinction coefficient for the region 360—370 mμ and the application of Beer's law, nitrite can be determined in presence of a very large excess of nitrate if the solution is first rendered slightly alkaline with sodium carbonate. For the determination of nitrate and nitrite together, the nitrite is determined as above and the sum of the two anions by measuring the extinction coefficient for the region 300—320 mμ, the magnitude of the absorption in this region being equal for both anions; nitrate is then found by difference. The results are within 1—2% of the theoretical. A. R. POWELL.

Determination of phosphorus in phosphorus alloys. B. SALKIN.—See B., 1927, 414.

Sources of error in the determination of phosphoric acid by the molybdate–magnesia method. II. J. M. MCCANDLESS and J. F. BURTON.—See B., 1927, 414.

Combustion by means of a copper oxide spiral. S. TSCHUMANOV (Z. anorg. Chem., 1927, **162**, 31).—Carbon monoxide in air is conveniently determined by oxidising to carbon dioxide by passing over an electrically-heated nickel wire coated with copper oxide by first copper-plating and then heating in air. R. CUTHILL.

Volumetric determination of carbon dioxide in carbonates. J. LINDNER and F. HERNLER.—See B., 1927, 408.

Determination of carbon dioxide in carbonates [in dyes]. T. CALLAN.—See B., 1927, 359.

Determination of silicon and silica in aluminium. PRETTNER.—See B., 1927, 414.

Determination of silica in ores, slags, fluxes, and refractory materials containing fluorine. A. STADELER.—See B., 1927, 414.

Determination of sodium, potassium, and chlorine in foods. A. D. HUSBAND and W. GODDEN.—See B., 1927, 397.

Colour reaction for magnesium, and colorimetric determination of traces of magnesium. I. M. KOLTHOFF (Chem. Weekblad, 1927, **24**, 254—255).—0·2 Mg. of magnesium per litre may be detected in alkaline solution by means of titan-yellow (azidine-yellow-5G) by the red coloration developed; this is also suitable for the determination, the blank being prepared with addition of a calcium salt if calcium is present in the sample. Both calcium and barium increase the intensity of the colour. Aluminium, tin, and zinc interfere. The method is very suitable for determination of magnesium in water, in salts of alkali metals etc. S. I. LEVY.

Volumetric determination of magnesium in magnesium chloride solutions. J. E. W. RHODES —See B., 1927, 364.

Separation and determination of metals by the use of 8-hydroxyquinoline. II. Separation and determination of magnesium. R. BERG (Z. anal. Chem., 1927, 71, 23—36; cf. this vol., 436).—Magnesium is precipitated quantitatively by the addition of a 2% alcoholic solution of 8-hydroxyquinoline to a feebly ammoniacal solution of a magnesium salt containing ammonium acetate or chloride. The precipitate is crystalline and contains $4H_2O$; after drying to constant weight at 100—105°, it contains $2H_2O$ and 6·98% Mg, and after heating at 130—140°, it becomes anhydrous and contains 7·78% Mg. It may also be ignited to obtain magnesium oxide for weighing after addition of 2—3 g. of anhydrous oxalic acid. For volumetric determination of magnesium, the precipitate is dissolved in hydrochloric acid and the 8-hydroxyquinoline liberated is titrated with standard bromide–bromate solution, using indigo-carmine as indicator, the colour change being from blue, through green, to a pure yellow. The method is available for the separation of magnesium from the alkaline earths, but a second precipitation is usually necessary; for this, the first precipitate is dissolved in hydrochloric acid, 1—2 g. of ammonium acetate are added, followed by ammonia until just alkaline, the solution is heated to boiling, and the precipitate collected immediately it becomes crystalline. For the separation of magnesium from the heavy metals other than copper, zinc, and cadmium, precipitation is effected from a solution containing 3 g. of sodium tartrate and 10—20 c.c. of 2*N*-sodium hydroxide solution. A. R. POWELL.

8-Hydroxyquinoline as an analytical reagent. Determination of magnesium, zinc, and aluminium; separation of aluminium or zinc from alkali metals, alkaline-earth metals, and magnesium, and of magnesium from alkali metals. F. L. HAHN and K. VIEWEG (Z. anal. Chem., 1927, **71**, 122—130; cf. Berg, this vol., 436, and preceding abstract).—Salts of certain bivalent and tervalent metals are able to react with 8-hydroxyquinoline, one metal atom replacing the phenolic hydrogen in two or three molecules, as the case may be, of the hydroxyquinoline, forming insoluble compounds, such as $(C_9H_6ON)_3Al$. The weakly acid or neutral solution of the salt, containing not more than 0·1 g. of the metal in 100 c.c., is warmed on the water-bath, and a 5% alcoholic solution of the reagent added, avoiding large excess, and then rather more ammonium acetate than corresponds with the acid liberated by the precipitation. The mixture is boiled, and filtered when cold, the precipitate being washed first with *N*-acetic acid, then with more and more dilute acid, and ultimately with water, finally being dried to constant weight, first at 100—120°, then at 140—160°. In the determination of magnesium, the solution should contain, instead of ammonium acetate, at least 3 g.-mols. of ammonia per g.-mol. of metal, and the precipitate is washed with ammonia. Small amounts of magnesium can thus be determined in presence of considerable amounts of alkali metals, although it may be necessary to dissolve the precipitate in acid and reprecipitate with ammonia. Zinc may be precipitated from a solution containing ammonia, or acetic acid, and ammonium acetate. If it is precipitated from acetic acid solution, magnesium can be precipitated from the filtrate by addition of the reagent and ammonia. R. CUTHILL.

Determination of zinc by means of membrane filters. W. AWE (Arch. Pharm., 1927, **265**, 147—149).—The method of Jander and Stuhlmann (A., 1921, ii, 711) has been applied to forensic specimens. The material is destroyed by hydrochloric acid and potassium chlorate, and excess of chlorine removed. The filtered solution is made alkaline, filtered, and the zinc precipitated as sulphide after addition of acetic acid. The precipitate is separated on a membrane filter and the zinc determined acidimetrically. The mean error is −0·16% and the time required 6 hrs. S. COFFEY.

Sodium sulphide. A detector for mercury vapour. B. W. NORDLANDER.—See B., 1927, 415.

Determination of mercury vapour. B. W. NORDLANDER.—See B., 1927, 415.

Determination of aluminium by cupferron. A. PINKUS and E. BELCHE (Bull. Soc. chim. Belg., 1927, **36**, 277—287).—Aluminium may be determined by precipitation with cupferron from neutral or very

slightly acid solutions. The precipitate is white, flocculent, easily filtered, and non-adsorbent. A procedure is also described for the separation by this method of aluminium from iron, copper, and magnesium. G. A. ELLIOTT.

Colorimetric determination of aluminium by Martin's method. M. L. DE BROUCKÈRE and E. BELCKE (Bull. Soc. chim. Belg., 1927, **36**, 288—291).—Cupferron produces no precipitate with aluminium in neutral or slightly acid solutions when the concentration is less than 10^{-4} g.-atom of the metal per litre, but a colloidal solution is obtained which appears yellow by transmitted and blue by reflected light (cf. Martin, Compt. rend. VI^{e} Cong. chim. ind., 1926). Details are given of the procedure necessary for the determination of traces of aluminium by the colorimetric comparison of such solutions. The method may also be employed in presence of coloured salts which are not precipitated by cupferron, the comparison being effected in this case by means of a nephelometer. G. A. ELLIOTT.

Electrometric titration of some aluminium solutions. F. O. ANDEREGG and G. W. DAUBENSPECK (Proc. Indiana Acad. Sci., 1925, **35**, 141—148).—Aluminium salts can be titrated electrometrically with sodium, potassium, barium, or calcium hydroxide, and titrated back with hydrochloric, nitric, sulphuric, or phosphoric acid. Ranges, rather than points, of precipitation and dissolution are to be considered. Calcium and barium ions retard the rate of re-dissolution of aluminium hydroxide formed by the addition of acid to aluminate solutions. In presence of sulphate, opalescence due to colloidal aluminium hydroxide may appear at p_H 2·0. Sulphate has little effect on the back titration curve. Inflexions were obtained from three aluminium phosphates at p_H 4·7 and 8·5. On back titration of an alkaline aluminium phosphate solution with hydrochloric acid, the buffer effect maintained a high p_H value at first, and only minor inflexions were observed for the three salts. CHEMICAL ABSTRACTS.

Determination of manganese in cobalt steels. A. HALLBAUER and P. KRÜGER.—See B., 1927, 447.

Determination of cobalt. G. SPACU and J. DICK (Z. anal. Chem., 1927, **71**, 97—101).—Cobalt is precipitated quantitatively as the compound $Co(CNS)_2,4C_5H_5N$ if to the boiling dilute solution of a cobalt salt containing 0·5 g. of ammonium thiocyanate for each 0·1 g. of cobalt there are added 1—3 c.c. of pyridine, and the mixture is allowed to cool at once. The precipitate is transferred to a Gooch crucible by means of a solution of 7 c.c. of pyridine and 5 g. of ammonium thiocyanate in 1000 c.c. of water. It is there washed six times with a solution prepared by mixing 130 c.c. of 95% alcohol, 855 c.c. of water, 15 c.c. of pyridine, and 1 g. of ammonium thiocyanate, then twice with absolute alcohol containing pyridine, and finally with ether containing pyridine. The precipitate is then dried in a vacuum at the ordinary temperature and weighed. The method is applicable to solutions containing alkali metals, magnesium, alkaline-earth metals, and mercury, but not to solutions containing copper, cadmium, nickel, manganese, or zinc. Strongly acid solutions should be evaporated and taken up with water before precipitation. Concentrated solutions of ammonium salts dissolve the precipitate. The accuracy attainable is equal to that of the electrolytic method. R. CUTHILL.

Determination of cobalt by the nitroso-β-naphthol method. J. E. CLENNELL (Min. Mag., 1927, **36**, 270—273).—In the precipitation of cobalt by means of nitroso-β-naphthol, the amount of precipitant used should be about twenty times the weight of the cobalt. Nickel, zinc, and ammonium salts, with the exception of nitrates, do not interfere, and iron is preferably removed by double precipitation of ferric hydroxide by zinc oxide emulsion. A. R. POWELL.

Test for molybdenum. P. FALCIOLA (Annali Chim. Appl., 1927, **17**, 261—262).—When a solution of molybdic acid containing hydrochloric acid is shaken with ethyl acetate and a considerable amount of about 25% sodium thiosulphate solution, the liquid is rendered coloured and turbid owing to separation of sulphur, whilst the ester separates on keeping with a colour varying from lilac to brownish-red or, sometimes, with that of molybdenum-blue. The reaction is detectable with a solution containing 1 part of molybdenum per 1,000,000 parts, but is somewhat less sensitive with alkali molybdates and phosphomolybdates. The colour of the ester is destroyed by alkali hydroxide and also by oxidising agents, although if the latter are pre-existent in the solution, their action is annulled by the thiosulphate. In moderate concentrations, tartaric, oxalic, citric, and tannic acids, ammonium salts, chromates, chlorates, and various cations which disturb other tests for molybdenum are without effect. T. H. POPE.

Identification of hydroxides in hydrogels. G. F. HÜTTIG and H. DÖBLING (Ber., 1927, **60**, [*B*], 1029—1031; cf. A., 1926, 798).—A reply to Kraut (this vol., 17), in which it is maintained that definite evidence of the presence of hydroxides in stannic oxide gels has not been adduced. H. WREN.

Stability of titanous sulphate solutions in air. H. WILKINSON and A. G. TYLER.—See B., 1927, 364.

Iodometric determination of vanadium. J. B. RAMSEY (J. Amer. Chem. Soc., 1927, **49**, 1138—1146).—A critical investigation of Stoppel, Sidener, and Brinton's method of determining vanadium iodometrically (A., 1925, ii, 73) shows that over a wide range of acid and iodide concentrations the method gives accurate results only when oxygen is excluded; when this gas is not excluded, more iodine is formed than is equivalent to the vanadium present. The method is improved so that accurate determinations may be carried out within 15 min. in a current of carbon dioxide. S. K. TWEEDY.

Separation of antimony from the alkali metals by distillation, and determination of very small quantities of antimony. G. JANDER and W. BRÜLL (Annalen, 1927, **453**, 332—337).—Antimony can be separated from the alkali metals, *e.g.*, in antimonates, by heating in a current of hydrogen

chloride. The residual alkali chloride is weighed, and the antimony chloride which distils over is collected and titrated. Before this treatment, substances containing large amounts of water should be partly dehydrated, whilst dry substances should be moistened with a little concentrated hydrochloric acid. Very small amounts of antimony can be determined accurately by the bromate method, provided certain precautions are observed. The solution for titration should be at 80°, and should contain 1—6% of hydrogen chloride. Reduction of small amounts of quinquevalent antimony to the tervalent state is best effected by heating at 100° for 2—3 hrs. with five times the theoretical amount of a 3% solution of potassium pyrosulphite. The excess of the reducing agent is destroyed by heating the solution and passing carbon dioxide through until all the sulphur dioxide is removed. R. CUTHILL.

Glow test for metals of the platinum group. C. W. DAVIS (J. Franklin Inst., 1927, **203**, 679—699).—Curtman and Rothberg's glow test for metals of the platinum group (A., 1911, ii, 661) may be applied safely only in the absence of copper, cobalt, nickel, and silver. Details are given of a procedure such that copper, cobalt, nickel, and silver will not give the glow reaction, the metals of the platinum group will give the test, and the detrimental effects of foreign salts are largely eliminated. The theory of contact catalysis and the factors which influence the glow reaction are discussed.

W. E. DOWNEY.

Detection and determination of the platinum metals. W. SINGLETON (Ind. Chem., 1927, **3**, 121—124).—The following tests are preferred: Platinum: addition of ammoniacal resorcinol solution, reduction with stannous chloride, microscopical test with hexamethylenetetramine or potassium chloride, addition of sodium thiocyanate and ammonium nitrate. Palladium: reactions with nitrosonaphthol, potassium or hydrogen iodide, mercuric cyanide, hexamethylenetetramine, formation of the compound $PdFe(CN)_5NO$. Rhodium: reduction by stannous chloride (the development of the red coloration is retarded by the presence of much rhodium). Osmium: reactions with potassium thiocyanate and ether or amyl alcohol, thiocarbamide, thiocarbanilide, or thiocarbonate and hydrochloric acid. Ruthenium: reaction with thiocarbamide or thiocarbanilide in hydrochloric acid. Iridium: reaction with sodium thiocyanate and ammonium nitrate solutions, reddish-brown crystals with hexamethylenetetramine.

CHEMICAL ABSTRACTS.

Portable laboratory bench units. A. D. LITTLE (Ind. Eng. Chem., 1927, **19**, 630).—Portable bench units of small-scale commercial apparatus, each carrying a set of related equipment, may be wheeled to the laboratory bench for intermittent use.

W. J. POWELL.

Mercury vapour trap. G. I. FINCH (Nature, 1927, **119**, 856).—A liquid alloy of sodium and potassium (1 : 2) is employed. The surface of the alloy is swept clean by means of a coil of iron wire controlled by an external electro-magnet.

A. A. ELDRIDGE.

M.-p. apparatus. M. SPETER (Chem. Weekblad, 1927, **24**, 269).—A modified form of the apparatus previously described (A., 1926, 378). S. I. LEVY.

Recording hydrostatic balance. F. G. TRYHORN and W. F. WYATT (Trans. Faraday Soc., 1927, **23**, 238—242).—Changes in weight occurring at one end of the beam of an ordinary balance are compensated by the resulting raising or lowering of a cylinder of metal or glass attached to the other end of the beam and partly immersed in a non-volatile liquid at constant temperature; the deflexions are automatically recorded on a photographic plate. The application of the balance to the measurement of adsorptive power, velocity of adsorption, and diffusion coefficients is discussed.

G. A. ELLIOTT.

Apparatus for maintaining a constant pressure in gas-collecting vessels and measuring burettes. G. AGDE, H. SCHMITT, and L. VON LYNCKER (Chem.-Ztg., 1927, **51**, 393—394).—The lower end of the measuring burette is provided with a side tube connected by means of rubber tubing with the side tube of a pear-shaped bulb blown on to the lower end of a long, narrow glass tube; the lower end of the bulb is itself connected with rubber tubing to a large bulb receiver, which acts as a reservoir of liquid for adjusting the height in the long tube so as to produce the desired pressure in the collecting burette. A modification of the apparatus for collecting larger volumes of gas in a large bottle and measuring the volume of liquid displaced is also described and illustrated.

A. R. POWELL.

Production of half-silvered mirrors. H. L. SMITH (J. Sci. Instr., 1927, **4**, 262—264).—The solution consists of 25 c.c. of 4% silver nitrate solution, to which ammonia solution is added until the precipitate redissolves, followed by a few drops of silver nitrate solution and then water to 50 c.c. The reducing agent is 0·5—1·0 c.c. of a mixture of equal volumes of 10% chloral hydrate solution and 40% formaldehyde, or a solution prepared by boiling 5 g. of sucrose and 0·6 g. of tartaric acid in 50 c.c. of water, cooling, and, after adding 10 c.c. of alcohol, diluting to 100 c.c. 2—3 C.c. of this solution mixed with 2 c.c. of 10% chloral hydrate solution are used with 50 c.c. of the ammoniacal silver solution. A satisfactory commercial method is described. H. J. DOWDEN.

Effectiveness of laboratory rectifying columns. M. J. MARSHALL and B. P. SUTHERLAND (Ind. Eng. Chem., 1927, **19**, 735—738).—The effectiveness of the lagged Hempel column with reflux and the same column unlagged and without reflux is investigated by rectification experiments with aqueous alcohol. The former column is from 2·4 to 41·5 times as efficient as the latter for the same rate of distillation. The efficiency increases with low alcohol concentrations and high rates of distillation. S. K. TWEEDY.

All-glass distillation column without constriction. H. J. LUCAS (Ind. Eng. Chem., 1927, **19**, 680).—The glass packing rests on a perforated glass nipple which is supported by three or four indentations in the wall of the column (cf. Peters and Baker, B., 1926, 175). S. K. TWEEDY.

Ebullioscope. W. SWIENTOSLAWSKI (Rocz. Chem., 1927, **7**, 30—33, and Bull. Soc. chim., 1927, [iv], **41**, 717—720).—Four types of ebullioscope are described, one being for the use of students and the others for various purposes. R. TRUSZKOWSKI.

Kipp's apparatus for the preparation of gases absolutely free from air. H. HILLER (Z. angew. Chem., 1927, **40**, 620—621).—The apparatus consists of the usual three bulbs with gas outlet from the middle one, but is fitted with a thistle funnel at the top and a 3-way tap on the outlet, one arm of which communicates with the top bulb and also with a mercury seal. The air in the apparatus is swept out with boiled water, and acid is added by the thistle funnel until it fills the bottom bulb. The liquor run-off tap is then closed. The acid and water are caused to mix by opening the 3-way tap with the finger on the gas-outlet tube, the excess of dilute acid is drawn off at the bottom, and the apparatus is ready for use. C. IRWIN.

Apparatus for measuring the adsorption of a gas at constant pressure. G. AGDE and H. SCHMITT (Z. angew. Chem., 1927, **40**, 600).—For measuring the adsorptive power of a substance, such as wood charcoal, for a gas under constant pressure preferably slightly above atmospheric, *e.g.*, 780 mm., the adsorption tube is connected by means of a 3-way tap with a vacuum pump and with the measuring burette containing the gas over mercury. The latter is connected with a movable counterbalanced reservoir and with a manometer tube, the mercury column in which is adjusted to give the desired pressure. During the adsorption, the reservoir is raised slowly so as to keep the pressure difference between the measuring burette and manometer tube constant. A. R. POWELL.

Laboratory steam superheater and evaporating bath with superheated steam. R. KATTWINKEL (Z. anal. Chem., 1927, **71**, 46—48).—The superheater comprises a metal cylinder containing two perforated discs carrying a series of metal tubes through which is passed saturated steam while heat is supplied by means of a flat Bunsen burner projecting through an opening in the side of the cylinder. The same principle is adapted to an evaporating bath in which steam from a small sheet-metal boiler is passed upwards through a bundle of metal tubes surrounded by a gas ring into a sheet-metal evaporating bath built on the same lines as the ordinary water-bath. Means are provided for allowing the condensed water to flow back into the boiler. A temperature of 200° is readily obtained in the bath. A. R. POWELL.

Rotating filter stand. L. BREMER (Z. anal. Chem., 1927, **71**, 49—50).—The apparatus consists of two metal or wood discs provided with collars and thumbscrews for attaching them to a loose collar fitted on the upright rod of the stand. The upper disc contains a number of holes for the funnels and the lower is sufficiently large to hold the beaker for the filtrate and the vessel containing the solution to be filtered. The whole rotates easily about the central rod so that six to eight filtrations may be carried out without the operator moving from his place. A. R. POWELL.

Primary cell. D. R. BARBER (Nature, 1927, **119**, 892).—A cell composed of zinc in a saturated solution of ammonium sulphate and carbon in an acidified, saturated solution of potassium permanganate, has an *E.M.F.* of 2·16 volts, with an internal resistance of 0·5 ohm for currents of 0·2—0·6 amp. There is practically no polarisation, and the amount of zinc dissolved is inappreciable. A. A. ELDRIDGE.

Silver accumulator. F. JIRSA and K. SCHNEIDER.—See B., 1927, 449.

Acid-resistance of asbestos. A. CALMON.—See B., 1927, 439.

Mineralogical Chemistry.

Chemical formulæ of mineral compounds. L. W. TIBYRIÇA (Nature, 1927, **119**, 815).—The only exceptions to the rule that the chemical formulæ of all true mineral species composed of any of the first 21 elements should conform to the equation $M=2a+8n$, where M is the molecular number (sum of the atomic numbers), a the number of atoms, excluding hydrogen, and n any integer, are the organic minerals, whewellite, oxammite, mellite, and fichtelite. A. A. ELDRIDGE.

[Chemical formulæ of mineral compounds.] J. W. E. (Nature, 1927, **119**, 815—816).—A theoretical interpretation of Tibyriça's observation (preceding abstract). A. A. ELDRIDGE.

Iodine content of some rocks and its relation to the chemical part of the goitre problem. E. WILKE-DORFURT (Annalen, 1927, **453**, 298—315; cf. von Fellenberg, A., 1925, ii, 321).—Many natural phosphorites contain much larger quantities of iodine than do most other minerals, this probably originating in organic remains. As would therefore be expected, the bituminous shales of the Lias also contain relatively large amounts of iodine. Certain types of Jurassic limestones contain even more iodine, apparently because it has remained in the form of insoluble organic compounds, such as occur in the shells of crustacea. In other cases, the iodine which has passed into solution when the softer portions of the bodies of marine animals and plants have decayed has been adsorbed by iron-containing strata in course of being laid down, and such rocks are relatively rich in iodine. The relation between the incidence of goitre in a particular district and the geology of the district may therefore be rendered complex by local use of phosphorites as manures, and by the passage of iodine into the air when coal is burned. R. CUTHILL.

Composition of the Lanzenkirchen meteorite. E. DITTLER (Mitt. Wien. Min. Ges., 1926, **88**, 26—30, in Tsch. Min. Petr. Mitt., 1927, **37**).—Two meteoric stones weighing 5 and 2 kg. fell on August 28, 1925,

near Lanzenkirchen in Lower Austria. They consist of darker (*d* 3·52) and lighter (*d* 3·45) portions, and detailed analyses are given of the magnetic, non-magnetic, and soluble (in hydrochloric acid) separations of each portion. The darker portion contains metal 9·33 (with Fe : Ni=7·6), troilite 5·72, chromite 1·21%; and its olivine has the composition $2{\cdot}4Mg_2SiO_4,Fe_2SiO_4$. The lighter portion contains metal 9·31 (Fe : Ni=6·5), troilite 4·72, chromite 0·06%; olivine $3{\cdot}4Mg_2SiO_4,Fe_2SiO_4$. Both portions belong to the Baroti type of the chondrites. The stone contains much olivine with bronzite and clinoenstatite, but no felspar, together with some merrillite and glass, and only traces of apatite. L. J. SPENCER.

Stony meteorite from Forksville, Mecklenberg County, Virginia. G. P. MERRILL (Proc. U.S. Nat. Mus., 1927, No. 2670, 1—4).—The meteorites contained metal 6·46, soluble silicates 52·71, insoluble silicates 40·83, total 100·00%. The metal consisted of Fe 87·61, Ni 12·13, Co 0·64, Cu 0·07, total 100·45%. The soluble silicate contained SiO_2 29·10, Al_2O_3 0·43, FeO 34·04, CaO 0·44, MgO 32·97, NiO 0·30, P_2O_5 0·43, S 2·16, total 99·87%. The insoluble silicate contained SiO_2 55·89, Al_2O_3 6·78, FeO 10·79, CaO 2·70, MgO 21·72, Cr_2O_3 0·22, Na_2O 1·21, K_2O 0·64, total 99·95%. The meteorite as a whole contained SiO_2 38·16, Al_2O_3 3·00, FeO 22·35, CaO 1·35, MgO 26·25, NiO 0·16, Cr_2O_3 0·09, MnO trace, Na_2O 0·49, K_2O 0·26, P_2O_5 0·23, Fe 5·66, Ni 0·78, Co 0·041, Cu 0·005, S 1·14, total 99·966%.

CHEMICAL ABSTRACTS.

Occurrence and origin of kaolin in the Lower Austrian Forests. L. KÖLBL (Tsch. Min. Petr. Mitt., 1927, **37** [for 1926], 173—200).—Deposits of kaolin have long been worked in the crystalline schists. They occur along crevices, and it is concluded that they have been formed *in situ* by weathering beneath a covering of peat (bands of lignite occur in the associated beds of Tertiary age). Analyses are given of the fresh rock (granulite) and of the portions soluble in concentrated hydrochloric acid and in sulphuric acid of the weathered rock, of the completely weathered sandy *débris*, and of the clay nodules. In the fresh rock, $SiO_2 : Al_2O_3$: bases=8·15 : 1 : 1·12, and in the hydrochloric extracts of the weathered products, $SiO_2 : Al_2O_3$: bases approximates to 2 : 1 : 0, suggesting kaolin. L. J. SPENCER.

Organic Chemistry.

Action of nitric acid on acetylene and ethylene. P. V. MCKIE (J.C.S., 1927, 962—965).—The action of nitric acid on ethylene is similar to its action on acetylene (Orton and McKie, *ibid.*, 1920, **117**, 283) and occurs in accordance with the scheme $CH_2{\cdot}CH_2 \longrightarrow CH_2(OH){\cdot}CH_2{\cdot}NO_2 \longrightarrow CH_2(NO_2){\cdot}CHO \longrightarrow CH_2(NO_2){\cdot}CO_2H \longrightarrow CH_3{\cdot}NO_2 \longrightarrow CH(NO_2){:}NOH \longrightarrow CH_2(NO_2)_2 \longrightarrow C(NO_2)_2{:}NOH \longrightarrow CH(NO_2)_3$, the intermediate β-nitroethyl alcohol being isolated. The yield of nitroform varies with the concentration of the nitric acid. Side reactions (chiefly oxidation to oxalic acid) account for 30—40% of the ethylene absorbed, but these are partly prevented by the addition of 0·66% of mercuric nitrate, which increases the speed of reaction and the ultimate yield of nitroform. J. W. BAKER.

Configurational relationships of butan-γ-ols and pentan-δ-ols. P. A. LEVENE, H. L. HALLER, and A. WALTI (J. Biol. Chem., 1927, **72**, 591—595).—*d-γ-Valerolactone*, b. p. 86—90°/14 mm., $[\alpha]_D^{20}$ +13·5°, gave, on reduction, *l-pentane-αδ-diol*, b. p. 95 96°/1·5 mm., $[\alpha]_D$ −4·90° (*diphenylcarbamate*, m. p. 131—133°, $[\alpha]_D^{20}$ −0·71° in alcohol). This was converted into *α-iodopentan-δ-ol*, which, on reduction, gave *l-pentan-δ-ol* (*α-naphthylcarbamate*, m. p. 71—73°, $[\alpha]_D^{20}$ −2·8° in alcohol). *l*-Pentan-δ-ol is therefore configurationally related to *l-γ*-hydroxyvaleric acid and hence to *l*-lactic acid. Since *d*-lactic acid is known to be related to *d*-butan-δ-ol, it follows that the latter is also related to *d*-pentan-δ-ol. *d*-Pentan-δ-ol, $[\alpha]_D$ +7·65°, gave an *α-naphthylcarbamate*, m. p. 88—91°, $[\alpha]^{20}$ +13·3° in alcohol.

C. R. HARINGTON.

Acetylenic erythritol [Δ$^{\gamma}$-hexinene-αβεζ-tetrol], HO·CH$_2$·CH(OH)·C:C·CH(OH)·CH$_2$·OH. R. LESPIEAU (Compt. rend., 1927, **184**, 1329—1332; cf. A., 1922, i, 103).—Hexinene-αβεζ-tetrol, m. p. 113—114°, on treatment with bromine gives a mixture of the isomeric dibromides from which only one *isomeride*, m. p. 184—185°, has been isolated. Ethylene dioxide, on treatment with excess of methyl alcohol in presence of sulphuric acid (cf. Blanchard, A., 1926, 1123), affords the *αζ-dimethyl ether* of *Δ$^{\gamma}$-hexinene-αβεζ-tetrol*, OMe·CH$_2$·CH(OH)·C:C·CH(OH)·CH$_2$·OMe, b. p. 143—143·5°/3 mm., *d*^{23} 1·122, n_D 1·477, which absorbs two atoms of bromine, giving a crystalline *dibromide*, m. p. 150—151°, and a liquid which probably contains isomeric dibromides. From the dimethyl ether of αζ-dichloro-Δ$^{\gamma}$-hexinene-βε-diol, two isomeric dibromides can be prepared. By removal of bromine, the dibromides furnish the two *isomerides* [(*a*) b. p. 136—137°/11 mm., m. p. 12—14°, *d*^{21} 1·110, n_D 1·4705, *dibromide*, m. p. 107°; (*b*) b. p. 138—139°/13 mm., m. p. 20—21°, *d*$^{-1}$ 1·112, n_D 1·4710, *dibromide*, m. p. 71—72°] of the dimethyl ether. E. H. SHARPLES.

Formation of geometrical isomerides by the reduction of acetylenic glycols. J. SALKIND (Ber., 1927, **60**, [*B*], 1125—1130; cf. A., 1923, i, 176).—The conception of rate of reaction introduced by Ott and Schroeter (this vol., 441) and connected with the activity of the catalyst has no bearing on the author's experiments with βε-dihydroxy-βε-dimethyl-Δ$^{\gamma}$-hexinene, since in all parallel experiments the same catalyst was employed and the "activity" factor may therefore be regarded as eliminated. The course of the reduction of acetylenic γ-glycols is influenced in a remarkable degree by the activity of different catalysts. αδ-Dihydroxy-ααδδ-tetraphenylbutinene is hydrogenated somewhat slowly, and the two stages are not very well marked. The initial products are the

isomeric *αδ-dihydroxy-ααδδ-tetraphenylbutenes*, α-form, m. p. 97·5° (also +EtOH, m. p. 76°, and +acetone, m. p. 71°), β-variety, m. p. 195—196°. The *cis*-configuration is assigned to the α-form, since, when heated with a little iodine at 200° or treated with boiling acetic anhydride, it yields 2 : 2 : 5 : 5-tetraphenyldihydrofuran (cf. Purdie and Arup, J.C.S., 1910, **97**, 1537), which could not be obtained from the β-variety. The latter compound passes at 210—220° into an unidentified substance, m. p. 199—201°, whereas it is transformed by boiling alcohol in presence of a little iodine into *αδ-diethoxy-ααδδ-tetraphenylbutene*, m. p. 121°. The ethylenic glycols do not react with bromine or alkaline permanganate. They are oxidised to benzophenone and a little benzilic acid.

Increase in the rate of reduction of the acetylenic glycol favours the formation of the α-form at the expense of the β-variety. H. WREN.

Walden inversion. IX. Mechanism of hydrolysis of optically active propylene oxides. P. A. LEVENE and A. WALTI (J. Biol. Chem., 1927, **73**, 263—274).—Hydrolysis of *d*-propylene oxide with acids leads to *d*-propane-αβ-diol; hydrolysis with alkalis to *l*-propane-αβ-diol. Since *l*-α-chloro-β-hydroxypropane is configurationally related both to *d*-propylene oxide and to *l*-propane-αβ-diol, the last two substances are related to one another, and it follows that the alkaline hydrolysis of propylene oxide proceeds normally, whilst the acid hydrolysis is accompanied by inversion. The results are discussed in relation to existing theories of Walden inversion occurring during hydrolysis. In experiments of this type, it is necessary to isolate the glycol formed, since the formation of condensation products, particularly during alkaline hydrolysis, may give fictitious values for the optical rotation of the crude reaction product.

C. R. HARINGTON.

Ethyl αβ-dichloro-β-bromovinyl ether. I. A. SMITH (J.C.S., 1927, 1099—1102).—Addition of bromine to ethyl αβ-dichlorovinyl ether (Crompton and Vanderstichele, *ibid.*, 1920, **117**, 691) followed by immediate treatment of the additive product with alcoholic potassium hydroxide solution yields *ethyl αβ-dichloro-β-bromovinyl ether*, b. p. 177°/754 mm., d_4^{20} 1·6565, n_D° 1·50427, which reacts with alcohols and phenols to yield the corresponding chlorobromoacetate, with sulphuric acid to yield ethyl chlorobromoacetate, and with acetic and benzoic acids to yield, in addition, the acid chloride. With bromine, it yields *αβ-dichloro-αββ-tribromodiethyl ether*, m. p. 28—29°, 2·2297, n_D^{34} 1·56833, which on heating in absence of moisture is converted into chlorodibromoacetyl chloride (*anilide*, m. p. 102—103°). Addition of chlorine probably takes place in a similar manner, but the ether could not be isolated. Ethyl αβ-dichlorovinyl ether has d_4^{20} 1·2037, 1·45584, and ethyl αβ$_p$-trichlorovinyl ether has d_4^{20} 1·3409, n_D^{16} 1·47551.

J. W. BAKER.

Crystalline form of sodium β-glycerophosphate. G. GILTA (Bull. Acad. roy. Belg., 1926, [v], **12**, 921—928).—*Sodium β-glycerophosphate tetrahydrate*, prepared by evaporation of an aqueous solution above 20° or by precipitation from aqueous solution by alcohol, forms monoclinic crystals, $a : b : c = 1·809008 : 1 : 0·997196$, whereas the *pentahydrate*, obtained by evaporation of the aqueous solution below 20°, gives monoclinic crystals, $a : b : c = 0·665590 : 1 : 0·516184$. C. W. GIBBY.

Methylation of hexosediphosphoric acid. H. H. SCHLUBACH and W. RAUCHENBERGER (Ber., 1927, **60**, [*B*], 1178—1179).—Silver hexosediphosphate, prepared from candiolin, is converted by methyl iodide into *tetramethyl hexosediphosphate*, n_D^{20} 1·4648, $[\alpha]_D^{18}$ +20·22° in methyl alcohol, which, when treated with silver oxide and methyl iodide, affords *tetramethyl trimethylhexosediphosphate*, b. p. 130—140°/0·01 mm., n_D^{20} 1·4457, $[\alpha]_D$ +20·77° in chloroform.

H. WREN.

Perchloromethyl mercaptan. A. GUTMANN (Z. anal. Chem., 1927, **71**, 43—45).—With alkaline sodium arsenite solutions, perchloromethyl mercaptan yields sodium carbonate, chloride, sulphide, and arsenate, whereas with boiling water hydrogen chloride, carbon dioxide, and sulphur are produced. In each case, a thioperoxide is probably an intermediate product. Thus the compound behaves more like a derivative of thiolcarbonic acid than of methyl mercaptan, and should more correctly be named trichlorothiolcarbonyl perchloride and formulated (I) $CCl_3{\cdot}S{:}Cl$ or (II) $CCl_3{\cdot}S{\cdot}Cl$. Formula (I) expresses its behaviour in alkaline solution and (II) its behaviour in neutral or acid solution. A. R. POWELL.

Interaction of alkali sulphites with some halogeno-compounds, and the optical resolution of α-phenylpropanesulphonic acid. E. B. EVANS, E. B. MABBOTT, and E. E. TURNER (J.C.S., 1927, 1159—1168).—The action of sodium sulphite either in the cold or in boiling saturated aqueous solution on various asymmetric and other halogeno-compounds has been studied. Contrary to the observations of Cohen and Clutterbuck (*ibid.*, 1923, **123**, 2507), β-phenylethyl chloride (or bromide) reacts with sodium or potassium sulphite to yield the *sodium* salt of *β-phenylethanesulphonic acid*, m. p. 91° (*potassium* and *barium* salts; *sulphonyl chloride*, m. p. 34°; *amide*, m. p. 119°; *anilide*, m. p. 77°). α-Phenylethyl chloride or bromide reacts similarly to yield *sodium α-phenylethanesulphonate* (*barium* and *potassium* salts; *sulphonyl chloride*, m. p. 79°). The acid was resolved by means of its *strychnine* salt, *strychnine* l-*α-phenylethanesulphonate*, $[\alpha]^{18}$ −20·5°, being the less soluble (*potassium* salt, $[\alpha]_D^{18}$ −11·8°). *Brucine* and *cinchonidine* dl-*α-phenylethanesulphonates* could not be resolved. Chlorination of pure ethylbenzene in diffused daylight yields a mixture of α- and β-phenylethyl chlorides (together with some higher chlorinated products), increased illumination increasing the proportion of the α-compound. Dimethylaniline does not react with β-phenylethyl chloride, but with the α-compound it yields *phenyldimethyl-α-phenylethylammonium chloride*, m. p. 95°. α-Phenylpropyl bromide, shaken with sodium sulphite solution in the cold, yields propenylbenzene and the *sodium* salt of *α-phenylpropanesulphonic acid* (*sulphonyl chloride*, b. p. 175°/20 mm.; *amide*; *anilide*), which, when heated with 0·5 equivalent of strychnine, yields *strychnine* d-*α-phenylpropanesulphonate*, $[\alpha]^{20}$ −23·7° (*sodium* salt, $[\alpha]_D^{25}$ +5·2°±0·1°), whilst the mother-liquor

treated with cinchonine yields *cinchonine* l-α-*phenylpropanesulphonate*, $[\alpha]^{25}$ +104·9° (*sodium* salt, $[\alpha]^{25}$ −5·2°±0·2°). *α-Phenylbutyl bromide*, b. p. 116°/28 mm., 126°/47 mm., *d* about 1·24, reacts with sodium sulphite at the ordinary temperature to yield mainly α-phenyl-Δ^{α}-butene and 10% of *sodium α-phenylbutanesulphonate*. The action of sulphur dioxide on magnesium α-phenylbutyl bromide yields only *di-α-phenylbutyl sulphide*, m. p. 96°. From α-bromobutane is obtained the *sodium* salt of *α-methylpropanesulphonic acid* (*cinchonine* salt), from which *strychnine* d-*α-methylpropanesulphonate*, $[\alpha]^{20}$ −29·3°, is obtained. The magnesium compound of 2 : 4-dichloroiodobenzene reacts with acetaldehyde to yield 2 : 4-*dichlorophenylmethylcarbinol*, b. p. 145°/20 mm., 154—155°/29 mm. (*bromide*, b. p. 154°/37 mm., which, on treatment with sodium sulphite, yields only the original carbinol). αβ-Diphenyl-αβ-dimethylethane-αβ-diol is readily obtained by the reduction of acetophenone in moist ether with powdered sodium under toluene. 3 : 5-Dichlorobromobenzene has m. p. 74° constant (Hartley, J.C.S., 1901, **82**, 1293, gives 77·5°; Hantzsch, A., 1898, i, 19, gives 82—84°).

J. W. Baker.

Compound containing a positive chlorine atom: trichloromethanesulphonyl chloride. J. F. Durand and R. Naves (Bull. Soc. chim., 1927, [iv], **41**, 632—633).—The authors suggest that the presence of three chlorine atoms in the molecule of trichloromethanesulphonyl chloride induces positive properties in the sulphonyl chlorine atom. The reactions observed by Battegay and Kern (this vol., 228) are interpreted thus: $\overset{-+}{CCl_3}\cdot\overset{-}{SO_2}\overset{+-}{Cl}$ $CCl_3\cdot SO_2H+Cl\cdot OH$; the hypochlorous acid then reacts with trichloromethanesulphinic acid in its tautomeric form $\overset{+-+-}{HOCl}$, affording chloroform, sulphuric and hydrochloric acids. Similarly with alcohol, ethyl hypochlorite, in which the chlorine is positive (A., 1925, i, 1231), is a first product, and this decomposes into acetaldehyde and hydrochloric acid.

R. Brightman.

Purification of acetic acid. Determination of acetic anhydride in acetic acid. K. J. P. Orton and A. E. Bradfield (J.C.S., 1927, 983—985).—Pure acetic acid, m. p. 16·2—16·4°, is obtained by the addition of the calculated quantity of acetic anhydride (equivalent to the water present) to a commercial sample, prior to distillation with 2% of chromic anhydride (cf. Orton and Bradfield, A., 1924, i, 607). The resulting sample (85—90% of the whole) contains less than 0·005% of acetic anhydride. A modification of the method of Orton and Edwards (J.C.S., 1911, **99**, 1181) for the determination of acetic anhydride in acetic acid consists in the determination of the unacetylated excess of 2 : 4-dichloroaniline by titration with a bromate–bromide solution, the method yielding accurate results.

J. W. Baker.

Preparation of pure oleic acid. H. W. Scheffers (Rec. trav. chim., 1927, **46**, 293—295).—Commercial oleic acid purified by Twitchell's method (B., 1921, 817) may have a good iodine value, but yet contain highly unsaturated and saturated acids. If treated with alcohol and neutralised by a lithium hydroxide solution such that the final alcohol concentration is 50% (cf. Moore, J.S.C.I., 1919, **38**, 220T), the lithium oleate which crystallises may be recrystallised and decomposed by hydrochloric acid. The resulting oleic acid solidifies to transparent crystals, m. p. 12°, which when preserved change to an opaque form, m. p. 15·4°, and to a liquid, which again crystallises in the form of low m. p.; oleic acid is thus dimorphous (cf. Kirschner, A., 1912, i, 533). Pure oleic acid has n^{15} 1·46140, n_D^{40} 1·45298, n_D^{65} 1·44399.

E. W. Wignall.

Polymorphism of higher fatty acids. J. Thibaud (Nature, 1927, **119**, 852—853).—For acids above C_{16}, the long spacing measured for a film of acid deposited from a solution ("*B*-modification") is greater than that obtained from a melted acid ("*C*-modification"). For stearic acid, two coexistent crystalline modifications have been obtained. The formula $C_{24}H_{48}O_2$ is ascribed to arachidic acid. The distribution of matter in a chain of the *B*-form of stearic acid is similar to that in the *C*-form, except for a small discrepancy in the situation of the terminal carboxyl groups. A study of the small spacings shows that for every saturated acid the arrangement of the carbon atoms in the chain is the same (Muller, this vol., 503).

A. A. Eldridge.

Preparation of carbonyl chloride from chloropicrin. Colour reaction for chloropicrin. S. Secareano (Bull. Soc. chim., 1927, [iv], **41**, 630—631).—Chloropicrin is rapidly decomposed when heated at 100° with sulphuric acid containing 20% of anhydride, affording carbonyl chloride (yield 73%) and nitrosyl chloride (cf. Erdmann, A., 1893, i, 681). The residue in the flask probably contains pyrosulphuryl chloride. Sulphuric acid containing a little diphenylamine on warming at 130° with chloropicrin gives an intense blue coloration, which can be applied to the colorimetric determination of chloropicrin.

R. Brightman.

[Non-]separation of optical antipodes of chlorobromopyruvic acid. M. Gabino and (Signa.) G. Bornate (Gazzetta, 1927, **57**, 330—332).—Chlorobromopyruvic acid forms a *quinine* salt, decomp. 135—250°, $[\alpha]^{18}$ in alcohol −115°; resinous *cinchonine* salt; *brucine* salt, decomp. 108—195°, $[\alpha]_D^{15}$ in alcohol −37·5°; *strychnine* salt, decomp. 150—185°, $[\alpha]_D^{15}$ in water −28·0°. From the aqueous solution of the last, crystals were obtained which on redissolving gave $[\alpha]_D^{15}$ −64·3°; the solution, however, quickly racemised.

E. W. Wignall.

Constitution of the chlorides of α-acetoxy-acids. E. E. Blaise and Herzog (Compt. rend., 1927, **184**, 1332—1333).—*α-Acetoxyisobutyryl chloride*, b. p. 70°/17 mm. (*anilide*, m. p. 100°), prepared by the action of thionyl chloride on α-acetoxy*iso*butyric acid, on treatment with benzene in presence of aluminium chloride gives a mixture of *phenyl α-acetoxyisopropyl ketone*, b. p. 135—137°/14 mm. (*semicarbazone*, m. p. 186—188°; p-*nitrophenylhydrazone*, m. p. 171°), *phenyl α-hydroxyisopropyl ketone*, b. p. 125°/12 mm. (*semicarbazone*, m. p. 184—185°; *oxime*, m. p. 106°), and the cyclo*acetal*, $\begin{matrix}CO & O\\ | & >\\ CMe_2\cdot O\end{matrix}$CMePh. Replacing benzene by *p*-xylene, the corresponding derivatives,

xylyl α-acetoxyisopropyl ketone, b. p. 148°/17 mm. [p-*nitrophenylhydrazone*, m. p. 212°; *xylyl α-hydroxyisopropyl ketone*, b. p. 136°/16 mm. (*semicarbazone*, m. p. 166°; p-*nitrophenylhydrazone*, m. p. 219°)], and the cyclo*acetal* are formed, but only the hydrolysis products of the last, 2 : 5-dimethylacetophenone (*semicarbazone*, m. p. 153°; p-*nitrophenylhydrazone*, m. p. 152°) and α-hydroxy*iso*butyric acid, can be isolated. It is concluded that the chlorides of acetoxy-acids can react in two isomeric forms; one of these forms, cyclic, corresponding with the *cyclo*acetals, isomerises into the second, acyclic, under the influence of aluminium chloride (cf. A., 1912, i, 236).

E. H. Sharples.

Condensation products of polyhydroxy-compounds with chloral. J. Boeseken (Proc. K. Akad. Wetensch. Amsterdam, 1927, **30**, 55—60).—Chloralides of α-hydroxy-acids and glycols are readily prepared by warming the acid or glycol with chloral hydrate and concentrated sulphuric acid.

[With (Miss) J. Blok.]—Lactic acid yields a chloralide, m. p. 45°, there being no indication of the formation of *cis*- and *trans*-isomerides. Citric acid yields an α-*monochloralide*, m. p. 166°, possibly a β-monochloralide and a dichloralide. On treating *d*-tartaric acid with the theoretical amount of chloral hydrate, a mixture is obtained from which two *dichloralides*, m. p. 116—118°, $[\alpha]_D^{17}$ −33·1°, and m. p. 159—161°, $[\alpha]_D^{18\cdot2}$ −53·9° in chloroform, have been isolated. Racemic and *meso*tartaric acids under similar conditions form a mixture of isomerides including possibly a meso*tartaric acid dichloralide*, m. p. 171°. Salicylic and amygdalic acids yield *chloralides*, m. p. 124—125° and 59—60°, respectively, on boiling the acids with excess of anhydrous chloral, the presence of sulphuric acid being unnecessary and undesirable.

[With J. Stok.]—*Glycol chloralide*, m. p. 40°, and *glycerol chloralide*, b. p. 142—144°/11 mm., d_4^{17} 1·5500, n_D^{17} 1·5053, are described. J. S. Carter.

Trifluoroacetoacetic acid and ethyl trifluoroacetoacetate. F. Swarts (Bull. Acad. roy. Belg., 1926, [v], **12**, 679—691, and Bull. Soc. chim. Belg., 1927, **36**, 313—322).—Theoretical; a discussion of the matter in the two following abstracts.

G. A. C. Gough.

Trifluoroacetoacetic acid. F. Swarts (Bull. Acad. roy. Belg., 1926, [v], **12**, 721—725, and Bull. Soc. chim. Belg., 1927, **36**, 323—345).—*Trifluoroacetoacetic acid*, b. p. 97°/8 mm., m. p. 72·8° (solubility in chloroform at 50°, 20%), obtained from the ethyl ester by hydrolysis with hydrochloric acid, forms a deliquescent *monohydrate*, m. p. 55·6°. Compared with the unsubstituted analogue, it is remarkably stable, undergoing but slight decomposition on distillation at the ordinary pressure. When heated with sodium hydroxide, the acid yields trifluoroacetone and sodium carbonate. A study is made of the conductivity of aqueous solutions of the acid.

G. A. C. Gough.

Ethyl trifluoroacetoacetate. F. Swarts (Bull. Acad. roy. Belg., 1926, [v], **12**, 692—720, and Bull. Soc. chim. Belg., 1927, **36**, 323—345).—*Ethyl trifluoroacetoacetate*, b. p. 131·5—132°, m. p. −39·1° (keto-form), prepared by the interaction of ethyl acetate, ethyl trifluoroacetate, and sodium ethoxide (80% yield), exhibits well-defined keto–enolic tautomerism. A sample at equilibrium at 22° contains 66·2% of the enolic form, which figure is rapidly reduced to about 0·8% by keeping at −16° or to 2·07% by the addition of water. Water stabilises the keto-isomeride through the formation of a *hydrate*, $CF_3{\cdot}C(OH)_2{\cdot}CH_2{\cdot}CO_2Et$, m. p. 25·7°. Addition of sodium hydroxide to an aqueous solution of the ester, however, produces an amount of the enolic isomeride equivalent to the alkali added. A study of the conductivity and the hydrogen-ion concentration of aqueous solutions of the ester is also made.

The *sodium* salt of ethyl trifluoroacetoacetate, m. p. 175—183°, yields, when heated at 190°, ethyl alcohol, ethyl trifluoroacetate, sodium fluoride, and resinous substances. The *copper* salt, m. p. 186·5°, subliming at 6 mm.; the *ferric* salt, b. p. 189°/16 mm., m. p. 95°; the *aluminium* salt, b. p. 192—194°/32 mm., m. p. 97°, and the *cobalt* salt are also described. By heating the *ammonium* salt, m. p. 86°, *ethyl γγγ-trifluoro-β-iminobutyrate*, b. p. 157·1—157·35°/145 mm., and *γγγ-trifluoro-β-iminobutyramide*, m. p. 137°, are formed. The *ammonium* salt of *trifluoroacetoacetamide*, m. p. 97° (closed tube), is formed by the passage of ammonia into an ethereal solution of ethyl trifluoroacetoacetate. *Ethyl trifluoroacetoacetate phenylhydrazone*, m. p. 61·2°, and *phenyltrifluoromethylpyrazolone*, m. p. 192·6° (corr.), are prepared in the usual ways. G. A. C. Gough.

Differentiation of *cis*- and *trans*-ethylenic compounds by catalytic hydrogenation. C. Paul and H. Schiedewitz (Ber., 1927, **60**, [*B*], 1221—1228).—Comparative experiments on the hydrogenation in alcoholic solution in presence of palladous hydroxide deposited on barium sulphate or calcium carbonate of maleic and fumaric acids, citraconic and mesaconic acids, oleic and elaidic acids, *cis*- and *trans*-cinnamic acids, and of their sodium salts in aqueous solution, show that the *cis*-compounds are uniformly more readily reduced than the corresponding *trans*-compounds. The heats of combustion of the *cis*-acids are somewhat greater than those of the *trans*-acids. H. Wren.

Properties of conjugated compounds. II. Addition to butadiene esters. E. H. Farmer and A. T. Healy (J.C.S., 1927, 1060—1067).—Addition of methyl sodiomalonate and ethyl methylcyanoacetate under varying conditions to methyl sorbate and methyl β-vinylacrylate always occurs in the αδ-positions, no trace of other additive products being obtained. Thus methyl sorbate and methyl malonate yield methyl β-methyl-Δ$^{\gamma}$-pentene-αα$^{\varepsilon}$-tricarboxylate (Kohler and Butler, A., 1926, 713), whilst from methyl β-vinylacrylate is similarly obtained methyl-Δ$^{\gamma}$-pentene-αα$^{\varepsilon}$-tricarboxylate, b. p. 172°/13 mm. (Kohler and Butler, *loc. cit.*, give b. p. 147—151°/11 mm.; *triamide*, m. p. 213°), which may be stabilised for a considerable period by the addition of a little quinol, and will not condense with methyl cyanoacetate, the double linking being non-mobile. By similar condensations are obtained *methyl ethyl* β-*cyano*-Δ-*hexene*-βζ-*dicarboxylate*, b. p. 182—185°/16 mm.; and

methyl ethyl β-*cyano*-γ-*methyl*-Δ^{δ}-*hexene*-βζ-*dicarboxylate*, b. p. 185—188°/16 mm., the structures of which were proved by ozonisation. δ-Vinylacrylic acid forms a liquid and a solid *dibromide*, m. p. 47° (*methyl* ester of the dibromo-acid, b. p. 136°/10 mm.). The solid on treatment in ether solution with diethylamine at 0° yields bromo-β-vinylacrylic acid, which readily polymerises (*methyl* ester, m. p. about 10°), whilst the liquid similarly yields a solid acid (*methyl* ester, b. p. 95—98°/16 mm.). Ozonisation of either dibromide yields α-*bromoacraldehyde*, b. p. 58°/21 mm. (*semicarbazone*, m. p. 160°). Sorbic acid dibromide (Auwers and Heyna, A., 1924, i, 8) (*methyl* ester, b. p. 146°/12 mm.), on treatment with diethylamine yields *bromosorbic acid*, m. p. 140° (*methyl* ester, b. p. 104—106°/10 mm.). Addition of bromine in each case occurs at the γδ double linking. J. W. Baker.

Sulphates and chlorides of complex bismuthotartrates. R. Portillo (Anal. Fís. Quím., 1927, **25**, 86—89; cf. A., 1926, 1025).—On dissolving the bismuthotartrate, $[BiC_4H_4O_6]Cl,3H_2O$, in a solution of potassium or sodium carbonate and keeping in a vacuum over sulphuric acid, crystalline *precipitates*, $[BiC_4H_4O_6]K_2Cl,H_2O$ and $[BiC_4H_4O_6]Na_2Cl,H_2O$, respectively, are obtained. Corresponding sulphate *compounds* may be obtained. G. W. Robinson.

Microchemical reaction for citric acid. M. Wagenaar (Chem. Weekblad, 1927, **24**, 258—259).—A drop of 0·1*N*-iodine in potassium iodide solution is warmed with one drop of the sample to be tested and a quantity of 30% acetic acid, and a tiny drop of 3% permanganate solution added. Crystals of iodoacetone separate at once if citric acid is present. No reaction is given by tartaric, malic, succinic, lactic, or oxalic acid. S. I. Levy.

Preparation of hexonic and bionic acids by oxidation of aldoses with barium hypoiodite. W. F. Goebel (J. Biol. Chem., 1927, **72**, 809—814).—The aldose is oxidised by the method of Willstatter and Schudel (A., 1918, ii, 337), with the difference that barium hydroxide is used as the alkali, and the solution is acidified with sulphuric acid and treated with excess of lead carbonate. The concentrated filtrate is freed from lead by means of sulphuric acid and from sulphuric and hydriodic acids with barium hydroxide and silver sulphate, respectively; the reaction product is isolated from the final solution as the calcium salt. The yields are 80—90% of the theoretical. C. R. Harington.

δ-Ketogluconic acid. H. Ohle and G. Berend (Ber., 1927, **60**, [*B*], 1159—1167).—The acid derived from lævulose di*iso*propylidene ether (A., 1926, 150) is identified as β-ketoglutaric acid, since it is oxidised by potassium permanganate in acid solution to -arabonic acid, which could not be derived from the isomeric ε-ketogluconic acid. Amended directions are given for the preparation of β-ketogluconic acid, of which the *barium* salt ($+2H_2O$), *calcium* salt, and *potassium* salt, $[\alpha]_D^{20}$ −69·95° in water, are described. With phenylhydrazine in concentrated acid solution, the acid gives the *phenylhydrazine* salt *acid phenylhydrazone*, m. p. (hydrated) 100°, (anhydrous) 121°, $[\alpha]_D$ −36·15° in aqueous pyridine; in acetic acid solution the product is not homogeneous. Treatment of barium δ-ketogluconate with sulphuric acid and acetone yields β-ketogluconic acid di*iso*propylidene ether. β-Ketogluconic acid does not appear to exhibit mutarotation. It is not converted by carboxylase into arabinose or other reducing substance. It is oxidised by alkaline permanganate to oxalic acid, the yield of which does not change appreciably with alteration in the concentration of alkali. For these reasons, it is improbable that it is isomeric with the β-ketogluconic acid of Honig and Tempus (A., 1924, i, 712), which is therefore considered to have the keto-group in other than the β-position, although it is not clear how such an acid could yield *d*-arabonic acid or *d*-arabinose. *Barium* d-*arabonate* is described. H. Wren.

Tautomerism of the ethyl dicarbethoxyglutaconates. H. Stobbe and F. Wildensee (J. pr. Chem., 1927, [ii], **115**, 163—177).—Colorimetric experiments with ethyl dicarbethoxyglutaconate and ferric chloride in alcoholic solution show that an equilibrium exists between the enolic and neutral forms of the ester. The original violet colour of the mixture slowly changes to yellow, due to the ketonising action of the hydrogen chloride liberated during the reaction. This change is hastened by the addition of hydrogen chloride, and is slowest at low concentrations of ferric chloride and at low temperatures. Whilst the attainment of equilibrium is instantaneous in alcohol, only the neutral form exists in ether, acetone, chloroform, benzene, and hexane.

These results are confirmed by a study of the absorption spectra of the ester, and it is deduced that the percentage of enol in alcohol increases with the dilution. It is calculated that a 0·01*N*-solution contains 0·1—0·3% of enol, a 0·001*N*-solution 32—34%, and a 0·0001*N*-solution about 55%. R. W. West.

Aldol condensation of formaldehyde and acetaldehyde. A. V. Stepanov and (Mlle.) M. Stchukina (J. Russ. Phys. Chem. Soc., 1926, **58**, 840—848).—By the action of sodium carbonate on a mixture consisting of 1 mol. of acetaldehyde and 2—3 mols. of formaldehyde, δ-*hydroxypropaldehyde*, together with β-hydroxybutaldehyde, is formed. The mixture on treatment with oxalic acid yields acraldehyde and crotonaldehyde, respectively. These cannot be separated by distillation, but yield a mixture of semicarbazones which are converted into the amides of the corresponding pyrazolinecarboxylic acids (cf. Nef, A., 1905, i, 3), and can then be separated. The mixture of aldols gives a mixture of semicarbazones, m. p. 54—55°, which undergoes the pyrazoline reaction, with loss of water. When kept in a desiccator, the mixture loses water, the m. p. is raised; and the resulting powder does not give the pyrazoline reaction. On adding water, the semicarbazones of the original aldols are re-formed.

E. Rothstein.

Polymerised formaldehyde as a model of cellulose. H. Staudinger, H. Johner, R. Signer, G. Mie, and J. Hengstenberg (Z. physikal. Chem., 1927, **126**, 425—448).—The insoluble polymerisation products of formaldehyde have been investigated, regarding them as being of similar structure to cell-

ulose. The soluble products formed from the higher polymerides by treatment with acetic anhydride contain from 1 to 20 formaldehyde groups, each group being similarly placed in the molecule. The insoluble polyoxymethylenes contain, therefore, probably not fewer than 50 formaldehyde groups.

A study of the α-, β-, γ-, and δ-polyoxymethylenes shows the α-compound to be a polyoxymethylene hydrate of high mol. wt., the β-modification an ester of sulphuric acid, and the γ a methyl ether.

X-Ray analysis shows the polyoxymethylenes to consist of very long molecules, formed by a series of CH_2·O-groups joined end to end in such a manner that the angles formed by two consecutive groups with the axis of the molecule differ by 180°, alternate groups thus occupying similar positions in the molecule. The Debye–Scherrer diagrams of the polyoxymethylene diacetates containing from 9 to 19 CH_2·O-groups exhibit the same rings as the higher polymerides, although the rings are less sharp and are sometimes divided into fine rings the radii of which differ very little from the radius of the corresponding ring of the higher polymerides. The molecules of the higher polymerides are therefore of the same structure as those of the lower. The mol. wt. of the soluble crystalline polyoxymethylene diacetates, obtained from the *X*-ray diagrams, agree with the values obtained from chemical and osmotic determinations.

By sublimation of β-polyoxymethylene in a vacuum, a γ-modification is obtained which, by *X*-ray measurement, is found to have the same fibrous structure as cellulose, the fibres being oriented along the length of the molecule. The size of highly-polymerised molecules may thus be determined by *X*-ray measurements. From the numerous parallels between the polyoxymethylenes and cellulose, it follows that the latter has a highly-polymerised molecule.

H. F. GILLBE.

Influence of monosaccharides and magnesium ions on sugar formation from formaldehyde. H. SCHMALFUSS (Biochem. Z., 1927, **185**, 70—85).—On heating an aqueous solution of formaldehyde with magnesium oxide at 120° under a pressure of 2 atm., or for longer periods at 100° and atmospheric pressure, there were obtained, in addition to the products already described (A., 1925, i, 116), 1—1·3% of hexose (calculated as dextrose) and small amounts of diacetyl and furfuraldehyde. The attainment of the final equilibrium is accelerated by increasing the amount of magnesium oxide up to that required for combination with the acids formed; it is still further quickened by addition of magnesium formate, acetate, or chloride, is not affected by sodium, potassium, or calcium formates, and is inhibited by copper formate; the accelerating effect is therefore due to the magnesium ion. The reaction is inhibited by acids, especially in presence of furfuraldehyde; it is not affected by diacetyl, but is much accelerated by addition of sugar. It takes place more rapidly in presence of sodium or calcium hydroxides than with magnesium oxide, but in these cases the yield of hexose is less, owing to secondary reactions.

C. R. HARINGTON.

Action of alkali and hydrogen peroxide on glyoxals. T. E. FRIEDEMANN (J. Biol. Chem., 1927, **73**, 331—334).—Methylglyoxal, on treatment with potassium hydroxide, is converted quantitatively into lactic acid, and, on treatment with potassium hydroxide and hydrogen peroxide, gives a quantitative yield of acetic and formic acids. Analogous behaviour was observed with glyoxylic acid and with hydroxymethylglyoxal (obtained by oxidising dihydroxyacetone with copper acetate).

C. R. HARINGTON.

Catalytic reduction of aliphatic oximes in presence of nickel at the atmospheric temperature. S. WASSILJEV (Ber., 1927, **60**, [*B*], 1122—1125).—Acetaldoxime is reduced to diethylamine, whereas propaldoxime and *iso*valeraldoxime yield the corresponding primary amine and ammonia. The rate and product of the actions are not sensibly influenced by the solvent (alcohol or water).

H. WREN.

Monobromoacetone and its cyanohydrin. A. CHRZĄSZCZEWSKA and W. SOBIERANSKI (Rocz. Chem., 1927, **7**, 79—86).—Pure monobromoacetone, b. p. 23·5—24·5°/3·5 mm. (*cyanohydrin*, b. p. 94·5—95·5°/5·5 mm.), is prepared by the action of bromine and sodium bromate on an aqueous solution of acetone in presence of sulphuric acid.

R. TRUSZKOWSKI.

***n*-Propyl*cyclo*butane and *cyclo*butyl ethyl ketone.** N. D. ZELINSKI and B. A. KASANSKI (Ber., 1927, **60**, [*B*], 1101—1102).—cyclo*Butyl ethyl ketone*, b. p. 154—155°/750 mm., d_4^{25} 0·8934, 1·4339 (*semicarbazone*, m. p. 153—155°), is prepared by passing a mixture of *cyclo*butanecarboxylic acid and propionic acid over a manganous and zinc oxide catalyst at 410—420°. Reduction of the corresponding hydrazone by Kishner's method affords *n-propyl*cyclo*butane*, b. p. 99—100°/736·2 mm., 0·7440, n_D^{25} 1·4119.

H. WREN.

Formation of diacetyl from carbohydrates and related substances. H. SCHMALFUSS and H. BARTHMEYER (Ber., 1927, **60**, [*B*], 1035—1036; cf. A., 1925, i, 116).—Diacetyl is produced when aqueous solutions of dihydroxyacetone or dextrose are heated at 120° or, preferably, 160°, and when glycollaldehyde, arabinose, sucrose, starch, filter-paper, or tartaric acid is subjected to dry distillation. The presence of 3 mg. of diacetyl in 1 c.c. of solution may be detected by addition of hydroxylamine hydrochloride and nickel sulphate, followed by sufficient ammonia to render the solution faintly alkaline. After being boiled for 1 min., the solution is rapidly cooled, when the nickel salt of diacetyldioxime separates. Before application of the reaction, formaldehyde must be removed by dimethyldihydroresorcinol.

H. WREN.

Oxidation of dextrose in alkaline solutions of iodine. W. F. GOEBEL (J. Biol. Chem., 1927, **72**, 801—807).—Quantitative oxidation of dextrose by the method of Willstatter and Schudel (A., 1918, ii, 337) is obtained only when the addition of the alkali occupies at least 2 min. This is accounted for by the fact that too rapid addition of alkali encourages the formation of iodate at the expense of hypoiodite, reducing the latter below the minimum concentration necessary to complete the reaction, and, further, by

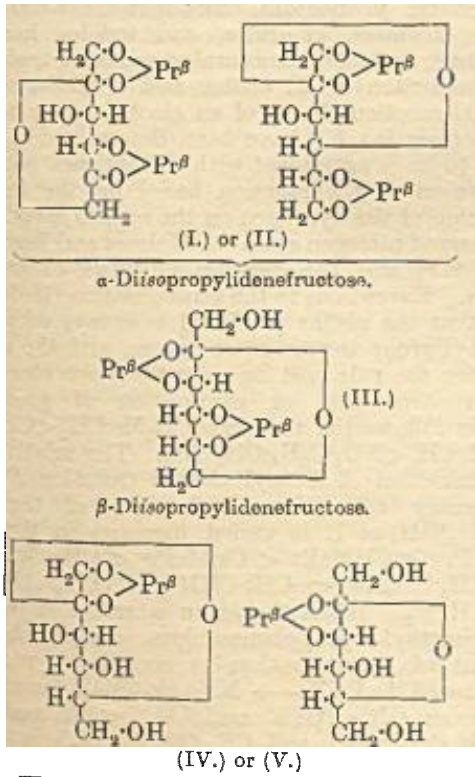
the effect of excess of alkali in converting a part of the dextrose into an unoxidisable ketose.

C. R. HARINGTON.

Mutarotation. I. Velocity of mutarotation of α-glucose in methyl alcohol and water. F. P. WORLEY and J. C. ANDREWS.—See this vol., 631.

Acetylated monosaccharides. III. Penta-acetyl-α-mannose. P. A. LEVENE and I. BENCOWITZ (J. Biol. Chem., 1927, **172**, 627—634).—An improved method is described for the preparation of penta-acetyl-α-mannose (cf. A., 1924, i, 615); the optical rotation of the product was determined for ten different wave-lengths. The relationship between the square of the wave-length and the reciprocal of the molecular rotation was expressed by a straight line, so that the optical rotatory dispersion followed a normal course. C. R. HARINGTON.

Ring structure of lævulose. H. OHLE (Ber., 1927, **60**, [*B*], 1168—1174).—On the general assumption that acetone condenses readily only with two neighbouring hydroxyl groups and that the hydroxyl groups retain the positions indicated for them by Fischer's projection formulæ when they are attached to carbon atoms which are members of a ring system, supported by individual arguments for which the original paper must be consulted, the following constitutions are assigned to the α- and β-di*iso*propylidenefructoses, the α- and β-*iso*propylidenefructoses, and the *iso*propylidenefructose of Irvine and Garrett (J.C.S., 1910, **97**, 1277).



(I.) or (II.)

α-Di*iso*propylidenefructose.

(III.)

β-Di*iso*propylidenefructose.

(IV.) or (V.)

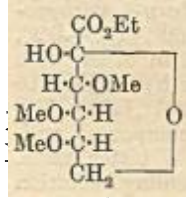
*iso*Propylidenefructose of Irvine and Garrett.

Study of the optical activity of the *iso*propylidene- indicates that the α-compounds are configuratively related to β-fructose and the β-compounds to α-fructose.

The difference in the products obtained by the action of acetone on lævulose in presence of copper sulphate or of mineral acid of differing concentration (cf. Ohle and Koller, A., 1924, i, 1168) is explained by the assumption that the main reaction leads to the production of α-di*iso*propylidenefructose without change of configuration or structure, whilst the liberated water converts a portion of the lævulose into the butylene oxide form, which is transformed into the corresponding *iso*propylidene ether. If lævulose in neutral aqueous solution is changed by water in the same manner as during acetonisation, it follows, when the magnitude of the specific rotation is taken into account, that the main chemical change during mutarotation consists in the transformation of the amylene oxidic β-form into the butylene oxidic β-form. This cannot occur without temporary opening of the oxygen bridge with production of the keto-form or its hydrate; sufficiently concentrated solutions of lævulose show the carbonyl absorption band.

H. WREN.

Structure of normal fructose: crystalline tetramethyl β-methylfructoside and crystalline tetramethylfructose (1 : 3 : 4 : 5). W. N. HAWORTH, E. L. HIRST, and A. LEARNER (J.C.S., 1927, 1040—1049).—Oxidation of normal tetramethylfructose with nitric acid (*d* 1·2) under the conditions used by Irvine and Patterson (*ibid.*, 1922, **121**, 2696) yields an *ethyl* ester, $C_{11}H_{20}O_7$, m. p. 86—87°, which cannot be the diethyl ester of hydroxydimethoxyglutaric acid, as stated by the earlier authors, since it is a monobasic ester and contains a reducing group.



The annexed constitution assigned to it is confirmed by the following series of reactions. It is converted by methyl alcohol and hydrogen chloride directly into the corresponding methyl ester, $C_{10}H_{18}O_7$, m. p. 119°, isolated by Haworth and Hirst (A., 1926, 1126), the methylated ester of which yields an *amide*, m. p. 118—119°, [α] (approximately) −137° in water. Further oxidation of the ethyl ester yields *d*-arabotrimethoxyglutaric acid, and finally *meso*-dimethoxysuccinic acid. Crystalline tetramethylfructose is therefore the αγδε-compound, both lævulose and the tetramethyl compound containing an amylene oxide ring. Tetramethyl-β-methylfructoside has been isolated as a crystalline compound, m. p. 33—34°, [α] −149·1° in water (cf. Irvine and Patterson, *loc. cit.*), by the action of alkali and methyl sulphate on tetra-acetyl-β-methylfructoside, deacetylation and methylation being effected in one operation.

J. W. BAKER.

Synthesis of coniferin. H. PAULY and K. FEUERSTEIN (Ber., 1927, **60**, [*B*], 1031—1034).—4-Hydroxy-3-methoxycinnamaldehyde is converted by the requisite alkali metal in methyl-alcoholic solution into the corresponding *sodium* or *potassium* derivative. The latter compound is transformed by acetobromoglucose into *tetra-acetylglucoconiferyl aldehyde*, $C_6H_7O_5Ac_4{\cdot}O{\cdot}C_6H_3(OMe){\cdot}CH{:}CH{\cdot}CHO$, m. p. 160°, hydrolysed by barium hydroxide to gluco-

coniferyl aldehyde, m. p. 206°. Reduction of the tetra-acetate to the corresponding primary alcohol appears impossible by purely chemical methods, but is smoothly effected biologically by adding it to a solution of sugar undergoing brisk fermentation by yeast. *Tetra-acetylglucoconiferyl alcohol*, m. p. 132°, so obtained, is converted by aqueous ammonia into coniferin, m. p. 185·5° (anhydrous), $[\alpha]_D^{20}$ −67·25°, identical with the natural glucoside. H. WREN.

Heptosides. E. GLASER and N. ZUCKERMANN (Z. physiol. Chem., 1927, **166**, 103—124).—Gluco-α-heptose is prepared from *d*-glucose by way of the cyanohydrin and the lactone of glucoheptonic acid (yield of lactone 57—62%). β-Hexa-acetyl-α-gluco-heptose (Fischer's "deca-acetyldiglucoheptose"), m. p. 135°, gives analytical and mol. wt. results confirming the views of Franchimont, and of Hudson and Yanowsky (A., 1916, i, 630). It is converted by hydrogen bromide in glacial acetic acid into *β-bromo-α-glucoheptosepenta-acetate*, m. p. 110°, which is applied to the synthesis of a number of α-glucoheptosides. *Penta-acetyl-β-geranyl-α-glucoheptoside*, m. p. 83·5—84·5°, $[\alpha]_D$ −21°, obtained from the bromo-compound by the action of geraniol and moist silver oxide, is hydrolysed by methyl-alcoholic ammonia to *β-geranyl-α-glucoheptoside*, m. p. 128—129°, $[\alpha]^{20}$ −24°. *Penta-acetyl*-β-cyclo*hexyl-α-glucoheptoside*, m. p. 140—140·5°, $[\alpha]_D^{20}$ −22°, and β-cyclo*hexyl-α-glucoheptoside*, m. p. 153—157°, $[\alpha]_D^{3}$ −9·2°, *penta-acetyl-β-benzyl-α-gluco-heptoside*, m. p. 116—117°, $[\alpha]_D$ −32°, and *β-benzyl-α-glucoheptoside*, m. p. 147—148°, $[\alpha]^{18}$ −43°, *penta-acetyl-β-bornyl-α-glucoheptoside*, m. p. 146—146·5°, $[\alpha]^{20}$ −65°, and *β-bornyl-α-glucoheptoside*, m. p. 217°, are similarly prepared. *Penta-acetyl-β-vanillin-α-glucoheptoside* [*penta-acetyl-β-(2-methoxy-4-aldehydo-phenyl)-α-glucoheptoside*], m. p. 179—180°, $[\alpha]_D^{18}$ −6·9°, obtained from the bromo-compound in ether with vanillin and *N*-sodium hydroxide, is hydrolysed to *β-vanillin-α-glucoheptoside*, m. p. 206—207°, $[\alpha]_D^{18}$ −17°, which is odourless, as is the geranyl compound, and, like the other glucoheptosides, has a bitter taste. None of the glucoheptosides reduces Fehling's solution until after fission by warm dilute mineral acid. They are not hydrolysed by emulsin or by yeast enzymes. The heptosides have in general a smaller optical activity than the corresponding glucosides. They are more readily prepared and crystallised, and more rapidly hydrolysed. C. HOLLINS.

Hydrolysis of starch by sulphuric acid. M. P. NOTTIN (Compt. rend., 1927, **184**, 1204—1206).—The hydrolysis of starch by sulphuric acid under varying conditions of temperature and concentration was investigated, using the copper acetate method of Le Grand (A., 1921, ii, 355) for direct determination of dextrose produced in the hydrolysis. The theory that starch is initially hydrolysed directly into dextrose, maltose, other reducing substances, and dextrins is supported, in opposition to the theory of Nanji and Beazeley (B., 1926, 685) that the breakdown of starch involves successive hydrolytic steps. M. CLARK.

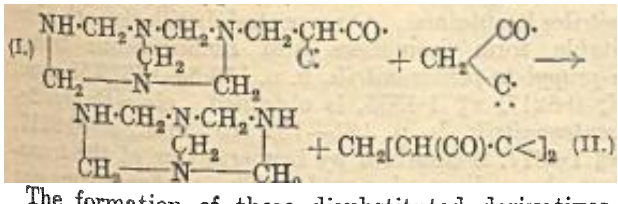
Crystalline substances isolated from lignin. G. J. RITTER (Ind. Eng. Chem., 1927, **19**, 624).—On extraction with ether, acetone, or alcohol, wood lignin prepared by the action of 72% sulphuric acid yields crystalline substances which are similar in form and general character to those obtained by Kürschner by biochemical methods (Z. angew. Chem., 1927, **40**, 224). This supports the view that ligneous material resulting from decay differs in composition from that in the original sound wood (cf. Bray and Andrews, B., 1924, 249). W. J. POWELL.

Thermal fissions of pine lignin. II. Treatment of technical Willstatter-lignin with steam. W. FUCHS (Ber., 1927, **60**, [*B*], 1131—1133; cf. this vol., 546).—Treatment of the material with superheated steam at 280—300° affords (*a*) an unsaturated, volatile hydrocarbon which appears to yield a sulphonic acid, (*b*) a tar containing the same components as that derived from the silver distillation (*loc. cit.*), (*c*) an aqueous distillate containing pyrocatechol and a far larger proportion of hydroxymethylfurfuraldehyde (apparently associated with analogous compounds) than is obtained by the silver treatment, and (*d*) a residue which does not differ very greatly from the initial material in composition. Consideration of the yield of hydroxymethylfurfuraldehyde and the composition of the residue indicates the presence of a hexal but not a hexose complex in lignin.
H. WREN.

Alternating effects in carbon chains. XVIII. Mechanism of exhaustive methylation and its relation to anomalous hydrolysis. W. HANHART and C. K. INGOLD (J.C.S., 1927, 997—1020).—The decomposition of a number of quaternary ammonium hydroxides, phenoxides, carbonates, *m*-nitrophenoxides, acetates, chlorides, and iodides has been examined, and the structural conditions underlying the production of an olefine and a tertiary amine (normal reaction *A*), or of an alcohol and a tertiary amine (reaction *B*), have been determined, and are found to be in agreement with the authors' suggested mechanism of the reaction based on the incipient ionisation of the hydrogen on the second carbon from the charged nitrogen atom (cf. Holmes and Ingold. A., 1926, 829) and the electron affinities of attached groups. Exceptions to the generalisation (Hofmann's rule) that the olefine produced is always ethylene if an ethyl group is present are given, and the reasons both for the rule and its exceptions are elucidated. The relative ease of elimination of groups as olefines follows the sequence $CH_2Me{\cdot}CH_2 < CH_2Me < CH_2Ph{\cdot}CH_2 < NO_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}CH_2$. The relative ease of elimination of methyl alcohol (reaction *B*) from quaternary ammonium hydroxides of the type $[NRMe_3]OH$, as R is varied, increases in the order $Et < Pr^{\beta} < CHMeEt < CHMePr^{\alpha} < CMe_3 < Pr^{\alpha} < CH_2{\cdot}CH_2{\cdot}CH_2Me < CH_2{\cdot}CHMe_2 < CH_2{\cdot}CHEt_2 < CH_2{\cdot}CHPr^{\alpha}_2$. When the anion is varied in the case of trimethyl-*n*-propylammonium compounds, the amount of decomposition in accordance with the reaction $[NMe_3Pr]X \longrightarrow NMe_2Pr + MeX$ increases in the order $OH' < (OPh'$ and $CO_3'') < (Cl'$ and $I') < [O{\cdot}C_6H_4{\cdot}NO_2'$ (*m*) and $CH_3{\cdot}CO_2']$, which, with the exception of chlorides and iodides, is in the anticipated order of increasing ionisation of the compounds HX in aqueous solution. The following compounds have been prepared in the course of the investigation: *dimethylethyl*-n-*propylammonium iodide* (*picrate*, m. p.

185—187°); *dimethyl*-n-*propylammonium picrate*, m. p. 108—109°; β-*phenylethyldimethylethylammonium iodide*, m. p. 158—159° (*picrate*, exists in two crystallographic modifications, m. p. 96—97° and 115—116°); dimethylethylammonium picrate has m. p. 202—203° (Kohn and Morgenstern, A., 1907, i, 681, give 193—194°). The interaction of β-phenylethyl chloride and β-*p*-nitrophenylethyldimethylamine yields *p*-nitrostyrene, β-phenylethyldimethylamine, and *di*-(β-*phenylethyl*)*dimethylammonium chloride*, m. p. 70° (*picrate*, m. p. 111—112°), the expected quaternary compound being unstable. Phthal-β-bromoethylimide condenses with dimethylethylamine to yield β-*phthalimidodimethyldiethylammonium bromide*, m. p. 280° (decomp.), which on hydrolysis and treatment with sodium picrate yields *dimethylethylethylenediammonium picrate*, m. p. 198° (decomp.). Tetramethylethylenediamine (which may be obtained in 40% yield when ethylenediamine sulphate is heated with paraformaldehyde at 130—140° for 4 hrs.) reacts with ethyl iodide to yield s-*tetramethyldiethylethylenediammonium di-iodide*, m. p. 233° (decomp.) [*dipicrate*, m. p. 261° (decomp.)]. β-*Dimethylaminodimethyldiethylammonium picrate*, m. p. 212—213° (not pure); *hexamethylethylenediammonium dipicrate*, m. p. 285° (decomp.); β-*hydroxydimethyldiethylammonium iodide* (*picrate*, two modifications, m. p. 237—239° and 258°); β-*chlorodimethylethylammonium picrate*, m. p. 126—127°; β-*chlorodimethyldiethylammonium iodide*, m. p. 198° (*picrate*, m. p. 192—193°); *trimethyl*-n-*propylammonium picrate*, m. p. 195—196° (free *base*, b. p. 65—66°); dimethyl*iso*butylamine, b. p. 80—81° (picrate, m. p. 124°); *trimethyliso*butylammonium *picrate*, m. p. 173—174°, and *dimethyl*-n-*propylamine*, b. p. 65—66°, are described. J. W. BAKER.

Action of substances containing an active methylene group on hexamethylenetetramine. M. V. IONESCU and V. N. GEORGESCU (Bull. Soc. chim., 1927, [iv], **41**, 692—706).—Substances of the types ·CO·CH_2·CO·, ·CO·CH_2·C<, and –CO·CH_2·C:N– containing a reactive methylene group, may be classified according to whether they react or do not react with hexamethylenetetramine in aqueous or in alcoholic solution. Deoxybenzoin, *cyclo*pentadiene, indene, fluorene, etc. do not react. The following substances react with increasing ease: ethyl malonate, ethyl acetoacetate, acetylacetone, indanedione, dimethyldihydroresorcinol, diphenyldihydroresorcinol, phenylmethylpyrazolone and its homologues, diindone. In the first stage of the reaction, an additive compound (I) is formed which is subsequently decomposed by a second molecule of the compound with a reactive methylene group, affording a methane derivative of the type (II).



The formation of these disubstituted derivatives of methane cannot be attributed to preliminary hydrolysis of hexamethylenetetramine to formaldehyde, since hexamethylenetetramine is decomposed by water only on prolonged boiling in presence of acids, whereas the reaction in question takes place rapidly in neutral solution and in anhydrous solvents such as benzene, toluene, or xylene. In certain cases, the methane derivative undergoes oxidation or dehydrogenation, yielding the corresponding methenyl derivative, >C·C(CO)·CH·CH(CO)·C<. Thus 5 : 5-dimethyl*cyclo*hexane-1 : 3-dione and hexamethylenetetramine in absolute alcohol afford, in addition to methylenebis-4 : 4-dimethyl*cyclo*hexane-2 : 6-dione, m. p. 190° (Vorländer, A., 1900, i, 99), the *amino*-derivative of *methenylbis*-4 : 4-*dimethyl*cyclo*hexane*-2 : 6-*dione*, $CMe_2<\begin{matrix}CH\\CH\end{matrix}\cdot CO>C.CH\cdot C\leqslant \overline{\quad\quad\cdot CH_2}>CMe_2$, m. p. 257—258°, together with a little tetramethyldecahydroacridinedione, m. p. 267° (Vorländer, *loc. cit.*); in aqueous solution the methylene derivative is obtained quantitatively. 5-Phenyl*cyclo*hexane-1 : 3-dione in alcohol affords methylenebis-4-phenyl*cyclo*hexane-2 : 6-dione, m. p. 213°, and a little diphenyldecahydroacridinedione. With ethyl acetoacetate the reaction is more complex, the mixture of methylene- and methenyl-bisacetoacetates first formed yielding, under the influence of ammonia formed in the reaction, ethyl dihydrolutidine-3 : 5-dicarboxylate, m. p. 182°, and a little ethyl lutidine-3 : 5-dicarboxylate. Similarly, acetylacetone in alcohol readily affords the compound $CAc<\begin{matrix}Me=CH\\CH\cdot CHAc\end{matrix}>C:NH$, m. p. 217°, obtained by Claisen (A., 1897, i, 592) by cyclisation of the methenyl derivative first produced. The non-reactivity of ethyl malonate with hexamethylenetetramine is in harmony with its low speed of reaction with aldehydes and with ethyl orthoformate (Claisen, *loc. cit.*) and with its smaller additive capacity towards heterogeneous asymmetric conjugated systems, and is attributed to a special structure in its valency field, the alkoxy-groups decreasing the electronegative action of the carbonyl groups on the attached methylene group. R. BRIGHTMAN.

Spermine. VI. F. WREDE, H. FANSELOW, and E. STRACK (Z. physiol. Chem., 1927, **163**, 219—228; cf. this vol., 264; Dudley, Rosenheim, and Starling, A., 1926, 1234).—The constitution of spermine, $NH_2\cdot[CH_2]_3\cdot NH\cdot[CH_2]_4\cdot NH\cdot[CH_2]_3\cdot NH_2$, is confirmed by synthesis. γ-Bromopropylphthalimide does not react with tetramethylenediamine in the desired manner, but by using γ-iodopropylphthalimide, m. p. 88°, and excess of the diamine, a product is obtained which on hydrolysis successively with alkali and hydrochloric acid gives spermine (*m*-nitrobenzoyl derivative, m. p. 172°), isolated as phosphate, m. p. 224—228°.

Tetramethylenediamine is converted into its *s*-dibenzenesulphonyl derivative, m. p. 131°, and methylated with methyl sulphate to give s-*dibenzenesulphonyldimethyltetramethylenediamine*, m. p. 151°. NN′-*Dimethyltetramethylenediamine*, b. p. 168° [*hydrochloride*, *chloroplatinate*, $C_6H_{16}N_2,H_2PtCl_6$, m. p. 242° (decomp.), and *di*-m-*nitrobenzoyl* derivative, m. p. 118°, described], obtained by hydrolysis of the dibenzenesulphonyl compound, condenses more

readily with γ-bromopropylphthalimide, giving after hydrolysis *dimethylspermine* (yielding a *chloroaurate*, $C_{12}H_{30}N_4,4HAuCl_4$, m. p. 200°, decomp. 205°), which is methylated with methyl-alcoholic potassium hydroxide and methyl iodide to hexamethylspermine tetramethiodide (decamethylspermine iodide) (tetramethochloride, mercuric chloride double salt, chloroaurate, and chloroplatinate identical with those from permethylated spermine). C. HOLLINS.

Unsaturated compounds from α-amino-acids and their conversion into α-keto-acids. E. ABDERHALDEN and E. ROSSNER (Z. physiol. Chem., 1927, **163**, 261—266; cf. this vol., 576).—When chloroacetyl-*d*-valine is treated with phosphorus pentachloride in acetyl chloride, ether, or carbon tetrachloride, there is obtained after treatment with water a *compound*, $C_7H_{11}O_3N$, m. p. 203°, which is probably α-acetamido-β-methylcrotonic acid. This, on hydrolysis with 25% sulphuric acid, isomerises to α-acetimido*iso*valeric acid, which is at once hydrolysed to dimethylpyruvic acid (*iso*propylglyoxylic acid), m. p. 24°, b. p. 85° [phenylhydrazone, m. p. 143° (decomp.)], isolated as its copper salt. The same keto-acid is obtained from α-bromo*iso*hexoyl-*d*-valine. Chloroacetyl-*l*-leucine on one occasion gave with phosphorus pentachloride in carbon tetrachloride an unsaturated *compound*, $C_8H_{13}O_3N$, m. p. 150°, $[\alpha]$ −22·4°, but the corresponding keto-acid was not obtained. The product, $C_{10}H_{16}O_4N_2$, described by Fischer and Könige (A., 1907, i, 486), probably resulted from bromo*iso*hexoylasparagine in a similar manner. C. HOLLINS.

Behaviour of hexoses and hexosemonophosphoric acids to serum and amino-acids. C. NEUBERG and M. KOBEL (Biochem. Z., 1927, **182**, 273—284).—In continuance of previous observations (A., 1926, 151, 1061; this vol., 378), it is shown that alterations of rotation occur when hexosemonophosphoric acids—Neuberg's, Robison's, and that obtained from sucrosemonophosphoric acid—are mixed with sodium aspartate and glutamate, *dl*-alanine, carbamide, and horse-serum. J. PRYDE.

Synthesis of tertiary leucine. E. ABDERHALDEN and E. ROSSNER (Z. physiol. Chem., 1927, **166**, 158; cf. this vol., 576).—Tertiary leucine ("ψ-leucine") has previously been synthesised by Knoop and Landmann (A., 1914, i, 257). C. HOLLINS.

Action of sodium hypochlorite on amides. IV. I. J. RINKES (Rec. trav. chim., 1927, **46**, 268—277; cf. this vol., 45).—Diethylmalonic acid, prepared by the hydrolysis of 5 : 5-diethylbarbituric acid with 33% potassium hydroxide, was converted through the acid chloride into the diamide, and this was treated with sodium hypochlorite solution at 0°, and the product decomposed with the calculated quantity of sulphuric acid. This liberated N-*chlorodiethylmalonamide*, m. p. 135°, which gave a strong chlorine reaction. When the solution was kept for 24 hrs. before being acidified, the product was αα-diethylhydantoin (cf. G.P. 310,426; B., 1919, 389A).

Maleamide (cf. Keiser and McMaster, A., 1913, i, 253), m. p. 180°, resolidifying and melting again at 266° (decomp.) owing to conversion into fumaramide, is converted by sodium hypochlorite at 0° and decomposition after 24 hrs. into uracil.

The monoamide of maleic acid (this vol., 45), when treated with aqueous sodium hypochlorite, gave a solution which, after heating to remove hypochlorous acid, contained *sodium* β-*carboxyvinylcarbamate*, $CO_2Na{\cdot}CH{:}CH{\cdot}NH{\cdot}CO_2Na$; this with dilute sulphuric acid evolved acetaldehyde, and when treated at 0° with semicarbazide hydrochloride formed β-*semicarbazinopropionic acid*, m. p. 116° (decomp.), and with hydroxylamine hydrochloride the oximinopropionic acid.

Maleimide when treated with sodium hypochlorite gave 2 : 6-*diketodihydrometoxazine*, $CO<\begin{matrix}CH{:}CH\\O—CO\end{matrix}>NH$, m. p. 158° (decomp.), a weakly acid substance which is at once decomposed by sulphuric acid to give acetaldehyde and carbon dioxide (cf. Mohr, Kohler, and Ulrich, A., 1909, i, 649).

Heptinamide (cf. A., 1920, i, 322) with sodium hypochlorite and acetic acid yielded heptinchloroamide, which with barium hydroxide gave *n*-heptonitrile.

Methyl styrylcarbamate is not hydrogenated by aluminium, but is hydrogenated by nickel and hydrogen to methyl β-phenylethylcarbamate, m. p. 30°, b. p. 161°/10 mm., hydrolysed by acid to β-phenylethylamine (cf. Weerman and Jongkees, A., 1906, i, 665).

The difficulty of decomposition of α-substituted αβ-unsaturated amides by hypochlorous acid is noted; α-phenylcinnamamide is not readily converted into the ketone (cf. Harrison and Wood, A., 1926, 835). E. W. WIGNALL.

Phenyl-α-hydroxycrotonamide — a ketone ether-oxide hydrate. J. BOUGAULT (Bull. Soc. chim., 1927, [iv], **41**, 668—676).—See A., 1926, 167, 404, 518, 613, 725.

Pyruvic guaneide. M. GARINO and (SIGNA.) A. DAGNINO (Gazzetta, 1927, **57**, 333—334).—Ethyl pyruvate condenses with guanidine to give *pyruvic guaneide*, $NH(NH{\cdot}CO{\cdot}Ac)_2$, m. p. 122° (decomp.). E. W. WIGNALL.

Phenyl-α-chloroacetonitrile and α-bromo*iso*butyronitrile. A. CHRZASZCZEWSKA and J. POPIEL (Rocz. Chem., 1927, **7**, 74—78).—α-*Bromo*iso*butyronitrile*, b. p. 61·2—61·6°/5 mm., is prepared by the action of phosphorus tribromide on acetonecyanohydrin. R. TRUSZKOWSKI.

Unsaturated aliphatic nitriles. A. MACQ (Bull. Acad. roy. Belg., 1926, [v], **12**, 753—774; cf. A., 1922, i, 817).—By the dehydrating action of thionyl chloride on di-*n*-propyl ketone cyanohydrin, a mixture of the two geometrically isomeric α-*propyl*-Δ^{α}-*pentenonitriles* is obtained. On repeated distillation, the less stable form isomerises and homogeneous trans-α-*propyl*-Δ^{α}-*pentenonitrile*, b. p. 175·8—176°/758 mm., d_4^{20} 0·8217, n_D^{20} 1·4355, is obtained. cis-α-*Propyl*-Δ^{α}-*pentenonitrile*, b. p. 181—182°/757 mm., d_4^{20} 0·8217, n^{20} 1·4377, is obtained by isomerisation of the *trans*-form by sodium phenoxide. The configurations are assigned by analogy of stability and physical properties with those of the corresponding unsaturated acids. By fractional crystallisation of the hydrolytic

product of either of the nitriles, the isomeric *α-propyl-α-pentenamides*, m. p. 89° and 115·5°, are obtained. These also undergo isomerisation with sodium phenoxide or sulphuric acid. *cis-α-Methyl-Δ^{α}-pentenonitrile*, b. p. 137·2—137·4°/763 mm., d_4^{20} 0·8170, n_D^{20} 1·4262, *trans-α-methyl-Δ^{α}-pentenonitrile*, b. p. 156° (not obtained pure), and the geometrically isomeric *α-methyl-Δ^{α}-pentenamides*, m. p. 65·5° and 96°, are obtained in a similar way from methyl *n*-propyl ketone cyanohydrin. Since these substances mutually isomerise, isomerism due to the position of the double linking is considered improbable.

α-Ethylcrotononitrile (Henry, A., 1899, i, 568) is separated by distillation into two forms: *stable*, b p. 139·4—139·6°/755 mm., d_4^{20} 0·8232, n_D^{20} 1·4279, and *labile*, b. p. 156—157° (not obtained pure, owing to traces of chlorinated substances). The hydrolytic product of the stable nitrile yields the isomeric *α-ethylcrotonamides*, m. p. 94° (33%) and m. p. 109° (66%) (cf. Mannich and Zernik, A., 1908, i, 399).

Diisopropyl ketone cyanohydrin, m. p. 59°, b. p. 111°/18 mm., yields similarly *β-methyl-α-isopropylcrotononitrile*, b. p. 178—179°/757 mm., d_4^{20} 0·8384, n_D^{20} 1·4472. G. A. C. Gough.

Action of organo-magnesium compounds on nitriles. α-Chloronitriles. M. Theunis (Bull. Acad. roy. Belg., 1926, [v], **12**, 785—796; cf. A., 1923, i, 311; 1926, 55).—α-Chloro-*n*-valeronitrile reacts with magnesium ethyl bromide (2 mols.) to give mainly *γδ-imino-γ-ethylheptane*, $\begin{matrix}\gamma & 2\\ CH & r^{\alpha}\end{matrix}\!>\!NH$, b. p. 68—69°/11 mm. (*chloroplatinate*, m. p. 177—178°; *phenylthiocarbamate*, m. p. 79—80°), together with (?) 3 : 3 : 6 : 6-*tetraethyl*-2 : 5-*di*-n-*propylpiperazine* (3—4% by weight of the nitrile), b. p. 128—131°/11 mm. (*dihydrochloride*, m. p. 183—184°).

γδ-Imino-γ-ethylheptane yields, on treatment with nitrous acid, *γ-ethyl-Δ^{γ}-heptene* (55%), b. p. 140—141°/759 mm., d_4^{20} 0·7477, n_D^{20} 1·4276, and *γ-ethylheptyl γ-nitrite*, b. p. 100°/11 mm. γ-Ethyl-Δ^{γ}-heptene, d_4^{20} 0·7482, n_D^{20} 1·4279, is also obtained by the dehydration of γ-ethylheptan-γ-ol (from ethyl *n*-valerate and magnesium ethyl bromide). The slight difference in the physical properties is attributed to admixture, in the second case, with small amounts of γ-ethyl-Δ^{δ}-heptene.

α-Chloroisohexonitrile reacts with magnesium ethyl bromide to give *γδ-imino-ζ-methyl-γ-ethylheptane*, b. p. 71—73°/11 mm., d_4^{20} 0·8170, n_D^{20} 1·4410.

G. A. C. Gough.

***cyclo*Propane derivatives.** P. Bruylants (Bull. Soc. chim. Belg., 1927, **36**, 153—164).—Known carbinols of the type CRR′(OH)·CH$<^{CH_2}_{H}$ show a smaller molecular exaltation than expected, and 14 new cyclo*propyldialkylcarbinols*, prepared by the Grignard reaction from ethyl *cyclo*propanecarboxylate or alkyl *cyclo*propyl ketones, are now examined. The b. p., and n_D, respectively, of the carbinols are: dimethyl, 123·4—123·6°/752 mm., 0·88063, 1·43257; methylethyl, 143·4—143·8°/762 mm., 0·88565, *methylpropyl*, 163·5—163·9°/761 mm., 1·44344; *methylbutyl*, 182—183°/752 mm., 120—121°/106 mm., (d_4^{26}) 0·87447, 1·44514; diethyl, 162·9—163·1°/759 mm., 0·88782, 1·44635; ethylpropyl, 182·0—182·5°/770 mm., 0·87908, 1·44745; *ethylbutyl*, 95—96°/18 mm., 0·87642, 1·45016; *ethylamyl*, 110·5—111·5°/19 mm., 0·87232, 1·45156; dipropyl, 197·8—198·2°/762 mm., 0·87284, 1·44846; *propylbutyl*, 103—104°/14 mm., 0·87148, 1·45046; *propylamyl*, 120—121°/18 mm., 0·86785, 1·45166; *propylhexyl*, 134·5—135·5°/16 mm., 0·86555, 1·45237; *dibutyl*, 117·5—118°/14 mm., 0·87008, 1·45207; *butylamyl*, 133·5—134°/18 mm., 0·86462, 1·45317. Substitution of ethyl for methyl brings about an increase in density, the increase being less marked in the higher members of the series. Substitution of higher alkyls for ethyl decreases the density, the differences being alternately smaller and larger. In all the tertiary alcohols examined, the molecular exaltation is less than is expected in *cyclo*propane derivatives. It is suggested that methyl is less saturated than ethyl, ethyl than propyl, and so on. The "conjugation" of the alkyl groups with the *cyclo*propane ring decreases the molecular exaltation, and the decrease is less as the homologous series is ascended.

C. Hollins.

Synthesis of dicyclo-[0 : 2 : 2]-hexane. N. D. Zelinski and K. A. Kozeschkov (Ber., 1927, **60**, [*B*], 1102—1108).—*cyclo*Hexane-1 : 4-dione is reduced by sodium amalgam in aqueous suspension in presence of carbon dioxide to a mixture of the *cis-* and *trans-*diols, which is converted by fuming hydrobromic acid at 100° into *trans*-1 : 4-dibromo*cyclo*hexane, *cis*-1 : 4-dibromo*cyclo*hexane, b. p. 111°/13 mm., and an isomeric *dibromide* (probably 1 : 2- or 1 : 3-dibromo*cyclo*hexane), m. p. 48°. The *cis*-dibromide dissolved in absolute *iso*amyl ether is transformed by sodium at 170—180° into *di*cyclo-[0 : 2 : 2]-*hexane*, b. p. 78·5—79·5°/732 mm., d_4^{19} 0·8245, n_D^{20} 1·4475, and Δ^{αε}-hexadiene, characterised by conversion into the tetrabromohexanes, m. p. 53—54° and 64—65°, respectively. [In an addendum, doubts are expressed regarding the structure of the di*cyclo*-compound, since, although its physical properties are in harmony with this conception, its unusual explosivity when mixed with oxygen suggests that it is a monocyclic compound with free valencies, $-CH<_{CH^2\cdot CH^2}^{H_2}>CH-$.] The "dicyclic" compound is very readily oxidised by permanganate and is converted by bromine exclusively into the liquid dibromide. *trans*-1 : 4-Dibromo*cyclo*hexane is transformed by sodium in presence of *iso*amyl ether mainly into Δ$^{1:3}$-*cyclo*hexadiene mixed with Δ^{αε}-hexadiene; the "dicyclic" compound is not produced.

H. Wren.

Piperidine as a general reagent for the determination of the constitution of halogenonitro-compounds. Nitration of 4 : 4′-dihalogeno-diphenylmethane and -*s*-diphenylethane. R. J. W. Le Fevre and E. E. Turner (J.C.S., 1927, 1113—1122).—Piperidine reacts more readily with labile halogen atoms in aryl halogenonitro-derivatives than do other reagents, and the resulting piperidino-compounds are usually crystalline, and are obtained free from by-products. The use of sodium acetate in the preparation of piperidino-derivatives is unsatisfactory, better results being obtained using piperidine

alone in the cold or at 100°. Thus from the appropriate halogen compounds are obtained: 3 : 3′-*dinitro*-4 : 4′-*dipiperidinodiphenylsulphone*, m. p. 183·5°; 4-*bromo*-2-*nitropiperidinobenzene*, m. p. 48—49°; 1-*nitro*-2 : 4-*dipiperidinobenzene*, m. p. 67—68°; 2-*chloro*-4-*nitropiperidinobenzene*, m. p. 47—48°; 4 : 5-*dichloro*-1-*nitro*-2-*piperidinobenzene*, m. p. 64—65°, which is obtained by the action of piperidine on either 1 : 2-dichloro-4 : 5-dinitrobenzene (best prepared by the nitration of 3 : 4-dichloronitrobenzene, separated from the nitration products of *o*-dichlorobenzene) or 2 : 4 : 5-trichloro-1-nitrobenzene; 5-*nitro*-2-*piperidinobenzoic acid*, m. p. 201—202° (*ethyl* ester, m. p. 78—79°); *ethyl* 3-*nitro*-4-*piperidinobenzoate*. Contrary to the observations of Borsche and Bahr (A., 1914, i, 28), both the chlorine atoms in 1 : 3-dichloro-4 : 6-dinitrobenzene are equally reactive, since in presence of a slight excess of piperidine 4 : 6-*dinitro*-1 : 3-*dipiperidinobenzene*, m. p. 130—131°, is formed, care being required to stop the reaction at the formation of 3-chloro-4 : 6-dinitropiperidinobenzene, which, moreover, readily reacts with aniline to yield 4 : 6-*dinitro*-3-*anilino*-1-*piperidinobenzene*, m. p. 148—148·5°. 1 : 3 : 5-Tribromo-2 : 4-dinitrobenzene reacts with 2 mols. of piperidine to yield 1 : 3-*dibromo*-2 : 4-*dinitro*-5-*piperidinobenzene*, m. p. 125—126°, whilst with an excess of piperidine it yields 2 : 4-dinitro-1 : 3 : 5-tripiperidinobenzene, m. p. 177—178° (Borsche and Trautner, A., 1926, 390, give 147—148°). 4 : 4′-Dichlorodiphenylmethane (conveniently obtained by the Sandmeyer reaction on the 4 : 4′-diamino-compound) on nitration yields 4 : 4′-*dichloro*-3 : 3′-*dinitrodiphenylmethane*, m. p. 198—199°, which with piperidine yields 3 : 3′-*dinitro*-4 : 4′-*dipiperidinodiphenylmethane*, m. p. 183—184°. 4 : 4′-Dibromo-*s*-diphenylethane on nitration yields 4 : 4′-*dibromo*-3 : 3′-*dinitro*-*s*-*diphenylethane*, m. p. 204°, from which a *dipiperidino*-compound, m. p. 235—240°, is similarly obtained. Piperazine reacts with 1-chloro-2 : 4-dinitrobenzene to yield 1 : 4-*di*-op-*dinitrophenylpiperazine*, m. p. 240° (decomp.), and with the trinitrochlorobenzene to yield 1 : 4-*di*-oop-*trinitrophenylpiperazine*, not melting at 260°. 4 : 4′-Dibromo-3 : 3′-dinitrodiphenyl reacts with piperazine to yield a *monopiperazine* derivative, m. p. 215°, and with benzidine to yield a *compound*, $C_{24}H_{17}O_4N_4Br$, m. p. 251°; in neither case was a Kaufler type of compound produced. J. W. Baker.

Aromatic fluoro-compounds. I. Preparation. G. Balz and G. Schiemann (Ber., 1927, **60**, [*B*], 1186—1190).—The necessary amine is diazotised in acid solution and the diazonium fluoborate is precipitated by 40% hydrofluoboric acid. The fluoborate is collected, washed successively with acid, alcohol, and ether, and dried. It is then gently heated in a glass flask, when it decomposes into nitrogen, boron trifluoride, and the aromatic fluoro-compound. The diazonium fluoborates are generally very stable substances, which may frequently be crystallised from warm water. They are not explosive. The following substances are described: *phenyldiazonium fluoborate*, decomp. 121—122° after darkening at 80°, d_4^{25} 1·53, and fluorobenzene, b. p. 85°/760 mm.; p-*tolyldiazonium fluoborate*, decomp. 110°, d_4^{25} 1·48; m-*xylyldiazonium fluoborate*, decomp. 108°, d_4^{25} 1·50, and 4-fluoro-*m*-xylene, b. p. 143—144°/749 mm.; α-*naphthyldiazonium fluoborate*, decomp. 113°, and α-fluoronaphthalene, b. p. 110°/17 mm., 215°/758 mm.; *diphenylene*-4 : 4′-*bisdiazonium fluoborate*, decomp. 157° after darkening at 130°, d_4^{25} 1·73, and 4 : 4′-difluorodiphenyl, m. p. 94—95°, d_4^{25} 1·328; o-, m-, and p-*nitrophenyldiazonium fluoborates*, decomp. 135°, 178°, and 156°, respectively, d_4^{25} 1·69, 1·66, 1·66, respectively, and *p*-fluoronitrobenzene.

H. Wren.

Disulphonation of *m*-dichlorobenzene and *s*-trichlorobenzene. W. Davies and H. G. Poole (J.C.S., 1927, 1122—1124).—When *m*-dichlorobenzene is heated with fuming sulphuric acid (45% SO_3) at 140—150° for 5 hrs. it yields 1 : 3-*dichlorobenzene*-4 : 6-*disulphonic acid* (*amide*, m. p. 276°; *potassium* salt $+0{\cdot}25H_2O$), which yields a disulphonyl chloride identical with that obtained by the action of phosphorus pentachloride on 1 : 3-dihydroxybenzene-4 : 6-disulphonic acid (Pollak and Weinerberger, A., 1915, i, 529). *s*-Trichlorobenzene on sulphonation yields *s*-*trichlorobenzenedisulphonic acid* (*amide*, m. p. 248°; *sodium*, *potassium*, and *barium* salts; *disulphonyl chloride*, m. p. 161·5°). The chlorine atoms in these sulphonic acids are unattacked by boiling potassium hydroxide solution. J. W. Baker.

Mechanism of the production of diphenyl from benzene. G. Pyl (Ber., 1927, **60**, [*B*], 1133—1134).—The formation of diphenyl from benzene in a sealed tube at 300° and its non-production at this temperature under atmospheric pressure is regarded as evidence in favour of the initial production of dihydrodiphenyl, since this change is accompanied by contraction in volume. A direct dissociation into phenyl and hydrogen involves an increase in volume. H. Wren.

Fluorene derivatives. C. Courtot and C. Vignati (Compt. rend., 1927, **184**, 1179—1181; cf. this vol., 234, 348).—Direct chlorination of fluorene in chloroform at 0—5° yields a mixture of 2-chlorofluorene and 2 : 7-dichlorofluorene, yielding, on oxidation, 2-chlorofluorenone and 2 : 7-dichlorofluorenone. Reduction of these compounds by zinc and alcoholic ammonia gives 2-*chlorofluorenol*, m. p. 142°, and 2 : 7-*dichlorofluorenol*, m. p. 154—155°. Nitration of the mixture of chlorofluorenes in acetic acid at 70—80° gives 2-*chloro*-7-*nitrofluorene*, m. p. 237°, leaving the dichloro-compound unattacked. Reduction of the nitro-derivative with zinc and alcoholic ammonia gives 2-*chloro*-7-*aminofluorene*, m. p. 134°, whilst oxidation yields 2-*chloro*-7-*nitrofluorenone*, m. p. 230°. The last-named compound is reduced by ammonium sulphide to 2-*chloro*-7-*aminofluorenone*, m. p. 203—205°, and by zinc dust to 2-*chloro*-7-*aminofluorenol*, m. p. 198—200°.

M. Clark.

Polymerisation of indene. Tetraindene. H. A. Bruson (Ber., 1927, **60**, [*B*], 1094—1096).—Indene is transformed when heated in a sealed tube for 25 hrs. at 260° into non-crystalline *tetraindene*, m. p. 100—110° according to the rate of heating, which, when more strongly heated under atmospheric pressure or in a high vacuum, is decomposed into indene, hydrindene, and truxene. H. Wren.

Synthesis of triphenyl. J. VON BRAUN (Ber., 1927, **60**, [*B*], 1180—1181).—The addition of *cyclo*hexyl bromide to a mixture of benzene and carbon disulphide containing a very small proportion of aluminium bromide gives *cyclo*hexylbenzene and p-*dicyclohexylbenzene*, m. p. 100°. The latter compound is not conveniently dehydrogenated by lead oxide or sulphur, but is transformed by bromine at 160° into triphenyl. H. WREN.

Jackson and White's synthesis of phenanthrene. J. KENNER and J. WILSON (J.C.S., 1927, 1108—1112).—The action of *o*-bromobenzyl bromide on hydrazine hydrate in alcohol yields *di*-o-*bromobenzylhydrazine* isolated as its *hydrochloride*, m. p. 214° (*benzylidene* derivative, m. p. 116°), and *tri*-o-*bromobenzylhydrazine hydrochloride*, m. p. 194°, which is readily oxidised in boiling alcoholic solution by cupric oxide or gradually by atmospheric oxygen to o-*bromobenzylidenedi*-o-*bromobenzylhydrazine*, m. p. 108°, which is, therefore, usually a product of the original reaction (cf. Busch and Weiss, A., 1900, i, 699). Tribenzylhydrazine hydrochloride is similarly oxidised to benzylidenedibenzylhydrazine, but dibenzylhydrazine does not undergo atmospheric oxidation. When the dibromodibenzylhydrazine is treated with yellow mercuric oxide, an almost quantitative yield of 2 : 2′-*dibromodibenzyl*, m. p. 84·5°, is obtained, and this, when refluxed in dry ether with sodium powder for 14 days, yields dibenzyl in more than 50% yield, together with phenanthrene and its dihydro-derivative, a 12% yield of phenanthraquinone being obtained on oxidation. These results are in agreement with the view that dibromodibenzyl rather than ditolyl is the intermediate in Jackson and White's synthesis (A., 1881, 822) of phenanthrene. The salt, m. p. 202°, described by Busch and Weiss (*loc. cit.*, who give the m. p. 200°) as the dihydrochloride of dibenzylhydrazine, is shown to be the *monohydrochloride*. J. W. BAKER.

Aluminium amalgam as an agent for the reduction of benzenesulphonyl chlorides to thiophenols. E. GEBAUER-FULLNEG (J. Amer. Chem. Soc., 1927, **49**, 1386—1387).—Benzenesulphonyl chlorides can be reduced to thiophenols by treatment with 1½ parts of aluminium amalgam (Wislicenus, A., 1896, i, 671) in alcohol–ether solution, the necessary water being added gradually. Yields of 50—70% of thiophenols were obtained from 2 : 5-dichlorobenzenesulphonyl chloride, naphthalene-β-sulphonyl chloride, and acetanilide-*p*-sulphonyl chloride. F. G. WILLSON.

Chlorination of anilides; directing influence of the acylamido-group. K. J. P. ORTON and A. E. BRADFIELD (J.C.S., 1927, 986—997; cf. *ibid.*, 1909, **95**, 1056; 1911, **99**, 1185, 1369).—Previous experiments on the chlorination of acylanilides have been repeated using a method which avoids dilution of the solvent during the reaction. Acetanilide is chlorinated by means of *p*-toluenesulphondichloroamide or acetchloroamide, or by direct transformation of *N*-chloroacetanilide in presence of 0·1 mol. of hydrogen chloride at 20° in (*a*) chloroform, (*b*) acetic acid (99·7%), (*c*) acetic acid (50%), and (*d*) methyl alcohol. After hydrolysis and steam distillation, the mixture of bases is reacetylated. The product, analysed by the f.-p. method and by fractional sublimation at 50—60°, which quantitatively removes *o*-chloroacetanilide, contains (*a*) 68·8%, (*b*) 67·5%, (*c*) 60·7%, and (*d*) 60·6%, respectively, of *p*-chloroacetanilide, the remainder being entirely *o*-derivative. When other acyl derivatives are chlorinated by the same method in 99·7% acetic acid, formanilide, benzanilide, and benzenesulphonanilide give mixtures containing 69·9%, 69·6%, and 65·0%, respectively, of *p*-derivative. Since the proportion *o*/*p* is only slightly affected by the nature of the acyl group, the velocity of chlorination affords a measure of the *o*- or *p*-directing power of the acylamido-group. Measurement of the velocity of chlorination of (*a*) benzanilide, (*b*) acetanilide, (*c*) formanilide, and (*d*) benzenesulphonanilide in 99·0% acetic acid gives the order (*a*) > (*b*) > (*c*), whereas from theoretical considerations (cf. Robinson, A., 1926, 397; Ingold, A., 1926, 833) which indicate that the directing power should increase as the strength of the acid corresponding with the acyl radical decreases, the order (*b*) > (*a*) > (*c*) was expected. Increase in the amount of hydrochloric acid present increases the velocity of chlorination of (*c*) and (*d*) and decreases that of (*b*). An attempt is made to explain the unexpectedly high directive power of the group $R{\cdot}SO_2NH$. H. E. F. NOTTON.

Anhydrides of *N*-carboxylic derivatives of α-amino-acids. IV. F. WESSELY and M. JOHN (Monatsh., 1927, **48**, 1—7).—The action of primary and secondary amines on α-amino-*N*-carboxylic anhydrides (Wessely, A., 1925, i, 1151) in which the basic character of the amino-group is not reduced by a substituent phenyl group, yields only high-molecular, peptide-like products, instead of the amide of the amino-acid. To overcome this difficulty, the picrates of aniline and methylaniline are employed instead of the free bases, and thus good yields of the picrates of the anilides of the corresponding amino-acids are obtained. Mol.-wt. determinations show the existence of the equilibrium aniline picrate aniline + picric acid, and it is assumed that the latter forms salts with the basic amino-group produced by hydrolysis of the anhydride and prevents further condensation to high-molecular products. Thus from phenylalanine-*N*-carboxylic anhydride are obtained the *picrates* of phenylalanineanilide, m. p. 242° (decomp.), and phenylalaninemethylanilide, m. p. 231° (decomp.). On decomposition with ammonia, these yield the free *anilide*, m. p. 80·5° (corr.) (*hydrochloride*, m. p. 212°), and *methylanilide*, oily [*naphthalene*-β-*sulphonyl* derivative, m. p. 190° (corr.)]. By similar methods, from sarcosine- and glycine-*N*-carboxylic anhydrides are obtained the *picrates* of sarcosinemethylanilide, m. p. 163°, glycinemethylanilide, decomp. 184°, and glycineanilide, m. p. 182·5°. Similarly, treatment of the anhydrides in alcohol with picric acid yields the picrates of the esters of the amino-acids, and thus are obtained the picrates of the ethyl esters of glycine and sarcosine. J. W. BAKER.

Destruction of amino-acids by irradiation. F. LIEBEN (Biochem. Z., 1927, **184**, 453—473).—The oxidation of tyrosine and tryptophan in the light of the mercury-vapour quartz lamp is increased by

sensitisers (hæmatoporphyrin or rose-Bengal). There is some effect in diffuse daylight with these sensitisers. The relations to intensity and duration of illumination, to the concentration and depth of the solution irradiated, and to the alkalinity are defined. The effects on melanin formation by light in presence of hydrogen peroxide, nitrite, and formaldehyde have been investigated. Similar studies on histidine and dihydroxyphenylalanine are reported. The reaction with ferric chloride of adrenaline and dihydroxyphenylalanine is exploited for the colorimetric determination of these substances. Protracted *X*-irradiation or exposure to radium of tyrosine solutions led to slight oxidation. R. K. CANNAN.

Action of alkali hydroxides on 3-halogeno-4-nitrosodimethylanilines. H. H. HODGSON and J. S. WIGNALL (J.C.S., 1927, 1144—1146).—3-Chlorodimethylaniline and 3-bromodimethylaniline, b. p. 245° (Wurster, A., 1879, 107, gives b. p. 259°), are obtained at 165°, and 3-*iododimethylaniline*, b. p. 215—216°/190 mm., at 175° when the corresponding 3-halogenoanilines are heated with methyl sulphate and methyl alcohol. 3-Chloro-4-nitrosodimethylaniline, m. p. 130° (decomp.), and 3-bromo-4-nitrosodimethylaniline, m. p. 129° (decomp.), for which various m. p. have been quoted (A., 1919, i, 320), are smoothly converted by boiling 10% sodium or potassium hydroxide into dimethylamine and 3-chloro- and 3-bromo-*p*-benzoquinone-4-oximes (cf. A., 1925, i, 1408), respectively. 3-*Iodo*-4-*nitrosodimethylaniline*, m. p. 128° (decomp.), is decomposed with loss of iodine by similar treatment, yielding compounds of indefinite character. H. E. F. NOTTON.

Basic character of acetoxylidides and its influence on the course of their substitution. H. E. DADSWELL and J. KENNER (J.C.S., 1927, 1102—1108).—Acetyl derivatives of xylidines and of mesidine form salts with mineral acids which are stable in fairly strong acid solutions. This salt formation is shown to influence the course of substitution in derivatives of 2 : 6- and 2 : 4-dimethylaniline, but the results do not conform to any general rule. *Aceto*-m-2-*xylidide hydrobromide* and *nitrate*, *aceto*-4-m-*xylidide hydrobromide* and *hydrochloride*, and the *hydrobromides* of *aceto*-p-, *aceto*-o-3-, and *aceto*-o-4-($+H_2O$)-*xylidides* and of *acetomesidide* are described. Bromination of aceto-*m*-2-xylidide in chloroform yields exclusively the 5-bromo-derivative, in glacial acetic acid (cf. Noeltling, A., 1901, i, 588) a little of the 4-bromo-derivative is also formed, whilst in sulphuric or 47% hydrobromic acid only the latter is obtained. It was identified by hydrolysis to 4-bromo-*m*-2-xylidine (m-*nitrobenzoyl* derivative, m. p. 170—171°). Bromination of *m*-2-xylidine in glacial acetic acid yields 5-bromo-*m*-2-xylidine (88% of theoretical) (m-*nitrobenzoyl* derivative, m. p. 186—187°), which is also the main product in 47% hydrobromic acid. 4-*Chloro*-2-*nitro*-m-*xylene*, m. p. 72—73°, from 2-nitro-*m*-4-xylidine, is reduced by tin and hydrochloric acid to 4-*chloro*-m-2-*xylidine*, b. p. 136—138°/17 mm. (*acetyl* derivative, m. p. 146—147°). ɔ-*Chloro*-2-*nitro*-m-*xylene*, m. p. 44—45°, gives 5-*chloro*-m-2-*xylidine*, m. p. 44—45° (*acetyl* derivative, m. p. 195°). The latter is formed in small yield when *m*-2-xylidine is chlorinated in glacial acetic acid. Although m-*nitrobenzo*-m-2-*xylidide*, m. p. 188—189°, shows no basic properties, it gives m-*nitrobenzo*-4-*nitro*-m-2-*xylidide*, m. p. 170·5°, when nitrated, instead of the expected 5-nitro-derivative. 6-Bromoaceto-*m*-4-xylidide is formed from aceto-*m*-4-xylidide and bromine in chloroform, glacial acetic acid, or hydrobromic acid. m-*Nitrobenzo*-m-4-*xylidide*, m. p. 162—163°, and nitric acid (*d* 1·42) at 5—10° afford m-*nitrobenzo*-5-*nitro*-m-4-*xylidide*, m. p. 210—211°, but in presence of sulphuric acid m-*nitrobenzo*-6-*nitro*-m-4-*xylidide*, m. p. 224—225°, is obtained. H. E. F. NOTTON.

Higher substitution products of 4-aminodiphenyl. H. A. SCARBOROUGH and W. A. WATERS (J.C.S., 1927, 1133—1140; cf. this vol., 236).—3-Chloro-4-aminodiphenyl and 3-nitro-4-aminodiphenyl readily undergo 5-substitution at the ordinary temperature and 5 : 4′-substitution on more vigorous treatment. The corresponding acetyl derivatives are substituted only with difficulty, the 4′-position being first attacked. It is suggested that the latter is a direct process, whereas 5-substitution takes place by way of the side-chain. Attempts to prepare derivatives of 4-*diacetamidodiphenyl*, m. p. 121°, and 4-*phthalimidodiphenyl*, m. p. 288° (from 4-aminodiphenyl and phthalic anhydride at 160°), in which indirect substitution is impossible, were frustrated by hydrolysis or complete decomposition. The former is converted by nitric acid (*d* 1·4) at 0° into 3-nitro-4-acetamidodiphenyl and 3 : 4′-dinitro-4-acetamidodiphenyl. Bromination of 3-chloro-4-aminodiphenyl in *glacial* acetic acid yields 3-*chloro*-ɔ-*bromo*-4-*aminodiphenyl*, m. p. 107° (all m. p. corr.) (*benzoyl* derivative, m. p. 222°). Deamination affords 3-*chloro*-5-*bromodiphenyl*, m. p. 29°, b. p. 22ɔ°/30 mm. [(*a*) product obtained by oxidation with chromic anhydride in acetic acid, 3-chloro-5-bromobenzoic acid]. Further bromination in boiling acetic acid yields 3-*chloro*-5 : 4′-*dibromo*-4-*aminodiphenyl*, m. p. 129° (*diacetyl* derivative, m. p. 147°). 3-Chloro-4-acetamidodiphenyl is brominated in presence of sodium acetate and pyridine at 100° to 3-*chloro*-4′-*bromo*-4-*acetamidodiphenyl*, m. p. 185° [(*a*) *p*-bromobenzoic acid], which is hydrolysed to 3-*chloro*-4′-*bromo*-4-*aminodiphenyl*, m. p. 108°. Nitration of 3-chloro-4-acetamidodiphenyl with nitric acid (*d* 1·4) at the ordinary temperature gives 3-*chloro*-4′-*nitro*-4-*acetamidodiphenyl*, m. p. 220·5° [(*a*) *p*-nitrobenzoic acid], and with nitric acid (*d* 1·5) 3-*chloro*-5 : 4′-*dinitro*-4-*acetamidodiphenyl*, m. p. 250° [(*a*) not attacked]. 3-Nitro-4-aminodiphenyl is brominated in glacial acetic acid to 3-*bromo*-5-*nitro*-4-*aminodiphenyl*, m. p. 99—101°, which contains traces of more highly brominated compounds. This base is converted on deamination into 3-*bromo*-ɔ-*nitrodiphenyl*, m. p. 72°, b. p. 240—250°/30 mm. [(*a*) 3-bromo-5-nitrobenzoic acid], and on further bromination at 100° into 5 : 4′-*dibromo*-ɔ-*nitro*-4-*aminodiphenyl*, m. p. 158° [(*a*) *p*-bromobenzoic acid], which is also formed on prolonged treatment of 3-nitro-4-acetamidodiphenyl with excess of bromine in glacial acetic acid. Chlorination of 3-nitro-4-acetamidodiphenyl in boiling acetic acid containing sodium acetate yields 4′-*chloro*-3-*nitro*-4-*acetamidodiphenyl*, m. p. 199° [(*a*) *p*-chlorobenzoic acid], which is hydrolysed to 4′-*chloro*-3-*nitro*-4-

aminodiphenyl, m. p. 174°; whilst bromination in presence of pyridine and sodium acetate at 100° yields 4′-bromo-3-nitro-4-acetamidodiphenyl (cf. Le Fevre and Turner, A., 1926, 1029), and nitration with nitric and sulphuric acids at 0°, 3 : 4′-*dinitro*-4-*acetamidodiphenyl*, m. p. 243—244° [(*a*) *p*-nitrobenzoic acid], erroneously described by Fichter and Sulzberger (A., 1904, i, 325) as 3 : 5-dinitro-4-acetamidodiphenyl. H. E. F. NOTTON.

Diphenyl series. V. Derivatives of 4-amino- and 4-hydroxy-diphenyl. F. BELL and P. H. ROBINSON (J.C.S., 1927, 1127—1133).—Methylation of p-*toluenesulphon*-2-*nitroanilide*, m. p. 110°, with methyl sulphate gives 2-*nitro*-1-p-*toluenesulphonmethylanilide*, m. p. 126°, which is also obtained together with the corresponding 4-nitro-derivative by nitrating *p*-toluenesulphonmethylanilide. 3-Nitro-4-methylaminodiphenyl (Garcia Banus, A., 1922, i, 333) is conveniently prepared by the hydrolysis of 3-*nitro*-4-p-*toluenesulphonmethylamidodiphenyl*, m. p. 157°, obtained by nitrating 4-*p*-toluenesulphonmethylamidodiphenyl. Like 3 : 5-dinitro-4-methylaminodiphenyl (A., 1926, 1241), it readily forms an *acetyl* derivative, m. p. 89°, the constitution of the former being accordingly confirmed. With nitrous acid it gives 3-*nitro*-4-*nitrosomethylaminodiphenyl*, m. p. 87°, which is converted into 3 : 5-dinitro-4-nitrosomethylaminodiphenyl by nitration. 3 : 3′-*Dinitro*-4 : 4′-*di*-p-*toluenesulphonamidodiphenyl*, m. p. 220°, from 4 : 4′-di-*p*-toluenesulphonamidodiphenyl and nitric acid (*d* 1·4), is hydrolysed to 3 : 3′-dinitrobenzidine. The directive actions of the *p*-toluenesulphonamido- and acetamido-groups are therefore similar. Bromination of 3-nitro-4-acetamidodiphenyl in acetic acid yields (5 ?)-*bromo*-3-*nitro*-4-*acetamidodiphenyl*, m. p. 94—95°, (5 ? : 4′)-*dibromo*-3-*nitro*-4-*acetamidodiphenyl*, m. p. 153°, which is also obtained by brominating 4′-bromo-3-nitro-4-acetamidodiphenyl, and a trace of a *compound*, m. p. 210—213°. 4′-*Bromo*-4-*hydroxydiphenyl*, m. p. 164—166°, is prepared from 4′-bromo-4-aminodiphenyl (cf. Le Fevre and Turner, A., 1926, 1029) (p-*toluenesulphonyl* derivative, m. p. 174°). When brominated in chloroform, it yields successively 3 : 4′-*dibromo*-4-*hydroxydiphenyl*, m. p. 117° (o-*nitro*-derivative, m. p. 189°), and 3 : 5 : 4′-*tribromo*-4-*hydroxydiphenyl*, m. p. 159°. Continued action of bromine on 4-hydroxydiphenyl in chloroform gives 3-*bromo*-4-*hydroxydiphenyl*, m. p. 96°, 3 : 5-dibromo-4-hydroxydiphenyl, m. p. 91—94° (Raiford and Colbert, A., 1925, i, 808, give m. p. 96°), and finally 3 : 5 : 4′-tribromo-4-hydroxydiphenyl. The last is converted by nitrous acid into 3 : 4′-dibromo-5-nitro-4-hydroxydiphenyl (above). 5-*Bromo*-3-*nitro*-4-*hydroxydiphenyl*, p. 76°, and 3 : 5-dinitro-4-hydroxydiphenyl are among the products formed by treating 3 : 5-dibromo-4-hydroxydiphenyl with nitrous acid, but the di romonitrophenol, m. p. 171°, which Raiford and olbert (*loc. cit.*) claim to have obtained in this way, could not be isolated. Nitration of 3-bromo-4-yaroxydiphenyl in acetic acid furnishes 3 : 5-di i ro-4-hydroxydiphenyl, 5-bromo-3-nitro-4-hydroxy- ip enyl, and a little 5-*bromo*-3 : 4′-*dinitro*-4-*hydroxy- p enyl*, m. p. 218°, which is also obtainable by nitrating 3-bromo-4′-nitro-4-hydroxydiphenyl. 4′-Nitro-4-hydroxydiphenyl and bromine in boiling chloroform afford 3-*bromo*-4′-*nitro*-4-*hydroxydiphenyl*, m. p. 132°. H. E. F. NOTTON.

Organo-metallic syntheses of triphenylamine and triphenylmethane derivatives. W. MADELUNG, E. REISS, and E. HERR (Annalen, 1927, **454**, 1—6).—The original Bindschedler's green, $NMe_2{\cdot}C_6H_4{\cdot}N{:}C_6H_4{:}NMe_2Cl,ZnCl_2$, reacts with magnesium phenyl bromide in a similar way to the quinoxalinium and phenazonium compounds of Freund (A., 1909, i, 417), giving pp′-*tetramethyldiaminotriphenylamine* (15—20% yield), m. p. 157° [*perchlorate*, $C_{22}H_{17}N_3(ClO_4)_2$; *methiodide*, m. p. 180° (decomp.)], besides diphenyl and *pp′*-tetramethyldiaminodiphenylamine (*ethiodide*, m. p. 210°). Aralkyl and alkyl Grignard reagents act as reducing agents, yielding only the latter compound. Crystal-violet and malachite-green are recovered unchanged from solutions containing magnesium phenyl bromide, whilst the zinc chloride double salt of *pp′*-tetramethyldiaminobenzhydrol is converted into leuco-malachite-green. H. E. F. NOTTON.

Relation between blue additive compounds and blue oxidation products of substituted di- and tri-phenylamines. W. MADELUNG, E. REISS, and E. HERR (Annalen, 1927, **454**, 7—37).—Evidence is adduced in favour of the view that the development of a blue colour when solutions of di- and triphenylamine derivatives are treated with oxidising agents is not primarily accompanied by oxidation or formation of quinonoid substances (cf. Wieland, A., 1907, i, 1076; 1910, i, 242). For example, the following consecutive reactions between triphenylamine and chromyl chloride have been followed : (*a*) formation of a blue equimolecular additive product, from which the base is recovered unchanged, (*b*) oxidation to tetraphenylbenzidine, and (*c*) formation of a stable blue chromyl chloride derivative of the latter. Nitrogen dioxide and triphenylamine give trinitrotriphenylamine. *Compounds* of *pp′*-tetramethyldiaminodiphenylamine with antimony pentachloride, $C_{16}H_{21}N_3,SbCl_5$, and with stannic chloride, $(C_{16}H_{21}N_3)_2,SnCl_4$, are described. *pp′*-Tetramethyldiaminotriphenylamine (cf. preceding abstract) gives dark blue additive *compounds* which are not decomposed by water or dilute acids, with antimony pentachloride, $C_{22}H_{25}N_3,SbCl_5$; stannic chloride, $(C_{22}H_{25}N_3)_2,SnCl_4$; thallic chloride, $C_{22}H_{25}N_3,TlCl_3$, and cupric chloride, $C_{22}H_{25}N_3,CuCl_2$; also less stable compounds with nitrogen dioxide, bromine, chromyl chloride, sulphur trioxide, and other highly oxidised substances, from all of which it may be recovered unchanged. Initially non-conducting cold aqueous solutions of the stable ferric chloride *derivative*, $C_{22}H_{25}N_3,FeCl_3$, rapidly increase in conductivity on keeping, and the three chlorine atoms become ionised. The blue colour of the solution, and consequently the mode of combination of the base, remains unchanged. Ferric ions are not present, since the product gives a colourless precipitate with potassium ferrocyanide, which decomposes on warming into ferric ferrocyanide and free base. The oxidising power of the compound is that of the ferric chloride it contains. It is suggested

that a co-ordinated complex, $\left[\begin{matrix}C_{22}H_{25}N_3 \\ 2H_2O\end{matrix}\!\!>\!\!FeCl_3\right]$, is first formed, the chlorine atoms of which are subsequently displaced into the outer zone by water. A second blue co-ordinated iron *derivative*, $[C_{22}H_{25}N_3,Fe(CN)_5]H_2,3H_2O$, in which the base replaces a cyanogen radical, is obtained with hydroferricyanic acid. It is converted by hydrocyanic acid into the green *ferricyanide*, $C_{22}H_{25}N_3,H_3Fe(CN)_6,3H_2O$. Since the colour of these additive products is independent of the nature of the inorganic component, they are all probably similarly constituted. The aminium salt formula proposed by Weitz and Schwechten (this vol., 49, 351) for the corresponding tri-*p*-tolylamine derivatives cannot apply to the above non-ionised ferric chloride compound, and these authors' compounds are better regarded as co-ordinated complexes in which the base functions as an ammine. The constitution of the base in the additive compound thus remains formally unchanged, and the production of the blue colour is due to an excitation of the molecule as a whole, induced by the high energy content of the inorganic component (cf. A., 1925, i, 1459). H. E. F. Notton.

Action of peracetic acid on acetyl derivatives of aromatic amines. D. Bigiavi (Atti R. Accad. Lincei, 1927, [vi], 5, 587—591).—Oxidation of aromatic amines by peracetic acid yields the corresponding nitro- and azoxy-compounds, but under similar conditions the acetyl derivatives of primary aromatic amines mostly give only the nitro-compounds. Apparently the acetyl group is detached only after the nitrogen has undergone oxidation and as a result of a perhydrolysis, $\cdot NHAc \longrightarrow \cdot NAc\cdot OH \longrightarrow \cdot N(OH)_2 + Ac\cdot OH$; the nitroso-compound thus formed is then rapidly oxidised to nitro-compound and, in the absence of arylhydroxylamine, cannot give the azoxy-derivative.

The action of peracetic acid on *p*-acetamidoazobenzene at 50—60° for some days gives the two *p*-nitroazoxybenzenes, m. p. 148° and 153°, but the principal products of the reaction are the acetyl derivatives of the two isomeric aminoazoxybenzenes: (1) $O{:}NPh{:}N\cdot C_6H_4\cdot NH_2$, m. p. 136°, the acetyl compound of which has m. p. 151° (Passerini, A., 1921, i, 624, gave 166°), and (2) $NPh{:}NO\cdot C_6H_4\cdot NH_2$, m. p. 133° (Passerini, 114°); the acetyl compound has m. p. 172° (Passerini, 143°). Aminoazoxybenzene (1) gives an *iso*diazotate, is unstable towards permanganate, condenses readily with nitrosobenzene, has slight dyeing properties, and is not reduced by stannite at the ordinary temperature; isomeride (2) gives an *iso*diazotate, is stable towards permanganate, condenses slowly with nitrosobenzene, has no dyeing properties, and is reduced by stannite. The fact that *p*-aminoazobenzene, dimethylaminoazobenzene, and *pp'*-diaminoazobenzene give intensely coloured salts with hydrochloric and sulphuric acids, whereas the two isomeric *p*-aminoazoxybenzenes form colourless salts, may be related to the impossibility of the latter salts being derived from a quinonoid form of the molecule. T. H. Pope.

Free ammonium radicals. IX. Ammonium character of the tetra-arylhydrazines. E. Weitz and H. W. Schwechten (Ber., 1927, 60, [*B*], 1203—1216; cf. this vol., 351).—The analogy between the tetra-arylhydrazines and hexa-arylethanes is incomplete, since the nitrogen atom of the former is not exerting its maximum valency. The extra attraction of the aryl groups is such that the nitrogen atom becomes quadrivalent and the hydrazine behaves as an ammonium radical. Confirmation of this view is found in the observation that tetra-*p*-tolylhydrazine is converted by iodine and silver perchlorate in presence of ether into *tetra*-p-*tolylhydrazinium perchlorate*, $[(C_7H_7)_2N\cdot N(C_7H_7)_2]ClO_4$, a somewhat unstable, blackish-violet, crystalline powder which liberates iodine from potassium iodide with re-formation of tetra-*p*-tolylhydrazine and has pronounced oxidising properties. Titrimetric reduction of it (and of tri-*p*-tolylaminium perchlorate) is conveniently effected with the dimeric *N*-alkylcollidinium radical in organic solvents. Only the monoperchlorate is produced when an excess of chlorine tetroxide is employed. Tetra-*p*-tolylhydrazine is converted by non-oxidising acids into dark violet compounds (cf. Wieland, A., 1907, i, 1076) which contain the hydrazinium salt, since after neutralisation of the acid by sodium acetate they immediately liberate iodine from potassium iodide. Tetra-*p*-tolylhydrazine behaves therefore towards acids as a "metal-like" ammonium radical, displacing hydrogen, which is utilised in the reduction of a portion of the hydrazine to di-*p*-tolylamine contained in the product as the corresponding salt. If neutralisation of the acid is omitted, the action of potassium iodide on the product results ultimately in the complete conversion of tetra-*p*-tolylhydrazine into di-*p*-tolylamine. Other reducing agents behave similarly in acid solution; with stannous chloride, the colour persists until 2 or 3 equivalents of the reagent have been used for 1 mol. of (originally used) free hydrazine or 1 mol. of hydrazinium salt and all the hydrazine has been converted into di-*p*-tolylamine. With glacial acetic acid or picric acid in benzene or chloroform, tetra-*p*-tolylhydrazine forms hydrazinium salts very slowly; the dark violet coloration is, however, developed immediately after addition of lead dioxide or lead tetra-acetate.

The tetra-arylhydrazines have a dual character, the intact hydrazine being a cation radical, whereas the diarylnitrogen radical derived from it is anionic, the character being illustrated by di-*p*-tolylaminotetramethylammonium (Schlenk and Holtz, A., 1917, i, 262), which in pyridine conducts electricity like a salt. Tetra-arylhydrazines are therefore potentially amphoteric. It thus appears possible for tetra-arylhydrazines to react with suitable salts, with the production of violet tetra-arylhydrazinium salts and of a compound derived from diarylamine and the metal or salt residue. The complex salts obtained by Wieland from tetra-arylhydrazines and antimony pentachloride, phosphorus pentachloride, and stannic and ferric chlorides (*loc. cit.*) are therefore regarded as hydrazinium salts of complex chloro-acids, *e.g.*, $[Ar_2N\cdot NAr_2']'(SbCl_5)'$. For the similar compounds from aluminium, mercuric, and zinc chlorides it appears reasonable to suppose the presence of hydrazinium salt and amine derivative of the type

$Ar_2N{\cdot}ZnCl$. The possibility of a simple additive reaction is excluded, since the products liberate iodine from potassium iodide even after addition of sodium acetate. H. WREN.

Superheating of uniform organic compounds. IV. *cyclo*Hexane derivatives. S. SKRAUP and W. BEIFUSS (Ber., 1927, 60, [*B*], 1070—1074).—*cyclo*Hexane is not appreciably altered when heated during 3 days at 350°, and contains only about 5% of methyl-*cyclo*pentane after 3 days at 420°. *cyclo*Hexanecarboxylic acid, conveniently prepared by the oxidation of the mixture of *o*- and *p*-*cyclo*hexylphenol derived from the interaction of *cyclo*hexanol and phenol in presence of phosphoric oxide, is converted through the chloride into the *phenyl* ester, b. p. 163—164°/21 mm., which at 350—370° yields *cyclo*hexene, *cyclo*hexanecarboxylic acid, phenol, and o-*hydroxyphenyl* cyclo*hexyl ketone*, b. p. 166—168°/14 mm., m. p. 41—42°. The constitution of the last substance is established by its production from *phenyl* cyclo*hexanecarboxylate* under the influence of zinc chloride. Phenyl *cyclo*hexyl ether, b. p. 136—140°/20 mm., passes at 373—377° into *cyclo*hexene and the products of its polymerisation, phenol, o-cyclo*hexylphenol*, m. p. 53° (cf. Schrauth and Görig, A., 1923, i, 1084), and (?) *di*-oo'-*di*cyclo*hexylphenol*, m. p. 62—65°. The probability that the action consists primarily of fission of the ether and secondarily of addition of phenol at the double linking of the *cyclo*hexene, is established by the observation that o-*cyclo*hexylphenol is obtained from these substances at 350°. Similarly, *cyclo*hexene and *p*-cresol afford di*cyclo*hexene, 3-cyclo*hexyl*-p-*cresol*, b. p. 162—164°/15 mm., and 3 : 5-*di*cyclo*hexyl*-p-*cresol*, b. p. 222—224°/15 mm. H. WREN.

Problem of benzene substitution. II. Displacement of isomeric relationships by acids. S. SKRAUP and W. BEIFUSS (Ber., 1927, 60, [*B*], 1074—1077; cf. A., 1925, i, 143).—The observation of Schrauth and Quasebarth (A., 1924, i, 724) that *cyclo*hexene and phenol in acetic–sulphuric acid give *p*-*cyclo*hexylphenol, whereas a mixture of *o*- and *p*-compounds is produced in presence of phosphoric oxide, and solely the *o*-compound in a non-acidic medium (Skraup and Beifuss, preceding abstract), taken in conjunction with the literature on substitution, make it probable that acids generally favour the entry of substituents in the *para*-position. This view is supported by the observation that phenol is converted by tetranitromethane in pyridine into a mixture of almost equal amounts of *o*- and *p*-nitrophenol. More convincing results are obtained with bromine and phenol in pyridine, when 54—64% of the monobromophenol mixture is found to be composed of the *ortho*-derivative. H. WREN.

The two racemic forms of 2-dimethylaminomethyl*cyclo*hexanol. C. MANNICH (Arch. Pharm., 1927, 265, 251—255).—2-Dimethylaminomethyl*cyclo*hexanol (Mannich and Braun, A., 1920, i, 851) exists in two racemic forms, termed provisionally α and β, since it has not yet been determined which is the *cis*- and which the *trans*-isomeride. The hydrochloride of the benzoyl derivative of the crude amino-alcohol is crystallised from three fourths of its weight of water. Almost pure α-benzoate hydrochloride, amounting to about two thirds of the whole, separates, whilst the β-isomeride is purified by recrystallising from acetone the residue contained in the aqueous mother-liquor.

α-2-*Dimethylaminomethyl*cyclo*hexanol* has b. p. 96—97°/12 mm. The *hydrochloride* (m. p. 222—223°) of the *benzoate* is strongly anæsthetic. The p-*nitrobenzoyl* derivative (m. p. 88·5—90°) and its *hydrochloride* (m. p. 222—223°), the p-*aminobenzoyl* derivative (m. p. 147—149°), and the p-*carbethoxyaminobenzoyl* derivative (m. p. 99°; *hydrochloride*, m. p. 179—182°) are described. β-2-*Dimethylaminomethyl*-cyclo*hexanol* has m. p. 40—41°. The *hydrochloride* (m. p. 196—197°) of the *benzoate* is weakly anæsthetic. The p-*nitrobenzoyl* (*hydrochloride*, m. p. 218—220°), p-*aminobenzoyl* (m. p. 116—119°), and p-*carbethoxyaminobenzoyl* (m. p. 125°) derivatives are described. W. A. SILVESTER.

2-Tetralol. [Derivatives of *ar*-tetrahydro-β-naphthol.] H. THOMS and W. KROSS (Arch. Pharm., 1927, 265, 336—347).—Esters of tetrahydro-β-naphthol are obtained in good yield by means of the acid chloride in pyridine. The following compounds are described: 4-*nitrobenzoate*, yellow, m. p. 106·5°; *cinnamate*, m. p. 77·5°; *carbonate*, m. p. 111°; *diphenylurethane*, m. p. 114°; *ethyl ether*, b. p. 129°/11 mm., 132—133°/15 mm., d_{20}^{20} 1·008. The *iso*propyl and *n*-butyl ethers could not be obtained. The dry sodium compounds of tetrahydro-β-naphthol and chloroacetone furnish *tetrahydro-β-naphthoxyacetone*, b. p. 178—184°/18 mm. (decomp.), in small yield, (p-*nitrophenylhydrazone*, red, blackening at 118°; *semicarbazone*, m. p. 167°). Anhydrous hydrogen cyanide and hydrogen chloride in presence of zinc chloride afford 2-*hydroxytetrahydronaphthaldehyde* (1- or 3-), m. p. 82° (*oxime*, m. p. 150°; *phenylhydrazone*, orange, m. p. 180°; p-*nitrophenylhydrazone*, dark red, blackening at 250°; *semicarbazone*, m. p. 190—191°). Attempts to oxidise the aldehyde to the corresponding acid for identification purposes failed. Nitration of tetrahydro-β-naphthol with nitric and sulphuric acids afforded only the 1 : 3-dinitro-compound (cf. Schroeter, A., 1922, i, 126), but tetranitromethane and nitrogen peroxide also furnished 3-*nitro*-2-*hydroxytetrahydronaphthalene*, m. p. 88—89°, which was reduced to 3-amino-2-hydroxytetrahydronaphthalene, m. p. 201—202° (piperonylidene derivative, m. p. 160—161°), described by Schroeter, and a *nitro*-compound, m. p. 77°, which was not studied in detail. The following are also described: *benzylidene*-3-*amino*-2-*hydroxytetrahydronaphthalene*, m. p. 85—86°; 2-*hydroxytetrahydronaphthyl*-3-*carbamide*, m. p. 192°, and 2-*hydroxytetrahydronaphthyl*-3-*thiocarbamide*, m. p. 173°. S. COFFEY.

Action of aromatic alcohols on aromatic compounds in presence of aluminium chloride. IV. Condensation of some secondary alcohols with phenol. R. C. HUSTON, W. C. LEWIS, and W. H. GROTEMUT (J. Amer. Chem. Soc., 1927, 49, 1365—1368; cf. A., 1925, i, 249).—Condensation of phenylmethylcarbinol with phenol in presence of aluminium chloride affords 4-hydroxy-αα-diphenylethane, m. p. 57—58°, b. p. 168—170°/5 mm. (*benzoyl* derivative,

m. p. 82—83°), in 33—35% yield (cf. Koenigs and Carl, A., 1892, 446). Phenylethylcarbinol yields similarly 4-*hydroxy-αα-diphenylpropane*, m. p. 64·5°, b. p. 175—177°/6 mm. (*benzoyl* derivative, m. p. 67—68°), whilst benzhydrol affords in the same way *p*-hydroxytriphenylmethane, m. p. 110°, in 40% yield. The relative yields of the products indicate that unsaturation of the carbon atoms adjacent to the alcoholic group increases the reactivity of the hydroxyl group. F. G. Willson.

Migration of the triphenylmethyl group in phenols. J. van Alphen (Rec. trav. chim., 1927, 46, 287—292).—The preparation of phenyl triphenylmethyl ether by the methods of Baeyer (A., 1909, i, 642) or Helferich (A., 1925, i, 790) depends on the absence of free hydrochloric acid, since the substance, although stable alone at 180°, is converted at that temperature by a trace of hydrogen chloride into *p*-hydroxytetraphenylmethane, also obtained by the action of zinc chloride on the ether, or on a mixture of phenol and triphenylmethyl chloride. The introduction of the triphenylmethyl group is thus indirect, through reaction on the hydroxyl group; this is supported by the failure of triphenylmethyl chloride to react with benzene or with anisole, in which there is no hydroxyl group for the preliminary reaction.

Similarly, *o*-βββ-triphenylethylphenol, obtained by Schorigin (this vol., 54) as a by-product both in the preparation of *o*-tolyl triphenylmethyl ether and in the decomposition of the latter by sodium, was obtained by the condensation of triphenylmethyl chloride and *o*-cresol, best in presence of zinc chloride, and as the main product of the treatment of the above ether with zinc chloride at 160°. There is thus a migration of the triphenylmethyl group into the side-chain *ortho* to the oxygen atom; the formation of *o*-βββ-triphenylethylphenol is an indirect process, and, correspondingly, toluene does not react with triphenylmethyl chloride.

p-Tolyl triphenylmethyl ether, m. p. 81°, was prepared in pyridine in a similar manner to the *o*-tolyl ether (Schorigin, *loc. cit.*); its constitution was proved by hydrolysis to triphenylcarbinol. When this substance, or a mixture of *p*-cresol and triphenylmethyl chloride, was heated with zinc chloride, the triphenylmethyl group did not migrate either to the nucleus or to the side-chain, but separated as triphenylmethane, whilst a red dye, belonging probably to the aurin group, was simultaneously formed. The equation $3C_6H_4Me\cdot O\cdot CPh_3 \longrightarrow 3CHPh_3 + O{:}C_6H_4{:}C(C_6H_3Me\cdot OH)_2$ is suggested for this reaction; it agrees with the yield of triphenylmethane obtained. E. W. Wignall.

Iodination of *o*-nitrophenol. H. H. Hodgson (J.C.S., 1927, 1141—1144).—Various formulæ (cf. Ber., 1874, 7, 461; Beilstein, II, 700; Keimatsu, A., 1924, i, 1059) have been ascribed to Hübner's α- and β-iodonitrophenols, m. p. 90—91° and 66—67°, respectively. These have now been identified as impure specimens of 4 : 6-di-iodo-2-nitrophenol, m. p. 98°, and 4-iodo-2-nitrophenol, m. p. 79—80°, whilst a little 6-iodo-2-nitrophenol has been isolated from the crude reaction product through its alcohol-insoluble potassium salt. With excess of iodine, the di-iodo-derivative forms the main product, and it is still formed when half the quantity of iodine theoretically required for monoiodination is used. Mercurous salts are also produced. No indication of iodination in the 3-position has been obtained. The predominance of 4- over 6-iodo-2-nitrophenol suggests that initial monoiodination occurs preferentially in the 4-position. H. E. F. Notton.

Formation of hydrocyanic acid by action of persulphates on aromatic nitro-derivatives. I and II. B. Ricca (Gazzetta, 1927, 57, 269—273, 274—277).—I. When aromatic nitro-derivatives, are boiled with aqueous ammonium persulphate, some hydrocyanic acid is formed. Seyewetz and Poizat (A., 1909, i, 376) proposed equations such as $C_6H_2(NO_2)_3\cdot OH + 9O = 5CO_2 + 2HNO_3 + HCN$; determinations, however, show that the amount of hydrocyanic acid formed is variable, and very much less, and the amount of nitric acid greater, than this equation would indicate, whilst small quantities of ammonia are also detected, when potassium persulphate is used. Yields of hydrocyanic acid from mono-, di-, and trinitro-derivatives of benzoic acid, phenol, benzene, and toluene are given; with nitrobenzene and with *p*-nitrotoluene, no hydrocyanic acid is obtained.

II. The schemes of oxidation proposed by Seyewetz and Poizat (*loc. cit.*) are criticised as involving improbable oxygen migrations, and are disproved experimentally. Thus *p*-nitrosophenol and a nitrosonaphthol when treated with potassium persulphate give no hydrocyanic acid. Further, esters of oximinomalonic and oximino-oxaloacetic acids, $CO_2Et\cdot CO\cdot C(:NOH)\cdot CO_2Et$, intermediate products on the above authors' scheme, give no hydrocyanic acid, whether treated with water, with dilute sulphuric acid, or with potassium persulphate; esters of *iso*nitromalonic and *iso*nitro-oxaloacetic acids on boiling with water give hydrocyanic acid, but the yield of this is gradually reduced by addition of more and more persulphate. E. W. Wignall.

Scission of diaryl ethers and related compounds by piperidine. I. Scope of the method; constitution of some nitro-derivatives. R. J. W. Le Fèvre, S. L. M. Saunders, and E. E. Turner (J.C.S., 1927, 1168—1173).—The action of piperidine on diaryl ethers, $R\cdot O\cdot R' + C_5H_{10}NH \longrightarrow R\cdot NC_5H_{10} + R'\cdot OH$, enables the strength of attachment of different aryl radicals to oxygen to be compared. Diphenyl ether does not react with piperidine at 100°, 2- and 4-nitrodiphenyl ether, and 2′-, 3′-, and 4′-chloro-2-nitrodiphenyl ether react slowly, whilst 2 : 4-dinitrodiphenyl ether, 4′-bromo-2 : 4-dinitrodiphenyl ether, 2 : 4-dibromo-2′ : 4′-dinitrodiphenyl ether, m. p. 131°, and 2 : 4 : 2′ : 4′-tetranitrodiphenyl ether rapidly yield 2 : 4-dinitrophenyl-1-piperidinobenzene and phenol, *p*-bromophenol, 2 : 4-dibromophenol, and 2 : 4-dinitrophenol, respectively. Similarly, 4-chloro-2 : 3′-dinitro-4′-phenoxydiphenyl and 4-bromo-2 : 3′-dinitro-4-phenoxydiphenyl are quantitatively converted into 4-chloro- and 4-bromo-2 : 3′-dinitro-4′-piperidinodiphenyl, and 3 : 3′-dinitro-4 : 4′-diphenoxydiphenyl more slowly into 3 : 3′-dinitro-4 : 4′-dipiperidinodiphenyl. 5-Chloro-2-nitrodiphenyl ether

and piperidine in chloroform give *5-piperidino-2-nitrodiphenyl ether*, m. p. 86—86·5°, and, on further treatment, 1-nitro-2 : 4-dipiperidinobenzene and phenol. *4-Bromo-4′-nitrodiphenyl ether*, m. p. 60°, b. p. 230°/15 mm., from *p*-bromophenol, *p*-chloronitrobenzene, and potassium hydroxide, is reduced with iron and water, and the amine converted by the diazo-reaction into 4 : 4′-dibromodiphenyl ether, m. p. 60·5°, b. p. 210°/11 mm., which is identical with the product of bromination of diphenyl ether (Hoffmeister, Annalen, 1871, **159**, 210, gives m. p. 53°). Nitration in glacial acetic acid gives a 4 : 4′-*dibromonitrodiphenyl ether*, m. p. 90—91°, whilst nitric acid (*d* 1·5) at 100° gives a *dinitro*-derivative, m. p. 167°. *4-Chloro-4′-nitrodiphenyl ether*, m. p. 75·5—76°, b. p. 215°/12 mm., is reduced by iron powder and water to *4-chloro-4′-aminodiphenyl ether*, m. p. 100°, from which 4 : 4′-dichlorodiphenyl ether, m. p. 30°, is obtained in the usual way. With excess of nitric acid (*d* 1·5), the last forms 4 : 4′-*dichloro-2 : 2′-dinitrodiphenyl ether*, m. p. 152°, identified by its smooth scission by piperidine into 4-chloro-2-nitropiperidinobenzene and 4-chloro-2-nitrophenol. Mononitration in glacial acetic acid gives 4 : 4′-*dichloro-2-nitrodiphenyl ether*, m. p. 75°, b. p. 215—220°/15 mm., which may also be prepared from *p*-chlorophenol, 2 : 5-dichloronitrobenzene, and potassium hydroxide. The non-occurrence of 3-nitration is ascribed to the powerful orienting effect of the halogenophenoxyl radical. H. E. F. Notton.

Phosphorus pyrocatechyl oxychloride and *o*-phenylene phosphate. L. Anschutz and W. Broeker (J. pr. Chem., 1927, [ii], **115**, 379—384).—In repetition of the work of Knauer (A., 1894, i, 587), pure *o*-phenylene phosphate, $(o\text{-}C_6H_4)_3(PO_4)_2$, m. p. 230°, when freshly distilled, b. p. about 300°/12 mm., has been prepared by boiling a solution of pyrocatechol and phosphoryl chloride in xylene. It is converted by heating at 150—160° with excess of phosphoryl chloride into phosphorus pyrocatechyl oxychloride, $C_6H_4\langle{}^{O}_{O}\rangle POCl$, m. p. 59—60° (Knauer gives 35°), b. p. 120°/9 mm., which is also obtained by heating phosphorus pyrocatechyl trichloride (this vol., 146) with anhydrous oxalic acid.

H. E. F. Notton.

3 : 3′ : 5 : 5′-Tetranitro-2 : 2′-dimethoxydiphenyl. W. Borsche and E. Feske (Ber., 1927, **60**, [*B*], 1220).—Methylation of 3 : 3′ : 5 : 5′-tetranitro-2 : 2′-dihydroxydiphenyl affords 3 : 3′ : 5 : 5′-tetranitro-2 : 2′-dimethoxydiphenyl, m. p. 177°, thus confirming the value found by Borsche and Scholten (A., 1917, i, 390; contrast Raudnitz, this vol., 453).

H. Wren.

Dehydrogenation of sitosterol. L. Schmid and M. Zentner (Monatsh., 1927, **48**, 47—50).—Dehydrogenation of sitosterol by means of palladised charcoal yields a hydrocarbon which, after purification by sublimation at 180°/11 mm., has m. p. 324—326°, and is identical with the hydrocarbon of m. p. 325° (mixed m. p. gives no depression) obtained by Diels and Gadke (this vol., 241) by similar dehydrogenation of cholesterol. J. W. Baker.

Methoxy-substituted triphenylcarbinols and their salts. H. Lund (J. Amer. Chem. Soc., 1927, **49**, 1346—1360).—*Tri-o-anisylmethyl chloride*, decomp. 170—175° (m. p. not below 185° when heated suddenly to that temperature), and *tri-o-anisylmethane*, m. p. 136—137°, were prepared from the corresponding carbinol (Baeyer, A., 1909, i, 641). 2 : 4 : 2′ : 2″-*Tetramethoxytriphenylcarbinol*, m. p. 122°, was obtained from *o*-iodoanisole and ethyl 2 : 4-dimethoxybenzoate by the Grignard reaction. 2 : 4 : 2′ : 4′-Tetramethoxytriphenylcarbinol, obtained similarly from 1-iodo-2 : 4-dimethoxybenzene and methyl benzoate, has m. p. 137° (cf. Kauffmann and Kieser, A., 1912, i, 853), 4 : 6-di-iodo-1 : 3-dimethoxybenzene, m. p. 202°, being obtained as a by-product. 2 : 4 : 2′ : 4′-*Tetramethoxytriphenylmethyl chloride*, decomp. about 80°, forms bronze crystals with a metallic reflex. 2 : 4 : 4′ : 4″-*Tetramethoxytriphenylcarbinol*, m. p. 111°; 2 : 4 : 2′ : 4′ : 2″-*pentamethoxytriphenylcarbinol*, m. p. 146—147°; 2 : 4 : 2′ : 4′ : 4″-*pentamethoxytriphenylcarbinol*, m. p. 91—92°; 2 : 6 : 2′ : 6′ : 2″-*pentamethoxytriphenylcarbinol*, decomp. 143—146°; 2 : 4 : 6 : 2′ : 4′ : 6′-*hexamethoxytriphenylcarbinol*, m. p. 184°, and 2 : 4 : 6 : 2′ : 4′ : 2″ : 4″-*heptamethoxytriphenylcarbinol*, m. p. 147°, are obtained by analogous Grignard syntheses. *Tri-o-anisylmethyl*, decomp. about 110°, exists almost completely as the free radical in benzene and *p*-bromotoluene solution. The corresponding *peroxide*, m. p. 157—160° (decomp.), is described.

Increase in the number of methoxyl groups in the above series of carbinols results in an increase in basicity, but not according to any simple rule. When more than three methoxyl groups are present, the normal salts of the carbinols are coloured, and probably ionised, in the crystalline state. Salts of the most basic carbinols are only slightly hydrolysed in aqueous solution, and these compounds can be used as indicators (cf. Kolthoff, this vol., 637). The absorption spectra of the carbinol salts, in both the visible and ultra-violet, indicate that these must be regarded as quinocarbonium salts, rather than as oxonium derivatives. F. G. Willson.

Relationship between *as*-phenylmethylethylene glycol and the corresponding anhydro-forms. S. Danilov and E. Venus-Danilova (Ber., 1927, **60**, [*B*], 1050—1069).—It is regarded as probable that glycols, apart from pinacols, in an acid medium are first converted into aldehydes which yield additive products with the reagent, and are subsequently changed in different directions and partly isomerised to ketones.

Phenyldimethylcarbinol, b. p. 102°/22 mm., prepared in almost 90% yield by the action of magnesium methyl iodide on acetophenone, is converted by oxalic acid at 130° into β-phenyl-Δ^{α}-propene, b. p. 56°/13 mm., d_{20}^{20} 0·9154, d_4^{20} 0·9139, which is oxidised by benzoyl peroxide in chloroform solution under specified conditions to *as-phenylmethylethylene oxide*, b. p. 81—81·5°/14 mm., d_4^{20} 1·0258, n_D 1·52325. The oxide is transformed by dilute hydrochloric acid at the atmospheric temperature into *as*-phenylmethylethylene glycol, b. p. 149—150°/11 mm., m. p. 44°, by distillation under atmospheric pressure or by 50% sulphuric acid at 140—150° into β-phenylpropaldehyde, and by concentrated sulphuric acid at —17°

into benzyl methyl ketone unaccompanied by phenyl ethyl ketone or β-phenylpropaldehyde. Dehydration of *as*-phenylmethylethylene glycol by concentrated sulphuric acid gives benzyl methyl ketone, whereas under milder conditions β-phenylpropaldehyde or a mixture of aldehyde and ketone results; dehydration can also lead to the substituted diethylene ether (*vide infra*) and to condensation products. β-*Phenylpropaldehyde*, b. p. 92—92·5°/12 mm., 94—94·5/14 mm., d_4^{20} 1·0089, n_D 1·52216 (*semicarbazone*, m. p. 153°), the constitution of which is established by oxidation to β-phenylpropionic acid (*silver* salt), is isomerised to benzyl methyl ketone and partly polymerised by concentrated sulphuric acid or hot mercuric chloride solution. Its semicarbazone affords the aldehyde and condensation products when treated with dilute sulphuric acid, but gives benzyl methyl ketone with 50% sulphuric acid; the ketone has b. p. 100—101°/14 mm., d_4^{20} 1·0157, n_D 1·51739. Phenyl ethyl ketone is not greatly affected by concentrated sulphuric acid at −10°.

During unsuccessful attempts to prepare *as*-phenylmethylethylene oxide and by the action of 20% sulphuric acid on the corresponding glycol, a *substance*, $C_{18}H_{20}O_2$ (probably the ether, PhMeC$<^{\cdot CH_2}_{CH_2\cdot O}>$CMePh), b. p. 190—192°/11 mm., is obtained, which on exposure to moist air affords a *dihydrate*, m. p. 73°. The latter compound loses water, but is otherwise unchanged by cold, concentrated sulphuric acid, whereas with dilute hydrochloric acid at 175—185° it gives β-phenylpropaldehyde. H. WREN.

Isomerisation of some ethylene oxides of the general formula Ph·[CH$_2$]$_n$·CH·CH$_2$·O. (MLLE.) J. LÉVY and M. SFIRAS (Compt. rend., 1927, **184**, 1335—1337).—A systematic study of the isomerisation of the oxides of some hydrocarbons of the general formula Ph·[CH$_2$]$_n$·CH:CH$_2$. Hydrocarbons having n=1—4 were prepared from allyl bromide and the corresponding magnesium phenylalkyl bromide, and from these the oxides were made by the action of perbenzoic acid. Isomerisation was effected either by heating the oxides with a trace of zinc chloride or by passing the vapours over aluminium at 260°, and ketones having the general formula CH$_2$R·COMe were obtained in 35—40% yield. Rupture of the oxygen bridge occurs between the oxygen atom and the least substituted carbon atom, and is followed by migration of a hydrogen atom according to the scheme R·CH$_2$·CH·CH$_2$·O ⟶ R·CH$_2$·CHO·CH$_2$ ⟶ R·CH$_2$·COMe. It is concluded that the affinities of the benzyl, phenylethyl, phenylpropyl, and phenylbutyl groups are inferior to that of the hydrogen atom (cf. Tiffeneau and Lévy, A., 1926, 383, 818). E. H. SHARPLES.

Hydroanthranilic acids. F. P. MAZZA and C. CRAPETTA (Gazzetta, 1927, **57**, 292—299).—Unsuccessful attempts were made to prepare Δ^2-tetrahydroanthranilic acid by the action of sodium hypochlorite on Δ-*-tetrahydrophthalimide*, m. p. 171°, obtained from the corresponding anhydride, owing to opening of the *cyclo*hexene ring. As sodium amalgam did not reduce anthranilic acid, small amounts of sodium were employed, in amyl alcohol. The product gave on acidification some pimelic acid; the residue was esterified and fractionated. A small amount of ethyl hexahydroanthranilate was obtained, followed by *ethyl* Δ^4*-tetrahydroanthranilate*, b. p. 145°/15 mm. (*hydrochloride*, m. p. 161—162°), hydrolysed slowly by water, oxidised in the air to ethyl anthranilate, and lastly by ethyl $\Delta^{2:6}$*-dihydroanthranilate*, b. p. 156—157°/15 mm. (*hydrochloride*, m. p. about 170°), not hydrolysed by water or oxidised in the air. Δ^4*-Tetrahydroanthranilic acid*, decomp. about 200° (*copper* salt), oxidises very rapidly in the air to anthranilic acid. Ethyl Δ^4-tetrahydroanthranilate distilled in a current of hydrogen decomposes to give ammonia and $\Delta^{1:3}$-dihydrobenzoic acid (cf. Aschan, A., 1891, 1482); the constitution of this acid is proved by its oxidation by permanganate to succinic and oxalic acids. $\Delta^{2:6}$*-Dihydroanthranilic acid*, m. p. about 210° (*copper* salt), on treatment with nitrous acid, gives $\Delta^{2:6}$-dihydrosalicylic acid. E. W. WIGNALL.

Cyclic alkamine esters of *p*-aminobenzoic acid. II. H. HECKEL and R. ADAMS (J. Amer. Chem. Soc., 1927, **49**, 1303—1307; cf. A., 1926, 834).—*cyclo*Hexene was converted into *o*-chloro*cyclo*hexanol by Detœuf's method (A., 1922, i, 327), and the latter heated with butyl-alcoholic diethylamine at 150° (cf. Osterberg and Kendall, A., 1921, i, 727), when trans-*o*-*diethylamino*cyclo*hexanol*, b. p. 106—106·5°/17 mm., 225°/740 mm., d_{25}^{25} 0·9280, n_D^{25} 1·4659 (*hydrochloride*, m. p. 170·5—171·5°), was obtained (cf. Brunel, A., 1905, i, 869). Condensation of this with *p*-nitrobenzoyl chloride affords trans-*o*-*diethylamino*cyclo*hexyl* p-*nitrobenzoate hydrochloride*, m. p. 192—194°. The following were obtained by catalytic reduction of the corresponding nitro-compounds (cf. Adams, Cohen, and Rees, this vol., 552) in ethyl or butyl alcohol with hydrogen in presence of platinum oxide–platinum-black: trans-*o*-*diethylamino*cyclo*hexyl*-p-*aminobenzoate hydrochloride*, m. p. 220—221°; m-*dimethylamino*-, m. p. 184—185°; m-*diethylamino*-, m. p. 184—186°; (? cis)-p-*dimethylamino*-, m. p. 226—228°, and (? trans)-p-*dimethylamino*-cyclo*hexyl* p-*aminobenzoate hydrochloride*, m. p. 268—269°. All the above derivatives are effective anæsthetics, both on mucous membrane and by injection, the *trans-p*-dimethylamino-compound being slightly more active than cocaine. The order of anæsthetic effect towards goldfish in equimolar concentrations is as follows: *m*-diethylamino- > *m*-dimethylamino- > *trans-p*-dimethylamino- > *cis-p*-dimethylamino- > *o*-diethylamino-*cyclo*hexyl *p*-aminobenzoate hydrochloride. F. G. WILLSON.

Principle of induced alternate polarity in organic compounds, and the general and *ortho* effects of substituents. C. F. VAN DUIN (Rec. trav. chim., 1927, **46**, 256—267).—Mainly theoretical. In the theory of Lapworth and Robinson (J.C.S., 1922, **121**, 416, 427), the general effect is not opposed to the alternate effect, as Verkade (Versl. Akad. Afdeel. Natuurk., 1926, **35**, 492—504) suggests, since the former corresponds with a general electronic displacement and the latter with a shorter or longer

presence of valency electrons in the neighbourhood of alternate atoms (cf. Højendahl, A., 1924, ii, 722).

The reaction of nitrobenzyl chlorides with benzene in presence of aluminium chloride is, contrary to the opinion of Olivier and Berger (A., 1926, 1239), in good agreement with the theory, if the *o*-position, in which there is a special influence, is left out of account. Following Højendahl (*loc. cit.*), if in a substituted benzyl chloride the effect of the substituent on the carbon atom to which it is attached is represented by unity, its effect transmitted to the chlorine atom will be equal to 0·188 if in the *o*-, 0·136 if in the *m*-, and 0·120 if in the *p*-position. Thus the velocity constants of hydrolysis of benzyl chlorides substituted *o*-, *m*-, and *p*- by a group favouring *o*- and *p*-hydrolysis will be $K_o=K+0{\cdot}188(A+B)+C$, $K_m=K-0{\cdot}136(A-B)$, $K_p=K+0{\cdot}120(A+B)$, and with a group favouring *m*-hydrolysis $K_o=K-0{\cdot}188(A-B)+C$, $K_m=K+0{\cdot}136(A+B)$, $K_p=K-0{\cdot}120(A-B)$, where K is the velocity constant for benzyl chloride, A and B are respectively the alternating and general effects of each substituent on its α-carbon atom, and C is the *o*-effect. On this basis, values of A, B, and C are calculated for the groups Me, Cl, Br, I, CO_2H, and NO_2. For Me alone, B has a positive value, and is about equal to A, whilst for the other groups the general effect is numerically greater than the alternating effect; Me has a strongly negative and NO_2 a moderate positive *o*-effect; the influence of temperature is small.

Examples of the great effect of an *o*-substituent are quoted; it is observed that although the *p*-isomeride is not changed, and the *m*- only slowly, *o*-carboxybenzenesulphonamide is rapidly converted by dilute hydrochloric acid into the ammonium hydrogen salt. Since *o*-methoxybenzophenone is hydrolysed by sodamide (Lea and Robinson, A., 1926, 1144) to give unsubstituted benzamide, in contrast with the *m*- and *p*-isomerides, it is argued that *ethyl o-methoxytranscinnamate* (m. p. 34·0—34·5°) should hydrolyse readily; actually, however, hydrolysis is difficult. Owing to the variability of the *o*-effect, it is suggested that theoretical work on substituted benzene derivatives should be confined to the *m*- and *p*-compounds. E. W. Wignall.

M. p. of acetylsalicylic acid. T. S. Carswell (J. Amer. Pharm. Assoc., 1927, **16**, 306—309).—The temperature observed in the determination of the m. p. of acetylsalicylic acid is a combination of the true m. p. with the decomposition point. The latter has no exact value, but is a function of the time of heating, and the longer the period of heating below the true m. p. the more nearly the observed value approaches the decomposition point. The fineness of the material also influences the observed m. p., and the nearest approach to the true m. p. is obtained by grinding the sample to pass a 200-mesh sieve, inserting the m.-p. tube in a bath preheated at 125°, and raising the temperature of the bath at the rate of 1° in 10—15 sec. Under these conditions, fifteen samples of acetylsalicylic acid melted at 135°±0·2°, whilst with a slower rate of heating (3° per min. until commencement of melting, thereafter 0·5° per min.) the same ground samples melted at 131·2°±0·7°.

W. J. Powell.

Synthetic medicinals. III. [Physiological] action of acetylsalicylic acid and attempts to produce analgetics. H. P. Kaufmann (Arch. Pharm., 1927, **265**, 226—238; cf. B., 1927, 155).—The general question of the mode of action within the body of medicaments that can (i) easily or (ii) only with difficulty decompose into two or more fragments is reviewed, with particular reference to the very different properties of salicylic acid and its acetyl derivative. The compounds described below have been prepared in efforts to produce a series of compounds consisting of antipyretic and narcotic components bound together by linkings of varying stability. α-Bromopropionylsalicylic acid (cf. G.P. 212,422) has m. p. 107°. *α-Bromo-*n*-butyrylsalicylic acid*, m. p. 87·5°, and *α-bromoisovalerylsalicylic acid*, m. p. 90·5°, are similarly prepared from salicylic acid and the acid chloride in pyridine. Salicylamide, already known to be strongly narcotic and analgetic, is substituted at the oxygen atom only when treated with acyl bromides in cold pyridine: O-*α-bromoisovalerylsalicylamide*, m. p. 136°, is obtained in this way. When *O*-acetylsalicylamide is similarly treated, but in warm pyridine, O-*acetyl*-N-*α-bromoisovalerylsalicylamide*, m. p. 96·5°, is produced. Salicoyl chloride and carbamide in ether solution yield salicoylcarbamide, m. p. 192° decomp. (not 184—186°, as given by Jacobs and Heidelberger, A., 1918, i, 69). O-*Methylsalicoylcarbamide* (*o-anisoylcarbamide*) has m. p. 192°; p-*anisoylcarbamide* has m. p. 215°. Diethylmalonyl chloride and *O*-acetylsalicylamide yield *NN*-diethylmalonylbis-*O*-acetylsalicylamide, m. p. 126—128°. *Salicyl-ββββ-trichloro-α-hydroxyethylamide* (I), m. p. 117—127° (decomp.), is obtained from a warm mixture of chloral and salicylamide, and when sulphuric acid is added to the mixture, a *compound*, m. p. 172·5° (cf. Moucka and Rogl, A., 1926, 626), is obtained. Acetylsalicylamide and chloral give the *acetyl* derivative of (I), m. p. 149—150°.

W. A. Silvester.

Aromatic derivatives of phosphoric acid and of the hypothetical orthophosphoric acid; hetero-rings containing phosphorus. L. Anschütz (Annalen, 1927, **454**, 71—120).—The compound, $C_7H_4O_2Cl_5P$, b. p. 178°/11 mm., d_4^{20} 1·635, n_D^{20} 1·5637, from salicylic acid and phosphorus pentachloride at 170°, to which Anschütz (A., 1887, 947; 1906, i, 500—508) ascribed the formula $CCl_3{\cdot}C_6H_4{\cdot}O{\cdot}POCl_2$, has now been prepared from salicoyl chloride and phosphorus pentachloride at the ordinary temperature. Since only the phenolic group could be attacked under these conditions (cf. A., 1924, i, 1195), the product must be phosphorus *o*-chloroformylphenoxytetrachloride [orthophosphosal chloride, $COCl{\cdot}C_6H_4{\cdot}O{\cdot}PCl_4$; cf. the following proposed trivial names: phosphosal for *o*-carboxyphenyl dihydrogen phosphate, $CO_2H{\cdot}C_6H_4{\cdot}O{\cdot}PO(OH)_2$; phosphosal chloride, $R{\cdot}O{\cdot}POCl_2$; metaphosphosal chloride, $R{\cdot}O{\cdot}PO_2$; metaphosphorosal chloride, $R{\cdot}O{\cdot}PO$ ($R-COCl{\cdot}C_6H_4{\cdot}$)]. The following by-products in the latter reaction are isolated by fractional distillation: (*a*) *o*-chlorobenzotrichloride, (*b*) metaphosphosal chloride, and (*c*) a *compound*, $C_{14}H_8O_6ClP$, m. p. 81—82°, probably $C_6H_4<_{O}^{O_2}>PO{\cdot}O{\cdot}C_6H_4{\cdot}COCl$. It is

rapidly converted by moisture into a *compound*, $C_{14}H_{15}O_{10}P$, m. p. 150—151°, which is decomposed by water into phosphosal and salicylic acid, and is probably formed by replacing 2 mols. of water in phosphosal trihydrate by 1 mol. of salicylic acid. The formation of these by-products is explained by the thermal decomposition of a hypothetical intermediate product, $(COCl\cdot C_6H_4\cdot O\cdot)_2PCl_3$ [which is probably present in the oily residues from which (*c*) is isolated], into (*a*) and (*b*). The latter may then react with salicylide, another by-product, to form (*c*).

[With F. WENGER.]—3 : 5-Dichloro-orthophosphosal chloride (phosphorus 3 : 5-dichloro-2-chloroformylphenoxytetrachloride), m. p. 102—104°, obtained by Anschutz (*loc. cit.*) from 3 : 5-dichlorosalicoyl chloride and phosphorus pentachloride at 60°, has also been synthesised in a second way. 3 : 5-Dichlorometaphosphorosal chloride, m. p. 55°, is converted by chlorine into 3 : 5-*dichlorophosphosal chloride*, b. p. 183°/11 mm., m. p. 56—58°, which with phosphorus pentachloride at 165° gives 3 : 5-dichloro-orthophosphosal chloride.

[With H. BÆDECKER.]—Since it has now been shown that phosphoryl chloride is not an intermediate product in the action of phosphorus pentachloride on salicylic acid, the effect of 3-substituents must be to protect the hydroxyl group against phosphorus pentachloride itself. The action of the latter on other di-*o*-substituted phenols has now been examined. At 20°, 2 : 4 : 6-trichlorophenol gives *phosphorus bis-2 : 4 : 6-trichlorophenoxyoxychloride*, $(C_6H_2Cl_3O)_2POCl$, m. p. 126—129°, and 1 : 2 : 4 : 6-tetrachlorobenzene; 2 : 4 : 6-tribromophenol gives 1-chloro-2 : 4 : 6-tribromobenzene, and mesitol gives monochloromesitylene; at 60—80°, picric acid gives 1-chloro-2 : 4 : 6-trinitrobenzene, and 3-nitro-*o*-cresol reacts. 3 : 5-Dichloro-*o*-cresol does not react with pure phosphorus pentachloride at 80°. Accordingly, the protective action of substituents is determined by their chemical nature as well as their spatial properties.

[With W. BRŒKER.]—Mainly a fuller account of work previously described (this vol., 146). Phosphorus pyrocatechyl trichloride is converted by anhydrous oxalic acid in boiling benzene into phosphorus pyrocatechyl oxychloride and a little *di-o-phenylene pyrophosphate*, $(C_6H_4)_2P_4O_7$, m. p. 136—138°, b. p. 222°/12 mm.; by aniline into NN′-*diphenyl-o-phenylenephosphamidine*,

$C_6H_4<_O>P(:NPh)\cdot NHPh$, m. p. 242—244° (decomp.),

and by *o*-toluidine into NN′-*di-o-tolyl-o-phenylenephosphamidine*, m. p. 226—228°. The two last resemble the parent substance phosphamidine (phosphamide), $NH_2PO{:}NH$, and the corresponding derivatives of metaphosphamidine (cf. Michaelis, A., 1915, i, 328). Phosphorus phenoxytetrachloride and pyrocatechol in boiling benzene afford *phenyl di-o-phenylene orthophosphate*, $P(OPh)(O_2C_6H_4)_2$, b. p. 245—250°/10—11 mm., m. p. 192°, when freshly distilled. *Triphenyl o-phenylene orthophosphate*, $P(OPh)_3(O_2C_6H_4)$, m. p. (indef.) 95—101°, and triphenyl phosphate are obtained from phosphorus triphenoxydichloride and pyrocatechol at 150°. The reactivity of the chlorine atoms in the phosphorus aryloxychlorides decreases as the number of aryl groups increases. H. E. F. NOTTON.

Constituents of the kawa root. IV. Synthesis of a methyl kawaate and of two isomerides of methysticin. W. BORSCHE, W. ROSENTHAL, and C. H. MEYER (Ber., 1927, **60**, [*B*], 1135—1139; cf. A., 1921, i, 862).—Cinnamylideneacetyl chloride is prepared by the action of thionyl chloride on cinnamylideneacetic acid, preferably in boiling light petroleum (b. p. 70°). The chloride is converted by methyl sodioacetoacetate into *methyl α-cinnamylideneacetylacetoacetate*, $CHPh{:}CH\cdot CH{:}CH\cdot CO\cdot CHAc\cdot CO_2Me$, m. p. 45° [*copper* derivative, m. p. 203—204° (decomp.)], which, with ammonia, yields *methyl γ-cinnamylideneacetoacetate*, m. p. 93° (*copper* derivative, decomp. 215—216°), not identical with the product obtained from kawa resin by 10% sodium hydroxide solution. *Cinnamylideneacetylacetone* (*εη-diketo-α-phenyl-*$\Delta^{\alpha\gamma}$*-octadiene*), m. p. 139—140°, is described. Piperoyl chloride and methyl sodioacetoacetate afford *methyl piperoylacetoacetate*, $C_{17}H_{16}O_6$, m. p. 165—167°, converted by ammonia in ethyl alcohol into *methyl β-keto-ζ-methylenedioxyphenyl-*$\Delta^{\gamma\epsilon}$*-hexadienoate* (*allomethysticin*), m. p. 135—137°, not identical with *iso*methysticin. *Methyl α-acetyl-δ-methylenedioxyphenyl-*$\Delta^{\alpha\gamma}$*-pentadienoate*, m. p. 103° (cf. Junge, Diss., Gottingen, 1923), also differs from *iso*methysticin.

H. WREN.

Catalytic reduction of hydrophthalic anhydrides. I. Reduction of Δ^2-tetrahydrophthalic anhydride. F. P. MAZZA and G. DI MASE (Gazzetta, 1927, **57**, 300—311).—Phthalic anhydrides reduced partly in the benzene ring may be reduced catalytically to phthalides without further reduction in the nucleus. Thus Δ^2-tetrahydrophthalic anhydride is reduced by the Sabatier–Senderens method at 220—240° to Δ^2-*tetrahydrophthalide*, m. p. 73—74°, b. p. 148°/15 mm., which is hydrolysed by potassium hydroxide to 2-*hydroxymethyl-*Δ^6*-tetrahydrobenzoic acid*, m. p. 79—80° (*silver* salt), which very readily loses water, reverting to the phthalide. The tetrahydrophthalide is reduced by sodium and amyl alcohol to *trans*-hexahydrophthalide (Einhorn, A., 1898, i, 407); its structure is established by its reduction by hydriodic acid and yellow phosphorus to Δ^2-*tetrahydro-o-toluic acid*, m. p. 79—80°, which is oxidised by permanganate to α-methyladipic acid. Δ^2-Tetrahydrophthalide reacts with carbamide at 150° to give Δ^6-*tetrahydrophthalimidine*, m. p. 150°, with aniline to give the N-*phenyl* derivative, m. p. 135°, and with *p*-anisidine to give the N-p-*anisyl* derivative, m. p. 98°, of the above. With phosphorus pentachloride, it gives an unstable substance, m. p. 170°, which is probably ω-*chloro-*Δ^2*-tetrahydrotoluoyl chloride*; with phenylhydrazine, it reacts in the cold, with evolution of heat to form 2-*hydroxymethyl-*Δ-*tetrahydrobenzphenylhydrazide*, m. p. 130° (decomp.).

E. W. WIGNALL.

Catalytic reduction of hydrophthalic anhydrides. II. Reduction of $\Delta^{2:6}$-dihydrophthalic anhydride. F. P. MAZZA and A. CALÒ (Gazzetta, 1927, **57**, 311—318).—By similar methods to those previously employed (preceding abstract), the following compounds are obtained from $\Delta^{2:6}$-dihydro-

phthalic anhydride: $\Delta^{2:6}$-*dihydrophthalide*, m. p. 215°, b. p. 150°/30 mm.; 2-*hydroxymethyl*-$\Delta^{2:6}$-*dihydrobenzoic acid*, m. p. 195° (decomp.) (*silver* salt), which readily reverts to the phthalide, and is oxidised to oxalic and succinic acids; *trans*-hexahydrophthalide; $\Delta^{2:6}$-*dihydro*-o-*toluic acid*, m. p. 175° (decomp.) (*silver* salt), which oxidises to acetic, oxalic, and succinic acids; $\Delta^{2:6}$-*dihydrophthalimidine*, m. p. 218°, and its N-*phenyl*, m. p. 164°, and N-p-*anisyl*, m. p. 150°, derivatives; a substance, m. p. about 90°, probably ω-*chloro*-$\Delta^{2:6}$-*dihydrotoluoyl chloride*; and 2-*hydroxymethyl*-$\Delta^{2:6}$-*dihydrobenzphenylhydrazide*, m. p. 212°. E. W. WIGNALL.

Catalytic reduction of hydrophthalic anhydrides. III. Reduction of Δ^1-tetrahydrophthalic anhydride. F. P. MAZZA and (SIGNA.) A. CREMONA (Gazzetta, 1927, **57**, 318—322).—From Δ^1-tetrahydrophthalic anhydride there are obtained (cf. preceding abstracts): Δ^1-*tetrahydrophthalide*, m. p. 65—66°; 2-*hydroxymethyl*-Δ^1-*tetrahydrobenzoic acid*, m. p. 85° (silver salt), which readily reverts to the phthalide; *trans*-hexahydrophthalide; Δ^1-tetrahydro-*o*-toluic acid (cf. Kay and Perkin, J.C.S., 1905, **87**, 1066), which oxidises to γ-acetylbutyric acid; Δ^1-*tetrahydrophthalamidine*, m. p. 164°, and its N-p-*anisyl* derivative, m. p. 105°; and 2-*hydroxymethyl*-Δ^1-*tetrahydrobenzphenylhydrazide*, m. p. 115°. E. W. WIGNALL.

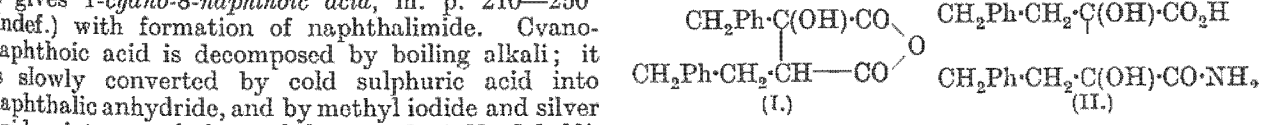
Phthalhydrazide. II. von Rothemburg's *N*-aminophthalimide. III. Mihailescu's *N*-aminophthalimide. D. RADULESCU (Bul. Soc. Chim. Romania, 1926, **8**, 117—119, 120—126).—A re-statement of work already published (Radulescu and Georgescu, A., 1925, i, 1185). S. K. TWEEDY.

1 : 8-Naphthalyl chloride. W. DAVIES and G. W. LEEPER (J.C.S., 1927, 1124—1127).—Attempts to isomerise 1 : 8-naphthalyl chloride (Mason, A., 1925, i, 34) by distillation [b. p. 195—200°/about 0·2 mm. (undecomp.)] or by heating with aluminium chloride were unsuccessful. Naphthalide was not obtained by catalytic reduction (cf. Rosenmund, A., 1921, i, 392). With ammonia in benzene solution, it gives 1-*cyano*-8-*naphthoic acid*, m. p. 210—250° (indef.) with formation of naphthalimide. Cyanonaphthoic acid is decomposed by boiling alkali; it is slowly converted by cold sulphuric acid into naphthalic anhydride, and by methyl iodide and silver oxide into methyl naphthoate. 1 : 8-*Naphthaldianilide*, m. p. 250—282° (decomp.), and 1 : 8-*naphthalois*-p-*dimethylanilide*, m. p. 245—246°, are obtained from naphthalyl chloride and the requisite amines. H. E. F. NOTTON.

Asymmetrical phenanthridones. I. 2-Nitro- and 7-nitrophenanthridone. F. J. MOORE and H. HUNTRESS (J. Amer. Chem. Soc., 1927, **49**, 1333—1334).—An improved method for the preparation of 4-nitrodiphenic acid, m. p. 220—221° (cf. Schmidt and Spoun, A., 1922, i, 665), is described. When heated at 150—160° with 2·5 parts of sulphuric acid, the latter is converted into 7-*nitrofluorenone*-4-*carboxylic acid*, yellow, m. p. 269—269·5° (methyl ester, m. p. 203—204°), the constitution of which is established by its oxidation to hemimellitic acid. *Fluorenone*-4-*carboxylic acid*, m. p. 223—224°, is obtained from the above nitro-derivative by the method of Graebe and Aubin (A., 1889, 145). On nitration, it yields the above 7-nitro-derivative, together with 5-*nitrofluorenone*-4-*carboxylic acid*, m. p. 238—239°, which is also obtained by heating 6-nitrodiphenic acid with sulphuric acid at 150—160°. Treatment of 7-nitrofluorenone-4-carboxylic acid with phosphorus pentachloride affords the acid *chloride*, m. p. 207·5—208°, from which, by the action of ammonia in benzene, the *amide*, m. p. 270·5—271°, is obtained, and this, on treatment with alkaline hypobromite, yields 7-*nitro*-4-*aminofluorenone*, scarlet, m. p. 292—293° (*acetyl* derivative, yellow, m. p. 307—308°). Conversion of the latter into 7-nitrophenanthridone could not be effected. Direct nitration of phenanthridone affords two *mononitro*-derivatives, yellow, m. p. 257—259°, and colourless, m. p. 368—370° (sealed tube), respectively, neither of which is the 2- or 7-nitro-derivative.

When boiled with acetic anhydride, 4-nitrodiphenic acid yields the *anhydride*, m. p. 211—211·5°, which, on treatment with ammonia solution, affords 4-*nitro*-2-*diphenamic acid* (4-*nitro*-4-*carbamidodiphenyl*-2′-*carboxylic acid*), m. p. 203—204°, and 4-*nitro*-2′-*diphenamic acid* (4-*nitro*-2′-*carbamidodiphenyl*-2-*carboxylic acid*), m. p. 164—165°. Treatment of the former with alkaline hypobromite yields 2-*nitrophenanthridone*, yellow, m. p. 348·5—349° (sealed tube), whilst the isomeride yields similarly 7-*nitrophenanthridone*, yellow, m. p. 292—293°. F. G. WILLSON.

Ether of a ketone hydrate. α-Benzylidene-β-(β-phenylethyl)succinic and benzyl-(β-phenylethyl)maleic acids. J. BOUGAULT (Compt. rend., 1927, **184**, 1255—1257).—The anhydride (I) prepared from the acid amide (II) (A., 1925, i, 921; 1926, 725), yields, on boiling with sodium hydroxide in amyl alcohol, α-benzylidene-β-(β-phenylethyl)succinic acid (cf. A., 1925, i, 1152), m. p. 161°, anhydride, m. p. 100°, which on further boiling yields the isomeric *benzyl*-(β-*phenylethyl*)*maleic acid* (III), m. p. 184° (*anhydride*, m. p. 106°). For the separation of the two acids, advantage is taken of the very slight

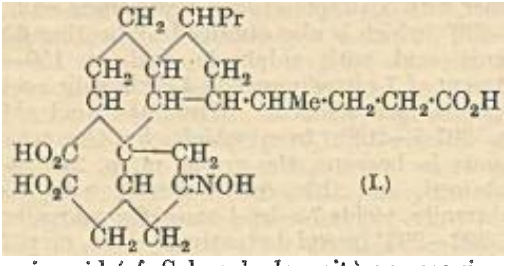


(I.) (II.)

solubility of the ammonium salt of the former in 3% ammonium chloride solution. The acid (III) is not hydrogenated by sodium amalgam. A third *isomeride*, $C_{19}H_{18}O_4$, m. p. 120° (*anhydride*, m. p. 112°), is produced when (I) is boiled with aqueous potassium hydroxide, the reaction being reversible. It is distinguished by the solubility of its calcium salt; it affords α-benzyl-β-(β-phenylethyl)succinic acid on reduction with sodium amalgam, and is converted by sodium hydroxide in amyl alcohol into (III). Each of the three acids yields a normal anhydride when heated with acetic anhydride for 10 min. at 100°, but prolonged treatment regenerates the anhydride (I) in each case. W. J. POWELL.

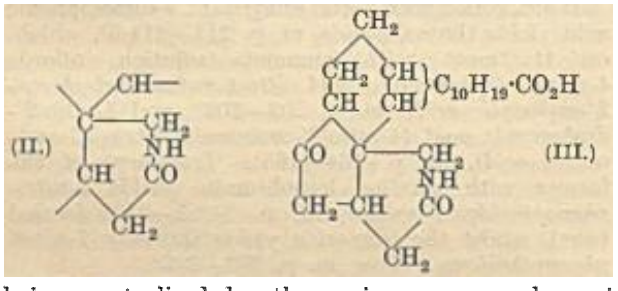
Bile acids. XVI. M. SCHENCK and H. KIRCHHOF (Z. physiol. Chem., 1927, **166**, 142—158; cf. Schenck, A., 1911, i, 10; 1919, i, 331).—The oxime

of deoxybilianic acid (I) (see Wieland, Schlichting, and Jacobi, this vol., 247) gives on isomerisation with



(I.)

sulphuric acid (cf. Schenck, *loc. cit.*) an *iso*oxime (II), m. p. 276°, hydrolysable by 20% hydrochloric acid to the corresponding amino-acid, $C_{24}H_{39}O_8N$, m. p. 195°, which regenerates the *iso*oxime when heated above its m. p. or in glacial acetic acid. The amino-acid titrates as a tribasic acid, one carboxyl group

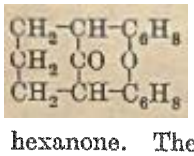


(II.) (III.)

being neutralised by the amino-group, and reacts with nitrous acid to form a nitrogen-free *compound*, not obtained pure. The amino-acid is converted by dry distillation in a vacuum into a *ketolactam-monocarboxylic acid*, $C_{23}H_{35}O_4N$ (III), m. p. 187—193° (sinters at 170°), a reaction similar to the conversion of choloidanic acid into pyrocholoidanic acid (Wieland, A., 1921, i, 113). There is also formed an impure *isomeride* of (III), m. p. 218—220° (sinters at 180°, completely clear at 225°). C. Hollins.

Condensation of benzaldehyde with organomagnesium compounds. A. P. Terentiev (J. Russ. Phys. Chem. Soc., 1927, **58**, 1265—1269).—See this vol., 152.

Action of sodamide on *cyclo*hexanone. R. Cornubert (Compt. rend., 1927, **184**, 1258—1259).—In the preparation of the sodium compound of *cyclo*hexanone, the latter should be in dilute solution, since in concentrated ethereal solution (20 g. in 80 c.c.) the product obtained after addition of water consists of *cyclo*hexylidene*cyclo*hexanone, together with a small quantity of the *substance*, $C_{18}H_{28}O_2$, m. p. 181—186° (corr.), which probably has the annexed formula, since with acetic anhydride and sodium acetate at 150° it yields neither an acetyl derivative nor di*cyclo*hexylidene*cyclo*hexanone. The amount of these condensation products formed depends on the quantity of solvent used (*e.g.*, with 20 g. of *cyclo*hexanone in 150 c.c. of ether less than 5% is obtained), and on the temperature and time of reaction, the maximum condensation occurring at 20°, but is not altered appreciably by the addition of an alkylating agent to the reaction mixture. W. J. Powell.

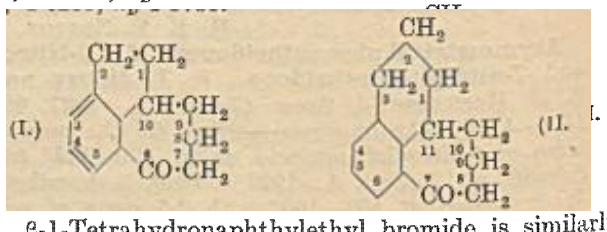


Alkyl*cyclo*-pentanones and -hexanones. III. Alkylation of 1-methyl*cyclo*hexan-2-one. A. Haller and R. Cornubert (Bull. Soc. chim., 1927, [iv], **41**, 367—383; cf. this vol., 152).—Further examination of the products obtained on methylating 1-methyl*cyclo*hexan-2-one with sodamide and methyl iodide or sulphate indicates that the dimethylation product consists of about 80% of 1 : 1- and 20% of 1 : 3-dimethyl*cyclo*hexanone, with traces of unchanged 1-methyl*cyclo*hexanone. The 1 : 1-dimethyl*cyclo*hexanone is readily obtained pure by fractional crystallisation of the semicarbazone. Further methylation of the dimethylated product affords a trimethyl*cyclo*hexanone, b. p. 178—179°/755 mm., d_4^{18} 0·9043, n^{18} 1·4493, possessing an odour of camphor, and finally a tetramethyl*cyclo*hexanone, b. p. 185—186°/770 mm., 100°/57 mm., $d_4^{17\cdot5}$ 0·8936, n_D^{18} 1·4470 (cf. A., 1913, i, 629), which, when freed from an unpleasant by-product, possesses an odour of camphor or menthol. Similarly ethylation of 1-methyl*cyclo*hexan-2-one with sodamide and ethyl bromide affords a product consisting of 83% of 1 : 1-methylethyl*cyclo*hexanone and 16% of the 1 : 3-isomeride with 1% of unchanged 1-methyl*cyclo*hexanone. Attempts to introduce the *iso*propyl group in the same way afforded in xylene solution only a small quantity of substance, $C_{10}H_{18}O$, b. p. 202—206°/760 mm. In ether or in benzene, only 12—14% of condensation product was obtained. The action of sodamide on the crude tetramethyl*cyclo*hexanones in xylene (cf. A., 1914, i, 291, 968) afforded small amounts of nitrogeneous liquids, b. p. 85—86°/24 mm. and 180°/17 mm., and nitrogeneous solid products, m. p. 120° and 146°.

R. Brightman.

Cyclanones and the ketonic function. R. Cornubert (Bull. Soc. chim., 1927, [iv], **41**, 541—606).—A lecture delivered on February 19, 1927.

Benzopolymethylene compounds. XIII. J. von Braun and E. Rath (Ber., 1927, **60**, [*B*], 1182—1196).—β-1-Hydrindylethyl bromide is converted by ethyl sodiomalonate into *ethyl* β-1-*hydrindylethylmalonate*, b. p. 212°/12 mm., and thence successively into β-1-hydrindylethylmalonic acid, γ-1-*hydrindyl*-n-*butyric acid*, b. p. 198°/11 mm., m. p. 92°, γ-1-*hydrindyl*-n-*butyryl chloride*, b. p. 172°/12 mm., and 6-*ketohomotetraphthene* (I), b. p. 172°/12 mm., d° 1·1118, n_D^{20} 1·5825 (*oxime*, m. p. 143°; *semicarbazone*, m. p. 203°). The ketone is reduced by Clemmensen's method to *homotetraphthene*, b. p. 127—128°/12 mm., d_4^1 1·0295, n_D^{20} 1·5750.



(I.) (II.)

β-1-Tetrahydronaphthylethyl bromide is similarly converted successively into *ethyl* β-1-*tetrahydronaphthylethylmalonate*, b. p. 229°/13 mm., β-1-tetrahydronaphthylethylmalonic acid, γ-1-*tetrahydronaphthyl*-n-*butyric acid*, b. p. 212°/12 mm., γ-1-*tetrahydronaphthyl*-n-*butyryl chloride*, b. p. 195°/19 mm.,

and *7-ketohomohexahydrobenznaphthene* (II), b. p. 182°/15 mm., m. p. 63°, d_4^{20} 1·1117 (*oxime*, m. p. 62°; *semicarbazone*, m. p. 221°). The new cyclic derivatives are obtained in very modest yield, although they are free from strain according to the Sachse–Mohr hypothesis. It appears doubtful if any theory based on considerations derived from tetrahedral models can fully explain the phenomena observed with di- and tri-cyclic compounds. H. WREN.

Thioethers of certain ketones, and their derivatives. A. CHRZASZCZEWSKA and S. CHWALINSKI (Rocz. Chem., 1927, **7**, 67—73).—The following substances of the type $(R{\cdot}CO{\cdot}CH_2)_2S$ are obtained by the action of various monochloroketones on sodium sulphide: *dibenzoyldimethyl sulphide*, m. p. 76·5—77·2° [*oxime*, m. p. 145—146° (decomp.), *phenylhydrazone*, m. p. 140—141°], and *di*-p-*chlorobenzoyldimethyl sulphide*, m. p. 121—121·6°.

R. TRUSZKOWSKI.

***N*-Alkylimines of benzophenone.** M. SOMMELET (Compt. rend., 1927, **184**, 1338—1339).—The following *N*-alkylimines of benzophenone have been prepared from benzophenone chloride and the corresponding amine by a modification of the method of Hantzsch and von Hornbostel (A., 1898, i, 195): methyl-, b. p. 168·5°/20 mm., m. p. 47—49°; *ethyl*-, b. p. 174·5°/21·5 mm., m. p. 61—62°; *allyl*-, b. p. 187°/22 mm., d_4^{22} 1·0475; cyclo*hexyl*-, b. p. 209—210°/17 mm., d_4^{21} 1·0268; benzyl-, 1·0358. These imines, with the exception of the allylimine, which was not examined, give stable methiodides which are hydrolysed quantitatively when their alcoholic solutions are boiled at 90°: $CPh_2{:}NRMeI + H_2O = CPh_2O + NHRMe.HI$ (cf., A., 1926, 946). E. H. SHARPLES.

Organic sulphur compounds. V. Action of Grignard's solutions on aromatic thioketones. A. SCHONBERG (Annalen, 1927, **454**, 37—46).—Diaryl thioketones react more or less readily with aromatic Grignard reagents, forming tetra-arylethylene sulphides (cf. Staudinger and Siegwart, A., 1921, i, 43). These are characterised by their reduction by zinc dust and acetic acid to the corresponding tetra-arylethylenes and by their tendency to form molecular *compounds*, *e.g.*, those of tetra-anisylethylene sulphide (A., 1925, i, 1300) with acetone (1 mol.) and with benzene (1 mol.). Xanthione is only slightly attacked by prolonged boiling with an ethereal solution of magnesium phenyl bromide, giving dixanthylene. The intermediate sulphide is not obtained. The difference in stability between tetraphenylethylene sulphide and dixanthylene sulphide thus resembles that between hexaphenylethane and 9 : 9′-diphenyl-9 : 9′-dixanthyl. Tetra-anisylethylene sulphide is quantitatively decomposed into tetra-anisylethylene and sulphur at 100°. 4 : 4′-Diethoxythiobenzophenone and 4 : 4′-diethoxy-5 : 5′-dimethylthiobenzophenone are converted by magnesium phenyl bromide into *tetra*-p-*phenetylethylene sulphide*, decomp. 156°, and *tetra*-6-*ethoxy*-m-*tolylethylene sulphide*, respectively. The latter is decomposed in boiling acetone solution, yielding tetra-6-ethoxy-*m*-tolylethylene (Gattermann, A., 1896, i, 179).

H. E. F. NOTTON.

Organic sulphur compounds. VI. Relation between constitution and stability to heat of organic compounds; thermal decomposition of mercaptols. A. SCHONBERG and O. SCHUTZ (Annalen, 1927, **454**, 47—53).—Dibenzylmercaptols of aromatic ketones, prepared by treating the latter with benzyl hydrosulphide in presence of hydrogen chloride and zinc chloride, or by heating ketone dichlorides with benzyl hydrosulphide, decompose on heating into the corresponding thioketone, *s*-diphenylethylene, and hydrogen sulphide. Their relative stability has been measured by observing the temperature at which they become coloured when heated in evacuated capillary tubes for 1 min. The following, in order of decreasing stability, (*a*) *dibenzylthioldibenzylmethane*, m. p. 103°, stable at 195°; dibenzylthioldiphenylmethane, decomp. 195°; 9 : 9-*dibenzylthiolxanthene*, m. p. 118—119° (decomp.), are compared with *s*-diphenyltetrabenzylethane, hexaphenylethane, and 9 : 9′-diphenyl-9 : 9′-dixanthyl; and (*b*) 9 : 9-*dibenzylthiolfluorene*, m. p. 101°, stable at 128°, > 9 : 9-dibenzylthiolxanthene, with diphenylbisdiphenyleneethane (Schlenk, A., 1910, i, 469) > diphenyldixanthyl. In general, substituents which increase the tendency to dissociation of the hexa-arylethanes produce a similar effect in the corresponding dibenzylthioldiarylmethanes. The preparation of xanthione from xanthone dibenzylmercaptole is described. *Dibenzylthioldi*-p-*anisylmethane*, m. p. 81·5°, decomposes on heating above its m. p.; phenyl αα-dibenzylthiolbenzyl ketone (Posner, A., 1902, i, 220) at about 200°, and p-*anisyl* αα-*dibenzylthiol*-p-*anisylmethyl ketone*, m. p. 112·5°, on heating above its m. p.

H. E. F. NOTTON.

Phenolic ketones and the Behn ketone synthesis. K. W. ROSENMUND and H. SCHULZ (Arch. Pharm., 1927, **265**, 308—319).—The reaction between phenols and acid chlorides with aluminium chloride in nitrobenzene solution to give phenol ketones (cf. Behn, G.P. 95,901, 1897) is of general applicability. The unique action of nitrobenzene is ascribed to its solvent action on the aluminium chloride complexes, but there exists the possibility of its entering into the reaction (cf. Scholl and Seer, A., 1922, i, 336). Monohydric phenols react readily except when the *p*-position to the hydroxyl group is occupied, but results are not so satisfactory with polyhydric phenols.

The following 4-hydroxy-2-methyl-5-*iso*propylphenyl (hydroxythymyl) ketones have been prepared from thymol: hydroxythymyl methyl ketone (*benzylidene* derivative, m. p. 167°); *ethyl ketone*, m. p. 112°, b. p. 200°/15 mm. (*oxime*, m. p. 153—154°); n-*propyl ketone*, m. p. 93°, b. p. 204°/14 mm. (*oxime*, m. p. 117—118°); iso*propyl ketone*, m. p. 80° (*oxime*, m. p. 161—162°); iso*butyl ketone*, m. p. 108 (*oxime*, m. p. 125—135°); *phenyl ketone*, m. p. 153° (*oxime*, m. p. about 157°). The ethyl and *iso*butyl ketones are reduced by amalgamated zinc and dilute hydrochloric acid to 6-n-*propylthymol*, b. p. 146°/14 mm. (*methyl ether*, b. p. 138°/15 mm.), and 6-iso*amylthymol*, b. p. 170°/15 mm. *o*-Propylphenol, prepared in quantitative yield from *o*-allylphenol by hydrogenation, gives an analogous series of *para*-ketones: 4-*hydroxy*-3-n-*propylphenyl methyl ketone*, m. p. 87° (*semicarbazone*, m. p. 192°); *ethyl ketone*, m. p. 81° (*semicarbazone*, m. p. 128°): n-*propyl ketone*, m. p. 54°,

b. p. 210°/14 mm. (*semicarbazone*, m. p. 151°); *isobutyl ketone*, amorphous solid, b. p. 220°/28 mm. (*oxime*, m. p. 87°; *semicarbazone*, m. p. 156°); *heptyl ketone*, m. p. 60—61° (*semicarbazone*, m. p. 137°). *p*-Cresol reacts with acetyl chloride and aluminium chloride to give 3 : 5-diacetyl-*p*-cresol, whilst resorcinol, pyrogallol, and phloroglucinol give resacetophenone, gallacetophenone, and phloroacetophenone, respectively. Benzoyl chloride and phloroglucinol furnish benzoylphloroglucinol and phloroglucinol tribenzoate. S. COFFEY.

Uranyl acetyl(and benzoyl)-acetone compounds. K. HAGER (Z. anorg. Chem., 1927, **162**, 82—86; cf. this vol., 358).—The following yellow, crystalline solids are obtained by adding to a methyl-alcoholic solution of uranyl nitrate the solution of the base and either acetylacetone or benzoylacetone in methyl alcohol: *ammonium, methylamine*, and *aniline triacetylacetoneuranates*, $NH_3,C_5H_8O_2,(C_5H_7O_2)_2UO_2$, etc.; *pyridine* and *quinoline diacetylacetoneuranates*, $C_5H_5N,(C_5H_7O_2)_2UO_2$, etc.; and *pyridine dibenzoylacetoneuranate*, $C_5H_5N,(C_{10}H_9O_2)_2UO_2$.

R. CUTHILL.

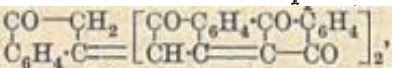
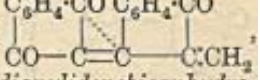
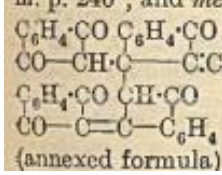
Action of ammonia and its derivatives on o-acetoacetylphenols. G. WITTIG and H. BLUMENTHAL (Ber., 1927, **60**, [*B*], 1085—1094).—3-Acetylaceto-*p*-cresol is converted by alcoholic ammonia into a mixture of 3-α-*amino*-β-*acetylvinyl*-p-*cresol*, m. p. 131·5—132° (decomp.), and 3-β-*aminocrotonyl*-p-*cresol*, m. p. 101—102° (also +benzene, m. p. 82—87°), the latter substance being also obtained under similar conditions from 3-acetyl-2 : 6-dimethyl- or 2 : 6-dimethyl-chromone. Treatment of 3-β-aminocrotonyl-*p*-cresol with methyl sulphate affords the corresponding *methyl ether*, m. p. 79·5—80°, and since this compound is also obtained by the action of alcoholic ammonia on the methyl ether of 3-acetylaceto-*p*-cresol, it follows that the open-chain structure must be assigned to the compounds mentioned above. The analogous compounds prepared by Wittig (A., 1925, i, 279; for 6- read 3-acetylaceto-*o*-cresol) and Schneider and Bode (A., 1923, i, 699) must also be regarded as open-chain compounds, and not as substituted chromanones. 3-Acetoacetyl-*p*-cresol and aniline in alcoholic solution give 3-β-*anilinocrotonyl*-p-*cresol*, m. p. 105—106°, converted by sulphuric acid into 2 : 6-dimethylchromone, by acetic anhydride and sodium acetate into 3-acetyl-2 : 6-dimethylchromone, and by semicarbazide into the semicarbazone of 3-acetoacetyl-*p*-cresol. 3-β-Aminocrotonyl-*p*-cresol is transformed by benzoyl chloride and sodium hydroxide into the corresponding *benzoate*, m. p. 162° (decomp.), hydrolysed by 2*N*-sulphuric acid to the *benzoate* of 3-*acetoacetyl*-p-*cresol*, and passing when heated at 170—180° into 3-*acetyl*-6-*methylflavone*, m. p. 108—109°. Treatment of 3-acetoacetyl-*p*-cresol or 3-β-aminocrotonyl-*p*-cresol with semicarbazide yields an impure semicarbazone, m. p. 190—220° (decomp.), converted by boiling sodium hydroxide into 5(3)-2′-*hydroxy*-5′-*methylphenyl*-3(5)-*methylpyrazole*, m. p. 103—104° (O-*acetate*, m. p. 138—139°; *diacetate*, m. p. 79—80°). 3-α-Amino-β-acetylvinyl-*p*-cresol similarly yields a non-homogeneous semicarbazone, m. p. 155—163°, which is converted by concentrated sulphuric acid into 5-6′-*hydroxy*-m-*tolyl*-3-*methylpyrazole*-1-*carbonamide*, m. p. 169—170° (decomp.), also obtained from 3-acetoacetyl-*p*-cresol and semicarbazide hydrochloride. 3-*Phenyl*-5-2′-*hydroxy*-5′-*methylphenyl*-5-*methylpyrazole*, m. p. 174—175°, is prepared from phenylhydrazine and 3-acetoacetyl-*p*-cresol or 3-β-aminocrotonyl-*p*-cresol.

3-Acetoacetyl-*o*-cresol and alcoholic methylamine afford 3-β-*methylaminocrotonyl*-o-*cresol*, m. p. 109—110°; 3-β-*anilinocrotonyl*-o-*cresol* has m. p. 90—91°. The semicarbazone of 3-acetoacetyl-*o*-cresol yields an *oxime*, m. p. 198°, transformed by hydrochloric acid into 5 : 2′-hydroxy-*m*-tolyl-3-methyl*iso*oxazole, m. p. 91° (cf. Wittig and Bangert, A., 1926, 177). Acetic anhydride and sodium acetate convert the semicarbazone of 3-acetoacetyl-*o*-cresol into the *lactone* of 5 : 2′-*hydroxy*-m-*tolyl*-3-*methylpyrazole*-1-*carboxylic acid*, m. p. 200—201°, and the O-*acetate* of 5(3)-2′-*hydroxy*-m-*tolyl*-3(5)-*methylpyrazole*, m. p. 137·5—138° (corresponding *diacetate*, m. p. 62·5—63·5°).

2-β-*Aminocrotonyl*-1-*naphthol*, m. p. 153—154°, and 2-β-*anilinocrotonyl*-1-*naphthol*, m. p. 156—157°, are described. 1-β-Aminocrotonyl-2-naphthol gives a *benzoate*, m. p. 159° (decomp.), converted by concentrated sulphuric acid into 2-methyl-5 : 6-benzochromone, and passing at 200° into 3-*acetyl*-5 : 6-*benzoflavone*, m. p. 170·5—171°. 2-Methyl-5 : 6-benzochromone and 5(3) : 2′-*hydroxynaphthyl*-3(5)-*methylpyrazole*, m. p. 144—145°, are obtained from semicarbazide and 1-β-aminocrotonyl-2-naphthol. 1-*Acetoacetyl*-2-*methoxynaphthalene*, m. p. 70—71°, is prepared by the action of sodium on 1-acetyl-2-methoxynaphthalene and ethyl acetate. H. WREN.

Compounds resembling curcumin. H. FINGER and W. SCHOTT (J. pr. Chem., 1927, [ii], **115**, 281—291).—Compounds in which the central methylene group of curcumin (A., 1910, i, 628) has been replaced by a *p*-phenylene or 4 : 4′-diphenylene group resemble this substance in showing characteristic colour changes to brown and red in alkaline solution, and to intense red or violet in sulphuric acid. In presence of glacial acetic and a little sulphuric acid, vanillin and *p*-diacetylbenzene give, first, yellow p-*feruloylacetophenone* (p-4-*hydroxy*-3-*methoxycinnamoylacetophenone*), m. p. 158° (*acetyl* derivative, m. p. 161°), and, on further treatment, p-*diferuloylbenzene*, yellow, m. p. 229 (*diacetyl* derivative, m. p. 259°). p-*Di*-5-*bromoferuloylbenzene*, m. p. 256°, from 5-bromovanillin and diacetylbenzene, forms a *tetrabromide*, decomp. 235°, which is also obtained by the direct bromination of diferuloylbenzene. In alcoholic sodium hydroxide, diacetylbenzene affords with piperonal, p-*di*-3 : 4-*methylenedioxycinnamoylbenzene*, m. p. 260°, and with *p*-dimethylaminobenzaldehyde, 4-p-*dimethylaminocinnamoylacetophenone*, m. p. 124—125°. Vanillin is converted by fuming sulphuric acid (20% anhydride) into *vanillin*-5-*sulphonic acid*, m. p. 123—125°, which gives 5-nitrovamllin with fuming nitric acid. p-*Diferuloylbenzene*-5 : 5′-*disulphonic acid* ($+6H_2O$) is reddish-brown, the anhydrous acid is nearly black. 4 : 4′-*Diacetyldiphenyl*, m. p. 190°, obtained in small yield by heating *p*-iodoacetophenone with copper powder at 235—260°, condenses with

vanillin, giving yellowish-brown 4 : 4′-*diferuloyldiphenyl*, m. p. 223°, and with vanillin-5-sulphonic acid, giving reddish-brown 4 : 4′-*diferuloyldiphenyl*-5″ : 5‴-*disulphonic acid* ($+n H_2O$), the anhydrous acid being dark brown. H. E. F. Notton.

Truxenequinone. Genetic relationships between indanedione, di-indone, and truxenequinone. M. Jonescu (Ber., 1927, **60**, [*B*], 1228—1235).—The view of Stobbe and Zschoch (this vol., 347) that the formation of truxenequinone from anhydrobisindanedione is due to initial fission into indanedione cannot be accepted, since this change cannot occur in media such as acetic anhydride, alcoholic hydrogen chloride, or concentrated sulphuric acid, which permit only the reverse change. Further, anhydrobisindanedione is converted by warm anhydrous pyridine in presence of piperidine into truxenequinone, whereas, under these conditions, its fission to indanedione is impossible. The conversion of anhydrobisindanedione by phenylhydrazine into indanedionediphenylhydrazone cannot be regarded as confirmation of Stobbe's views. It is considered probable that anhydrobisindanedione undergoes autocondensation with production of a compound, which by loss of water and indandione yields truxenequinone or reacts further with anhydrobisindanedione. Thus in cold pyridine solution in presence of piperidine, anhydrobisindanedione affords truxenequinone and the *compound*  , m. p. 328—329°. Anhydrobisindanedione is converted by hexamethylenetetramine in boiling xylene into *methyleneanhydrobisindanedione*,  , m. p. 240°, and *methyleneindanedionylidenebisanhydrobisindanedione*, $C_{46}H_{24}O_7$, m. p. 234°. Methylenanhydrobisindanedione and indanedione in alcohol–xylene in presence of piperidine give the *compound*  (annexed formula), m. p. 220°. H. Wren.

Quinonethiolimines. E. Gebauer-Fullnegg and H. A. Beatty (J. Amer. Chem. Soc., 1927, **49**, 1361—1365; cf. this vol., 52).—4-Chloro-2-nitrophenylthiol-*p*-hydroxyanilide is reduced by aluminium amalgam in ether–alcohol with quantitative formation of *p*-aminophenol. Treatment of 4-aminoresorcinol hydrochloride in ether with 4-chloro-2-nitro-1-chlorothiolbenzene and magnesium carbonate affords 4-chloro-2-nitrophenylthiol-2 : 4-dihydroxyanilide, orange-brown, amorphous, m. p. 133° (decomp.) [*silver* salt ($+1AgOAc$)]. On reduction with zinc dust and acetic acid in presence of sodium acetate, this yields 4-chloro-1-methylbenzthiazole, together with the tetra-acetyl derivative of aminoresorcinol (cf. Henrich and Wagner, A., 1903, i, 88), whilst oxidation with hydrogen peroxide affords 4-*chloro-2-nitrophenyl-2′-hydroxybenzoquinonethiolimine*. The latter dyes wool directly in yellowish-brown shades, a deeper brown being obtained by previous treatment with chromium salts. F. G. Willson.

Colouring matter of Paprika. L. Zechmeister and L. von Cholnoky (Annalen, 1927, **454**, 54—71).—After preliminary treatment with aqueous acetone to remove fats, capsicum-red, the colouring matter of *Capsicum annuum*, may be extracted from the dried fruit skins by light petroleum. On recrystallisation, it forms a red, microcrystalline powder, which still contains traces of fat, and in solution is 2—3·6 times as intensely coloured as carotin. It cannot therefore be identical with the latter (cf. Pabst, A., 1892, 1263; Kohl, Diss., Leipzig, 1902). If the fats are hydrolysed by treating a crude light petroleum extract with 30% methyl-alcoholic potassium hydroxide at the ordinary temperature, the pigment is precipitated. Its principal constituent (0·09—0·2% of the dried skins), *capsanthin*, $C_{34}H_{48}O_3$ or $C_{34}H_{50}O_3$, dark red, m. p. (indef.) 167—168° (corr.), is easily purified by recrystallisation. This resembles fucoxanthin in many respects; an ethereal solution is decolorised by bromine, gives a blue colour with sulphuric acid, and a characteristic dark greenish-blue with hydrochloric acid. Iodine in carbon disulphide gives a black iodide, permanganate in acetone is decolorised. The alcoholic solution shows absorption bands at about λ 490 and λ 450; in carbon disulphide and ether, the absorption is more general. The close resemblance in chemical properties and in absorption spectra shown by the products isolated with and without the use of alkali indicates that capsanthin is probably present as such in the raw material. Determination of the total colouring matter (0·38% calc. as capsanthin) shows that only subsidiary amounts of other pigments are present. H. E. F. Notton.

Protoretenes. A. Tschirch (Arch. Pharm., 1927, **265**, 347—352).—Natural resins such as storax, asafœtida, elemi, benzoin, and the balsams, undergo changes on keeping, the amount of material soluble in ether and insoluble in light petroleum increasing with age. Hence the protoretenes must be present in the ether-soluble portion. It is advisable to break down resins by means of indifferent solvents rather than by chemical means. S. Coffey.

Carotinoid pigments of the higher plants. H. Kylin (Z. physiol. Chem., 1927, **163**, 229—260).—Capillary analyses of alcoholic and ethereal extracts of the fruits, flowers, etc. of various plants have shown the presence of the known pigments lycopin, carotin, xanthophyll, phylloxanthin, and rhodoxanthin. Besides these, other pigments probably identical with those described by Lubimenko (Mem. Acad. Sci. Petrograd, 1916, **33**, 8) have been found, and are named as follows: *capsumin*, α, β, and γ, in ripe fruit of *Capsicum annuum*; *taxorhodin*, in the arillus of *Taxus baccata*; *arumin*, accompanying lycopin in the fruits of *Lycopersicum esculentum*, *Solanum Balbisii*, *S. dulcamara*, *Arum italicum*, and *Rosa canina*, and in the roots of *Brassica napus*; *physalin*, in the calyx and fruit of *Physalis Alkekengi*, and in the fruit of *Lycium carolinium* and *Solanum pseudocapsicum*; sorbusin, in the fruit of *Sorbus aucuparia*, *S. suecica*, and *Rosa canina*. A new orange-red pigment *calendulin* occurs in the flowers of *Calendula officinalis*. C. Hollins.

Pulegone oxide. N. Prileschaev (Bull. Soc. chim., 1927, [iv], **41**, 687—691; cf. A., 1912, i, 633).—

Pulegone is slowly converted by activated oxygen in ice-cold ethereal solution into *pulegone oxide*, $CHMe{\cdot}CH_2{\cdot}CH_2$ / $CH{:}C(OH){\cdot}C(O)CMe_2$, b. p. 137—138°/24 mm., m. p. 43—44°, which is optically inactive and yields no crystalline oxime, semicarbazone, or *p*-bromophenylhydrazone. The *phenylhydrazide*, m. p. 56·5—57·5°, has a composition varying between $C_{10}H_{16}O{:}N{\cdot}NHPh$ and $C_{10}H_{16}O{:}N{\cdot}NHPh,PhNH{\cdot}NH_2$. When gently heated with dilute sulphuric acid, the oxide affords acetone and the αδ-dialdehydo*iso*pentane, b. p. 90—91°/13 mm., d_{15}^{15} 1·0555, n_D^{15} 1·4729 (*diphenylhydrazone*, m. p. 138—139°), oxidised to β-methyladipic acid with moist silver oxide. Repeated distillation or heating at 200° changes the oxide into an unsaturated *substance*, $C_{10}H_{16}O_2$, b. p. 123—124°/25 mm., d_{15}^{1} 1·0038, n_D^{16} 1·4666 (*semicarbazone*, m. p. 210·5—211·5°) (cf. Tiffeneau, A., 1926, 383, 818). The above facts indicate that the resistance of compounds of the type CHR:CH·COR to oxidation by perbenzoic acid (cf. Boeseken, A,. 1926, 681) is not a general behaviour, although it is possible that enolisation of pulegone precedes its oxidation. It is suggested that the velocity of oxidation of aldehydes and ketones may depend on their degree of enolisation. R. Brightman.

Irreversible catalysis of unsaturated cyclic hydrocarbons. V. Contact transformation of thujene. N. D. Zelinski and B. A. Kasanski (Ber., 1927, **60**, [*B*], 1096—1100; cf. A., 1925, i, 821).—Thujene is converted by hydrogen in presence of palladised charcoal at 155° into a hydrocarbon, $C_{10}H_{20}$, b. p. 149—151°/739·7 mm., d_4^{22} 0·8254, n_D 1·4486, possibly 1 : 2- or 1 : 3-dimethyl-3-*iso*propyl*cyclo*pentane. Under analogous conditions, thujane gives the same product. The irreversible catalytic decomposition of thujene at 197—200° in presence of palladised asbestos affords cymene, thujane, and a cyclic hydrocarbon, $C_{10}H_{20}$, b. p. 158·5—161·5°/745 mm., d_4^{20} 0·7920, n_D^{18} 1·4388. H. Wren.

Action of carbonyl chloride on pinene. M. Garino and S. Boidi (Gazzetta, 1927, **57**, 329—330).—Carbonyl chloride, unlike sulphuryl chloride, has no action on pure pinene. E. W. Wignall.

Preparation of camphor from pinene. H. M. Mulany and E. R. Watson.—See B., 1927, 426.

Action of potassium cyanide on pernitroso-derivatives. M. Passerini (Ber., 1927, **60**, [*B*], 1201—1202; cf. A., 1926, 726; Houben and Pfankuch, this vol., 364).—Pernitrosocamphor is converted by potassium cyanide into menthonecyanohydrin, m. p. 145—146°, $[\alpha]_D^{20}$ +95·88°, which is hydrolysed by acids to the *lactone*, $C_{10}H_{18}{<}\begin{matrix}O\\CO\end{matrix}$, of a hydroxymenthanecarboxylic acid, m. p. 78—79°, $[\alpha]_D^{23}$ +20·46°. Reduction of 2-cyano-2-nitrosohydroxylaminocamphane with aluminium amalgam affords *d*- and *l*-bornylamine. The silver salt of the former compound decomposes when warmed into camphor and oily products; it is converted by alkyl iodides into the ethers (I) (*methyl*, m. p. 104—106°, $[\alpha]_D$ −20·49°; *ethyl*, m. p. 51—53°). H. Wren.

Fenchene series. I. Synthesis of *apo*fenchocamphoric acid. W. F. Short (J.C.S., 1927, 961—962).—By the condensation of ethyl propane-αα'γγ'-tetracarboxylate with *iso*butylene bromide in presence of toluene and powdered sodium (1·5 atoms), hydrolysis of the resulting ester, and heating the tetracarboxylic acid, m. p. 170—179°, at 220—230°, a mixture of *cis*- and *trans*-*apo*fenchocamphoric acids is obtained in 5% yield (*iso*butylene and other products being formed). The two forms are separated by conversion of the *cis*-acid into its anhydride by heating with acetyl chloride for 2 days. This synthesis establishes the constitution of *apo*fenchocamphoric acid as 4 : 4-dimethyl*cyclo*pentane-1 : 3-dicarboxylic acid. J. W. Baker.

Formation of coumaranones and chromanones from phenols. K. von Auwers, H. Baum, and H. Lorenz (J. pr. Chem., 1927, [ii], **115**, 81—106; cf. A., 1924, i, 1219).—When *p*-chloroanisole and α-bromo-*iso*butyryl bromide are treated in carbon disulphide with aluminium chloride, a product is obtained from which may be isolated 4-*chloro*-2-α-*hydroxy*iso*butyryl*-*phenol*, m. p. 73° (*semicarbazone*, m. p. 233—239°; *diacetyl* derivative, m. p. 65—66°). p-*Chlorophenyl* iso*butyrate*, m. p. 29°, b. p. 120°/11 mm., when heated with aluminium chloride at 110°, yields 4-*chloro*-2-iso*butyrylphenol*, b. p. 130°/20 mm., d_4^{20} 1·192, n_{He}^{20} 1·5521, which reacts with bromine, giving a yellow, oily *bromo*-derivative. The bromo-derivative is converted by alcoholic potassium hydroxide into 4-*chloro*-1 : 1-*dimethylcoumaranone* (I), m. p. 67—68°, $d_4^{20\cdot6}$ 1·1484, 1·51605, and 4-chloro-2-(α-hydroxy*iso*butyryl)phenol. o-*Tolyl* iso*butyrate*, b. p. 112°/15 mm., d_4^{20} 1·001, n_{He}^{20} 1·4911, with aluminium chloride yields 5-iso*butyryl*-o-*cresol*, m. p. 122°, and 3-iso*butyryl*-o-*cresol*, d_4^{20} 1·047, 1·5368, which reacts with acetic anhydride, yielding a *substance*, $C_{15}H_{18}O_4$, m. p. 64—65° (either α-2-acetoxy-3-methylbenzoyl-αα-dimethylacetone or 2-acetoxy-2 : 3 : 3 : 8-tetramethylchromanone), and yields an *acetyl* derivative, b. p. 152—154°/12 mm., d_4^{20} 1·074, n_{He}^{20} 1·5136. This acetyl derivative yields an oily *bromo*-derivative, which with alcoholic potassium hydroxide gives 1 : 1 : 6-*trimethylcoumaranone*, m. p. 67—68·5°, 1·0010, $n_\alpha^{160\cdot6}$ 1·50063 (*semicarbazone*, m. p. 240°), and with diethylaniline gives 3 : 8-*dimethylchromanone*, m. p. 65—66° (*semicarbazone*, m. p. about 220°). The preparation of 3-*iso*butyryl-*p*-cresol (*semicarbazone*, m. p. 193—194°; *oxime*, m. p. 149—150°; *phenylhydrazone*, m. p. 126·5—127·5°) is described. By reactions similar to those detailed above, as-m-*xylenyl* iso*butyrate*, b. p. 245°, yields 5-iso*butyryl*-as-m-*xylenol*, b. p. 129—131°/13 mm., d_4^{20} 1·028, n_{He}^{20} 1·5729 (*acetyl* derivative, b. p. 150—152°/14 mm.), 1 : 1 : 4 : 6-*tetramethylcoumaranone*, m. p. 68—69°, and 3 : 6 : 8-*trimethylchromanone* as a colourless oil (*semicarbazone*, m. p. 232—235°).

When 4 : 6-dimethylcoumaranone (*semicarbazone*, m. p. 235°) is treated with *p*-nitrophenylhydrazine in dilute ethyl alcohol it yields 2-*hydroxy*-3 : 5-*dimethyl*-

phenylglyoxal-pp'-dinitro-osazone as a reddish-brown powder, m. p. 270°. *4-Nitro-2-chloroacetylphenol*, m. p. 163—164°, which cannot be obtained by the action of aluminium chloride on *p-nitrophenyl chloroacetate*, m. p. 94°, is prepared by the nitration of *o*-chloroacetylphenol and reacts with dilute sodium hydroxide, giving a poor yield of *4-nitrocoumaranone*, m. p. 152°. The following substances are described: *p-tolyl diphenylacetate*, m. p. 76°, which with aluminium chloride yields a *substance*, $C_{21}H_{16}O_2$; *p-tolyl dibenzylacetate*, m. p. 78—79°; *2-chloroacetoxydiphenyl*, b. p. 198—200°/20 mm., which with aluminium chloride yields a *substance*, $C_{28}H_{20}O_4$, m. p. 275°, corresponding with a bimolecular phenylcoumaranone.

The influence of the substituents on the case of ring formation is discussed. R. W. WEST.

[Derivatives of 5 : 6-dihydroxycoumaranone.] K. FEIST and (FRL.) E. SIEBENLIST (Arch. Pharm., 1927, **265**, 196—211).—5 : 6-Dihydroxycoumaranone cannot be methylated by any of the usual methods, but the acetyl derivative furnishes *5 : 6-dimethoxycoumaranone*, m. p. 122—123°, when treated with methyl-alcoholic potassium hydroxide and methyl iodide. 5 : 6-Diacetoxycoumaranone condenses with veratraldehyde and resorcylaldehyde dimethyl ether, forming *5 : 6-diacetoxy-3' : 4'-dimethoxybenzylidenecoumaranone* and the corresponding *3' : 5'-dimethoxy-compound*, yellow needles, m. p. 184° and 190—191°, respectively. The former affords a crystalline *dibromide*, as does also the benzylidene derivative of 4-methyl-2-coumaranone (*dibromide*, m. p. 154°). 5 : 6-Diacetoxycoumaranone and the above-mentioned dimethoxybenzylidene derivatives form deep red, crystalline *oxonium* salts with perchloric and hydrochloric acids. The keto-group in diacetoxycoumaranone does not react with hydroxylamine or semicarbazide, whilst the veratrole derivative does not react with magnesium phenyl bromide. 5 : 6-Diacetoxycoumaranone also condenses with acetyl-β-naphtholaldehyde, acetyl-5-bromosalicylaldehyde, cuminal, and *o*-aminobenzaldehyde to give *β-acetoxynaphthylidene-5 : 6-diacetoxycoumaranone*, m. p. 135°, *5 : 6 : 2'-triacetoxy-5'-bromobenzylidenecoumaranone*, blackening at 205°, *5 : 6-diacetoxy-4'-isopropylbenzylidenecoumaranone*, m. p. 183°, and *5 : 6-diacetoxy-6-aminobenzylidenecoumaranone hydrochloride*, respectively. The last-named and the corresponding *5 : 6-dimethoxy*-derivative undergo ring closure when boiled with acetic anhydride, with the formation of *diacetoxycoumarinoline*, m. p. above 250°, and *dimethoxycoumarinoline*, m. p. 176° (cf. Stoermer and Barthelmes, A., 1915, i, 152).

Attempts to condense diacetoxycoumaranone with aliphatic aldehydes, aryl ketones, and camphor or the corresponding ketone-anils invariably lead to the recovery of unchanged yellow diacetoxycoumaranone (m. p. 106°), but with acetophenone and menthone a colourless *substance*, m. p. 104°, having the same composition but twice the mol. wt. is obtained.

S. COFFEY.

Furfuraldehyde derivatives. IV. Nitro-derivatives of the furylethylene series. I. KASI- Chem. Soc. Japan, 1927, 2, 110—113).—4-Dinitrotoluene condenses with furfuraldehyde in presence of piperidine, forming *2 : 4-dinitro-ω-furylstyrene*, orange, m. p. 135—135·5° (yield 67%); 2 : 4 : 6-trinitrotoluene yields *2 : 4 : 6-trinitro-ω-furylstyrene*, red, m. p. 123—124°, but 2 : 6-dinitrotoluene gives no condensation product under similar conditions. Furfuraldehyde with phenylnitromethane in presence of methylamine affords *α-nitro-ω-furylstyrene*, m. p. 87—87·5°, whilst with nitroethane it yields *β-nitro-α-furyl-Δ^α-propene*, m. p. 48—48·5°. Those derivatives which are nitrated in the side-chain give coloured solutions with alcohol, the colour vanishing on addition of alkali and returning when mineral acid is added. W. J. POWELL.

Fluorescein and some of its derivatives. W. R. ORNDORFF and A. J. HEMMER (J. Amer. Chem. Soc., 1927, **49**, 1272—1280).—When a dilute alkaline solution of fluorescein is acidified at the ordinary temperature with acetic acid, the fluorescein is precipitated in a yellow, finely granular state, of no recognisable crystal form (I). If the acidification is carried out at the b. p. with mineral acids, the fluorescein separates as bright red prisms, apparently rhombic, m. p. (sealed tube) 314—316° (decomp.) (II). (I) is converted into (II) by boiling with water and by heating at 260°. Neither form is hydrated (cf. Baeyer, A., 1877, i, 195) and no other forms of yellow fluorescein could be obtained (cf. Liebig, A., 1912, i, 376). The lactoid structure is ascribed to (I) (cf. Orndorff and Hitch, A., 1914, i, 542), whilst (II) is considered to be *p*-quinonoid. Yellow fluorescein crystallises from methyl alcohol +2MeOH, removal of which leaves red fluorescein. Fluorescein also crystallises with $2Ph\cdot NO_2$. Certain other solvents also effect conversion of (I) into (II), and *vice versa*. Both (I) and (II) combine with dry hydrogen chloride, with formation of different yellow *hydrochlorides*. Dry ammonia is practically without action on (I), but is absorbed to the extent of 2·5 mols. by (II); alcoholic ammonia converts either form into a product containing 1 mol. of NH_3 and 0·5 mol. of EtOH. Phenylcarbimide converts either form into a diphenylcarbamate, m. p. 197—198° (cf. Haller and Guyot, A., 1893, i, 409). The following derivatives of the lactoid fluorescein were also prepared: diacetate, m. p. 200°; *hydrazide* (+H_2O), decomp. 280° (*tetra-acetate*, m. p. 233·5—234·5°). Methyl alcohol, in presence of hydrochloric or sulphuric acid, converts either form into the *methyl* ester, m. p. 269—270° (*hydrochloride*; *acetate*, m. p. 210—211°). Bromination of either form in glacial acetic acid yields first *dibromofluorescein*, decomp. 280—290° (*dibenzoate*, m. p. 239—240°; *monohydrochloride*; *dihydrochloride*; *diammonium* salt), and then eosin, which is obtained in a colourless form crystallising with 2·5 or 1·5 mols. of H_2O, m. p. 295—296·5° to a dark red liquid, after becoming pink at 200°, by hydrolysis of the diacetate with alcoholic sodium hydroxide. *Di-* and *tetra-ammonium* salts of colourless eosin, and *monohydrates* of these, were prepared. F. G. WILLSON.

Pyrogallolbenzein and some of its derivatives. W. R. ORNDORFF and C. WANG (J. Amer. Chem. Soc., 1927, **49**, 1284—1289; cf. A., 1925, i, 277).—2 : 3 : 4-Trihydroxybenzophenone has been identified as a by-product in the preparation of pyrogallol-

benzein from benzotrichloride and pyrogallol. Dry pyrogallolbenzein absorbs about 2 mols. of ammonia. It forms a *sulphate*, a *perchlorate* (anhydrous and as *trihydrate*), and a *triacetate* ($0{\cdot}5Ac_2O$). By boiling pyrogallolbenzein with acetic anhydride and a trace of sulphuric acid, the *tetra-acetate* of the corresponding *carbinol*, decomp. 150—155°, is obtained. The analogous *tetrabenzoate*, m. p. 185—187°, was prepared. Bromination of pyrogallolbenzein in formic acid affords a *dibromo*-derivative, purplish-red, decomp. 260—263° (*triacetate*, bluish-green, +AcOH and +HBr), which combines feebly with 2 mols. of ammonia or hydrogen chloride. *Dinitropyrogallolbenzein*, decomp. 195—200°, is described. *Pyrogallolbenzein trimethyl ether*, brick-red, m. p. 187—189°, is obtained by the Claisen method (A., 1913, i, 1175). A *trisodium* salt of pyrogallolbenzein, reddish-bronze, triclinic, was prepared. Reduction of pyrogallolbenzein with zinc dust and formic acid affords 3 : 4 : 5 : 6-*tetrahydroxy*-9-*phenylxanthen* ($+3H_2O$) (*tetra-acetate*, m. p. 225—226°). F. G. Willson.

Thioacetaldehyde. E. Müller (with G. Schiller) (J. pr. Chem., 1927, [ii], **116**, 175—191).—Hydrogen sulphide converts acetaldehyde in presence of hydrochloric acid into *monothioparaldehyde*, m. p. 55°, which is converted by 2*N*-hydrochloric acid into α-trithioacetaldehyde; by acetyl chloride into β-trithioacetaldehyde; by phosphorus pentachloride partly into β-trithioacetaldehyde; by thionyl chloride into αα′-dichlorodiethyl sulphide (?), b. p. 53—55°/15 mm., and by potassium permanganate into the corresponding *sulphone*, m. p. 152°. Hydrogen sulphide reacts with paraldehyde, giving α-trithioacetaldehyde and a *substance*, b. p. 83—87°/15 mm. β-Trithioacetaldehyde is converted by sodium hypochlorite solution into *αα-dichlorodiethyl sulphide-α′-sulphonyl chloride*, $CMeCl_2{\cdot}S{\cdot}CHMe{\cdot}SO_2Cl$, b. p. 50—52°/0·1 mm., together with a small quantity of *α-chlorodiethyl sulphoxide α′-sulphonyl chloride*, $CHMeCl{\cdot}SO{\cdot}CHMe{\cdot}SO_2Cl$, decomp. 130°, whilst chlorine reacts with an aqueous suspension in presence of a trace of iodine, yielding *α-chloroethanesulphonyl chloride*, b. p. 72—73°/13 mm. H. Burton.

Pyrrolidones. (Mme.) Ramart-Lucas and Fasal (Compt. rend., 1927, **184**, 1253—1255).—The sodium compounds of 3 : 3 : 5-trimethyl- and of 5-methyl-3 : 3-diethyl-pyrrolidone condense with halogenated compounds to form products which are not attacked by hydrogen chloride or bromide at 180°, and are therefore *N*-derivatives, indicating that the parent pyrrolidone reacts exclusively in the lactam form (cf. the behaviour of carbostyril and hydrocarbostyril, Friedländer and Ostermaier, A., 1882, 201). At 210°, however, fission of the pyrrolidone ring takes place, forming an *N*-substituted γ-amino-αα-dimethyl(or diethyl)valeric acid, which at once reacts with the halogen acid present, yielding γ-amino-αα-dimethyl-(or diethyl)valeric acid and the halide of the substituent. The *N*-substituted pyrrolidones are not affected by sodium ethoxide and are inert towards organomagnesium derivatives unless a side-chain contains a group capable of reacting with them. The following were prepared: 3 : 3 : 5-*trimethyl*-1-*allyl*-2-*pyrrolidone*, 1-*benzyl*-3 : 3 : 5-*trimethyl*-2-*pyrrolidone*, *ethyl* 3 : 3 : 5-*trimethyl*-2-*ketopyrrolidinoacetate*, 5-*methyl*-3 : 3-*diethyl*-1-n-*butyl*-2-*pyrrolidone*, and 1-*benzyl*-5-*methyl*-3 : 3-*diethyl*-2-*pyrrolidone*. W. J. Powell.

1-Amino-5-phenyl-2-pyrrolidone and 1-amino-2-pyrrolidone-5-carboxylic acid. A. Darapsky (J. pr. Chem., 1927, [ii], **116**, 129—162).—[With J. van der Beck.]—β-Benzoylpropionic acid [*semicarbazone*, m. p. 181° (decomp.)], is converted by hydrazine into 3-phenylpyridazinone, which on reduction with sodium amalgam and alcohol gives 1-*amino*-5-*phenyl*-2-*pyrrolidone*, m. p. 38° (*hydrochloride*, m. p. 168°; *acetyl* derivative, m. p. 109°; N-*phenylthiocarbamido*-derivative, m. p. 251°; *benzylidene*, m. p. 180°; *salicylidene*, m. p. 170°; *cinnamylidene*, m. p. 159°, and p-*methoxybenzylidene* derivatives, m. p. 93°). Nitrous acid converts the 1-amino-compound into 5-*phenyl*-2-*pyrrolidone*, m. p. 110°, which is hydrolysed by barium hydroxide solution to γ-*amino*-γ-*phenylbutyric acid*, m. p. 216° (*hydrochloride*, m. p. 180°). Boiling hydrochloric acid hydrolyses the 1-amino-compound to hydrazine and γ-hydroxy-γ-phenylbutyric acid (isolated as lactone), but the substance is unaffected by hot barium hydroxide solution. Reduction of β-benzoylpropionic acid semicarbazone with sodium amalgam yields 5-*phenyl*-1-*carbamido*-2-*pyrrolidone*, m. p. 144°, which is also obtained by the action of cyanic acid on 1-amino-5-phenyl-2-pyrrolidone.

[With E. Philipp.]—α-Ketoglutaric acid reacts with hydrazine, yielding pyridazinone-3-carboxylic acid, which is reduced to 1-*amino*-2-*pyrrolidone*-5-*carboxylic acid*, m. p. 158° (*hydrochloride*, m. p. above 270°; *hydrobromide*, decomp. 220°; *benzylidene* derivative, m. p. 196°; *salicylidene* derivative, m. p. 195°; *ammonium* salt, m. p. 107°; *barium* salt). The *ethyl* ester (*hydrochloride*, m. p. 143°; *salicylidene* derivative, m. p. 136°), and *methyl* ester [*hydrochloride*, m. p. 159° (decomp.); *benzylidene* derivative, m. p. 134°], are described. Silver nitrite reacts with the 1-amino-acid, giving two substances having m. p. 198° (decomp.), and above 270°, whilst the action of nitrogen trioxide gives an unrecognisable product. Nitrous acid converts the ethyl ester into an unrecognisable oil. H. Burton.

Piperidyl- and substituted piperidyl-alkyl *p*-aminobenzoates. III. O. A. Barnes and R. Adams (J. Amer. Chem. Soc., 1927, **49**, 1307—1315).—Condensation of sodium *p*-nitrobenzoate with ethylene bromide or trimethylene bromide in presence of diethylamine affords, respectively, β-bromoethyl *p*-nitrobenzoate, m. p. 52—53°, and γ-*bromopropyl* p-*nitrobenzoate*, m. p. 39—40°. Catalytic reduction of methyl nicotinate with hydrogen in absolute-alcoholic acetic acid in presence of platinum oxide platinum-black yields methyl hexahydronicotinate, and this condenses with the above bromo-esters to give, respectively, β-(3-*carbomethoxypiperidyl*)*ethyl* p-*nitrobenzoate hydrochloride*, m. p. 197—198°, and γ-(3-*carbomethoxypiperidyl*)*propyl* p-*nitrobenzoate hydrochloride*, m. p. 207—208°. Catalytic reduction of these nitro-derivatives affords β-(3-*carbomethoxypiperidyl*)*ethyl* p-*aminobenzoate hydrochloride*, m. p. 186—188°, and γ-(3-*carbomethoxypiperidyl*)*propyl*

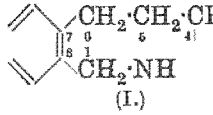
p-*aminobenzoate*, m. p. 195—196°. Condensation of methyl nicotinate with ethylenechlorohydrin at 120° yields β-*hydroxyethyl-3-carbomethoxypyridinium chloride*, liquid. Catalytic reduction of β-hydroxyethylpyridinium chloride affords N-β-hydroxyethylpiperidine, b. p. 89—91°/20 mm., n_D^{25} 1·4749, 0·9732 (*hydrochloride*, m. p. 122—124°) (cf. Ladenburg, A., 1881, 1157). *γ-Hydroxypropylpyridinium chloride*, liquid, and N-*γ-hydroxypropylpiperidine*, b. p. 108—109°/20—21 mm., n_D^{25} 1·4742, d_{25}^{25} 0·9529 (*hydrochloride*, m. p. 139—141°), are obtained analogously. Treatment of the above piperidine derivatives with *p*-nitrobenzoyl chloride affords β-*piperidylethyl* p-*nitrobenzoate hydrochloride*, m. p. 203—204° (cf. Einhorn, A., 1910, i, 170), and *γ-piperidylpropyl* p-*nitrobenzoate hydrochloride*, m. p. 206—208°, respectively, and these, on reduction, yield β-piperidylethyl *p*-aminobenzoate hydrochloride, m. p. 213—214° (cf. Einhorn, *loc. cit.*), and *γ-piperidylpropyl* p-*aminobenzoate hydrochloride*, m. p. 214—215°. β-Piperidylethyl benzoate hydrochloride, m. p. 179—181° (cf. Brill, A., 1925, i, 833), and γ-piperidylpropyl benzoate hydrochloride, m. p. 191—193°, were prepared. Treatment of γ-bromopropyl *p*-nitrobenzoate with pyridine at 130° affords γ-p-*nitrobenzoxypropylpyridinium bromide*, m. p. 191—193° (decomp.), and this, on reduction, yields γ-p-*aminobenzoxypropylpyridinium bromide*, m. p. 114—115°. The last-named product has no anæsthetic properties. The above β-piperidylethyl and γ-piperidylpropyl derivatives are anæsthetics, the propyl group being more effective than the ethyl group. Introduction of the carbomethoxy-group reduces the anæsthetic properties, which are also much less in absence of the *p*-amino-group. F. G. Willson.

Action of benzoyl chloride on isatin salts. A. Hantzsch and W. Krober (J. pr. Chem., 1927, [ii], **115**, 126—136).—The authors have been unable to repeat the preparation of Heller's isatol (A., 1925, i, 1166), only the bimolecular isatoid or its transformation products being obtained. By the action of benzoyl chloride, sodium isatin yields *N*-benzoylisatin, but if alcohol be present, the product is ethyl *N*-benzoylisatoate, and not the alcoholate of *O*-benzoylisatin. This is confirmed by a comparison of the absorption curves of *N*-benzoylisatoic acid and its ethyl ester. The amide, m. p. 218°, undergoes hydrolysis with alkalis, yielding ammonia and salts of benzoic and isatoic acids. Under conditions similar to those required for amide formation, 4-hydroxy-2-phenylquinazoline is formed by the action of ammonia on ethyl *N*-benzoylisatoate. This is explained on the assumption that benzoylanthranilamide is formed intermediately. The products and mechanism of the reaction of ethyl chloroformate with sodium isatin are discussed. R. W. West.

Constitution of α-naphtholisatin. A. Steopoe (Ber., 1927, **60**, [*B*], 1116—1117).—Under conditions such that isatin condenses to colourless compounds with thionaphthenquinone, phenol, and dimethylaniline (cf. Danaila, A., 1910, i, 411), it is not possible to effect condensation with α-naphthol or its ethyl ether. The latter compound with isatin and concentrated sulphuric acid affords αα-diethoxydinaphthyl, m. p. 210—211°. H. Wren.

Synthesis of the eight-membered 7 : 8-benzoheptamethyleneimine. J. von Braun and O. Bayer (Ber., 1927, **60**, [*B*], 1257—1262).—Whereas in the monocyclic series the formation of cyclic imines by the authors' methods cannot be extended beyond a seven-membered ring, an eighth member can be introduced in the case of dicyclic benzoderivatives, the two carbon atoms of the benzene ring appearing to behave like a single methylene group.

δ-Phenyl-*n*-butylamine and ethyl bromoacetate in benzene afford *ethyl δ-phenyl-n-butylaminoacetate*, b. p. 188—194°/16 mm. (non-crystalline *picrate*; *hydrochloride*), which is converted by hot hydrochloric acid into *δ-phenyl-n-butylaminoacetic acid hydrochloride*, m. p. 220°. *Benzenesulphonyl-δ-phenyl-n-butylaminoacetic acid*, m. p. 95°, is converted by successive treatment with phosphorus pentachloride and aluminium chloride in nitrobenzene or, preferably, by phosphoric oxide in benzene into a mixture


(I.)

δ-phenyl-*n*-butylamine and 7 : 8-*benzoheptamethyleneimine* (I), b. p. 123°/13 mm., d_4^{18} 1·0190, which is oxidised by nitric acid to phthalic acid free from benzoic acid. The *hydrochloride*, m. p. 129—130°, *picrate*, m. p. 175°, *phenylthiocarbamate*, m. p. 124°, non-crystalline *nitroso*-derivative, and quaternary *methiodide*, m. p. 250°, are described. *Ethyl ε-phenyl-n-amylaminoacetate*, b. p. 194°/14 mm. (very hygroscopic *hydrochloride*), is converted into *ε-phenyl-n-amylaminoacetic acid hydrochloride*, m. p. 191—193°, from which non-crystalline *benzenesulphonyl-ε-phenyl-n-amylaminoacetic acid* and p-*toluenesulphonyl-ε-phenyl-n-amylaminoacetic acid*, m. p. 76—77°, are derived. The last-named substance evolves carbon monoxide when treated with phosphorus pentachloride and aluminium chloride or phosphoric oxide, but the product, after hydrolysis, gives ε-phenyl-*n*-amylamine and complex substances.

The synthesis of tetrahydro*iso*quinoline and *as*-homotetrahydro*iso*quinoline from benzenesulphonyl-β-phenylethylaminoacetic acid and *p*-toluenesulphonyl-γ-phenyl-*n*-propylaminoacetic acid is extraordinarily simplified by the use of phosphoric oxide in place of phosphorus pentachloride and aluminium chloride.

The conversion of benzenesulphonylbenzylaminoacetic acid into dihydro*iso*indole could not be effected. H. Wren.

Pyridine compounds of salts of bivalent heavy metals. R. Weinland, K. Effinger, and V. Beck (Arch. Pharm., 1927, **265**, 352—379).—Perchlorates of certain bivalent metals react with pyridine in aqueous solution to give sparingly soluble compounds having a cation composed of a metal and 6 mols. of pyridine, such as *hexapyridinecobaltous perchlorate*, $[Co(C_5H_5N)_6](ClO_4)_2,4H_2O$ (I), and the corresponding *nickel* ($4H_2O$), *copper*, and *cadmium* ($4H_2O$) compounds. *Manganese perchlorate* ($10H_2O$) forms a *compound* containing 5 mols. of pyridine and 3 mols. of water. Compounds of type (I) on recrystallisation, warming, or dehydration over sulphuric acid furnish a series of anhydrous *cobalt*, *nickel*, *copper*, *zinc*, *cadmium* (also $2H_2O$), and *manganese*

tetrapyridine perchlorates. *Aquopentamminecobalt perchlorate* and *cobalt hexa-aquoperchlorate* are quite stable towards heat, which differentiates them from other cobalt salts of the aquopentammine series. Attempts to replace the perchlorate ion in (I) by other anions failed; sodium phosphite and phosphate furnished the following *double* salts, $3CoHPO_3,C_5H_5N,5H_2O$ and $Co_3(PO_4)_3,C_5H_5N,6H_2O$.

The corresponding *tetrapyridine chloride*, *bromide*, and *iodide* are obtained by the action of the appropriate pyridine salt on tetrapyridinecobalt perchlorate, but pyridine phosphate and sulphate furnish the *compounds* $Co_2(HPO_4)_2,7C_5H_5N,8H_2O$ and $CoSO_4,3C_5H_5N,2H_2O$ (cf. Reitzenstein, A., 1899, i, 162), respectively. Ferrous iron forms two main series of complex compounds containing 4 and 2 mols. of pyridine per mol., respectively (cf. Costachescu and Spacu, Chem. Zentr., 1916, i, 404). *Tetrapyridine ferrous bromide*, *iodide*, *sulphate*, and *phosphate* $(2MeOH,4H_2O)$ are yellowish-green solids, readily converted into dipyridine derivatives, of which the following are described: *dichlorodipyridineiron*, $[Fe(C_5H_5N)_2Cl_2]$, *oxalatodipyridineiron*, *dibromodipyridineiron* $(2H_2O)$, and *diformatodipyridineiron*. A complex *oxalate*, $Fe_2(C_2O_4)_2,H_2C_2O_4,2C_5H_5N,2H_2O$, and *phosphate*, $Fe'''PO_4,Fe''HPO_4,4C_5H_5N,4MeOH,8H_2O$, and *nickel* $(7H_2O)$, *copper* $(6H_2O)$, *zinc* $(7H_2O)$, and *cadmium* $(5H_2O)$ *perchlorates* are described incidentally.

S. Coffey.

Product of the action of sulphuryl chloride on pyridine, its transformation into *N*-pyridiniumsulphonic acid and its application to acylation. P. Baumgarten (Ber., 1927, **60**, [*B*], 1174—1178).—Pyridine and sulphuryl chloride in presence of ether give a non-crystalline product which appears to contain the substances $C_5H_5NCl{\cdot}SO_2Cl$ and $(C_5H_5NCl)_2SO_2$. It readily decomposes into sulphur dioxide and chloropyridines. With water, it yields sulphur dioxide, chloropyridines, and pyridine-1-sulphonic acid. The last compound is obtained in good yield if an excess of pyridine is used and ether is replaced by chloroform; decomposition is then effected in the solution. The chloro-compound is decomposed by ethyl alcohol, acetic or benzoic acid, with production of ethyl, acetyl, and benzoyl chlorides, respectively. The acid chlorides thus produced may be used directly for acylations; thus, β-naphthyl acetate is prepared by addition of β-naphthol to a solution of pyridine and sulphuryl chloride in glacial acetic acid.

H. Wren.

Metallic derivatives of 8-hydroxyquinoline and their analytical application. R. Berg (J. pr. Chem., 1927, [ii], **115**, 178—185).—8-Hydroxyquinoline readily forms salts of the type $C_9H_6N{\cdot}OM$ with the metallic elements. In general, these salts are yellow or greenish-yellow in colour, but the ferric (black), ferrous (red), and uranium (reddish-brown) are distinctive. In presence of sodium acetate, the precipitation of these salts is a very delicate reaction, the zinc salt being precipitated from a solution containing 1 part of zinc in a million parts, and as the insoluble salts are quite crystalline and easily filtered and washed, they may conveniently be used for the determination of metals. In such determinations the salts may (*a*) be weighed directly, (*b*) be decomposed by heat in the presence of oxalic acid and the metal weighed as oxide, or (*c*) be determined volumetrically by means of bromide–bromate solution, the reaction depending on the equation $C_9H_7ON+2Br_2=C_9H_5ONBr_2+2HBr$.

R. W. West.

Synthesis of methyl 2:4-dihydroxyquinoline-3-carboxylate. G. Koller (Ber., 1927, **60**, [*B*], 1108—1111).—*Methyl* 2:4-*dihydroxyquinoline*-3-*carboxylate*, m. p. 203—204° (*sodium* derivative), is prepared by the action of methyl anthranilate on ethyl malonate in presence of sodium ethoxide at 140—150°. It is hydrolysed to 2:4-*dihydroxyquinoline*, m. p. above 330°, which with phosphoryl chloride gives 2:4-dichloroquinoline, m. p. 67—68°, and with phosphorus pentachloride affords a *trichloroquinoline*, m. p. 104—105°. Reduction of the chlorinated product by zinc dust gives quinoline.

H. Wren.

Quinoline-4-carboxylic acids. S. Berlingozzi and A. Turco (Annali Chim. Appl., 1927, **17**, 244—249).—2-*Phenyl*-6-p-*acetamidophenylquinoline*-4-*carboxylic acid*, prepared by the interaction of acetylbenzidine, pyruvic acid, and benzaldehyde, decomposes at about 250° and forms heavy metal salts of various colours. Acetylbenzidine and pyruvic acid give: with anisaldehyde, 2-*methoxyphenyl*-6-p-*acetamidophenylquinoline*-4-*carboxylic acid*, m. p. 199° (decomp.); with cinnamaldehyde, 2-*styryl*-6-p-*acetamidophenylquinoline*-4-*carboxylic acid*, m. p. about 210° (decomp.); with piperonal, 2-*methylenedioxyphenyl*-6-p-*acetamidophenylquinoline*-4-*carboxylic acid*, m. p. about 245° (decomp.); with vanillin, 2-*hydroxymethoxyphenyl*-6-p-*acetamidophenylquinoline*-4-*carboxylic acid*, m. p. about 175° (decomp.); with acetaldehyde, 2-*methyl*-6-p-*acetamidophenylquinoline*-4-*carboxylic acid*, decomp. above 260°.

T. H. Pope.

β-Substituted quinolines. S. Berlingozzi and W. E. Burg (Annali Chim. Appl., 1927, **17**, 250—256).—p-*Methoxyphenacylphthalimide*, $OMe{\cdot}C_6H_4{\cdot}CO{\cdot}CH_2{\cdot}N<\begin{matrix}CO\\CO\end{matrix}>C_6H_4$, m. p. 164°, obtained by the condensation of *p*-chloroacetylanisole with potassiophthalimide, condenses with *o*-aminobenzaldehyde in presence of sodium hydroxide to form 3-o-*carboxybenzamido*-2-p-*anisylquinoline*, m. p. 156—158°. Hydrolysis of this compound by means of 30% hydrochloric acid yields 3-*amino*-2-p-*anisylquinoline*, m. p. 138°, which gives fluorescent solutions, yields an *acetyl* derivative, m. p. 165°, and a *picrate*, m. p. 218°, and gives 3-hydroxy-2-*p*-anisylquinoline (A., 1923, i, 483) when treated with nitrous acid.

Condensation of isatoic acid with *p*-methoxyphenacylphthalimide gives 3-o-*carboxybenzamido*-2-p-*anisylquinoline*-4-*carboxylic acid*, m. p. 255° (decomp.), which, when boiled with hydrochloric acid, yields 3-*amino*-2-p-*anisylquinoline*-4-*carboxylic acid*, m. p. about 150° (decomp.); this acid forms an *acetyl* derivative, m. p. 212° (decomp.), and is converted into 3-amino-2-*p*-anisylquinoline when heated at 150—155°, and into 3-hydroxy-2-*p*-anisylquinoline-4-carboxylic acid (A., 1924, i, 1345) when treated with nitrous acid.

T. H. Pope.

Hydroxyazoquinoline derivatives. S. Berlingozzi (Annali Chim. Appl., 1927, **17**, 256—261).—Experiments on the coupling of diazo-compounds with 2-, 3-, and 4-hydroxyquinolines show that hydroxyazo-compounds are obtained only when the hydroxyl group is in the 3- or 4-position. Thus, 2-hydroxyquinoline behaves in this respect like β-naphthols with the α-position occupied by a substituent.

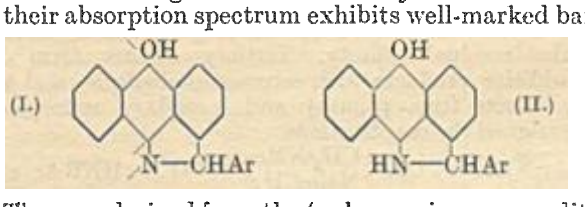
4-*Benzeneazo*-3-*hydroxy*-2-*phenylquinoline*, obtained from benzenediazonium chloride and 3-hydroxy-2-phenylquinoline, has m. p. 140°. Similarly, 3-hydroxy-2-methylquinoline forms 4-*benzeneazo*-3-*hydroxy*-2-*methylquinoline*, m. p. 133°, and 4-hydroxy-2-methylquinoline, 3-*benzeneazo*-4-*hydroxy*-2-*methylquinoline*, m. p. 208°. Diazotisation of 3-amino-2-methylquinoline and coupling with 3-hydroxy-2-methylquinoline gives 4-(2′-*methylquinoline*-3′-*azo*)-3-*hydroxy*-2-*methylquinoline*, m. p. about 255° (decomp.). 4-(2′-*Phenylquinoline*-3′-*azo*)-2-*hydroxy*-3-*phenylquinoline*, has m. p. about 235° (decomp.); 3-*benzeneazo*-2-*methylquinoline*, m. p. 160°; 3-β-*naphtholazo*-2-*methylquinoline*, m. p. 240—241°; 3-*benzeneazo*-2-*phenylquinoline*, m. p. 71—72°, and 3-β-*naphtholazo*-2-*phenylquinoline*, m. p. 228°. T. H. Pope.

Constitutive factors governing the pharmacological activity of atophan. J. von Braun and L. Brauns (Ber., 1927, **60**, [*B*], 1253—1257).—Displacement of the carboxyl group of atophan into the benzenoid nucleus or the aromatic substituent destroys the pharmacological activity of the substance. Full activity is observed only when the carboxy-group is attached directly to the pyridine nucleus, but it is immaterial whether it is in position 3 or 4.

2-*Phenyl*-6-*methylquinoline*, b. p. 270°/12 mm., m. p. 69° (*hydrochloride*, m. p. 209°; *picrate*, m. p. 208°), obtained by decarboxylation of 2-phenyl-6-methylquinoline-4-carboxylic acid, is oxidised by chromic acid to 2-phenylquinoline-4-carboxylic acid, m. p. 277° (*sodium* and *silver* salts). *p*-Tolyl methyl ketone and isatin afford 2-p-*tolylcinchoninic acid*, m. p. 211° (*silver* salt; *methyl* ester, m. p. 101°), which is decarboxylated to 2-p-*tolylquinoline*, b. p. 240°/15 mm., m. p. 83° (*picrate*, m. p. 194°; *methiodide*, decomp. 192°). Oxidation of the latter substance gives 2-*phenylquinoline*-4′-*carboxylic acid*, m. p. 248° (*silver* salt; *methyl* ester, m. p. 154°). 2-*Phenyl*-3-*methylcinchoninic acid*, m. p. 299° (decomp.), from isatin and phenyl ethyl ketone, is converted into -*phenyl*-3-*methylquinoline*, b. p. 250°/vacuum, m. p. 43° (*picrate*, m. p. 205°; *methiodide*, m. p. 235°), which is oxidised to 2-*phenylquinoline*-3-*carboxylic acid*, m. p. 226° (*ethyl* ester, b. p. 195°/13 mm.; *methyl* ester, m. p. 84°). Isatin and β-benzoylpropionic acid give 2-*phenyl*-3-*carboxymethylcinchoninic acid*, m. p. -60° (decomp.), which could not be smoothly decarboxylated. δ-Benzoyl-*n*-valeric acid and isatin give -*phenyl*-3-γ-*carboxypropylcinchoninic acid*, m. p. 278° (decomp.), which is converted by loss of carbon dioxide 2-*phenyl*-3-γ-*quinolyl*-n-*butyric acid*, m. p. 187° (*sodium* and *silver* salts; *methyl* ester). H. Wren.

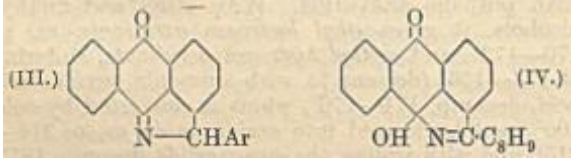
Synthesis and derivatives of acridinic acid. ozer and S. von Niementowsky (J. pr. Chem., 1927 [ii], **116**, 43—56).—Acridinic acid (quinoline-dicarboxylic acid, cf. Graebe and Caro, A., 1880, 398) is conveniently prepared from *o*-aminobenzaldehyde and ethyl sodio-oxalacetate in strongly alkaline aqueous alcoholic solution. It is also formed from equilibrium solutions of ethyl oxalacetate in indifferent solvents and *o*-aminobenzaldehyde, the yield running parallel with the degree of enolisation of the ester. Treatment of a mixture of the two with alcohol gives a *substance*, m. p. 210°. Contrary to the statement of Graebe and Caro, the acid is reprecipitated from cold alkaline solutions as the *trihydrate*, converted into a monohydrate at 68°, the two forms being non-interconvertible in cold aqueous solution. With boiling acetic acid and acetic anhydride, the monohydrate yields the anhydrous acid; it is decomposed slowly at 100—105° and rapidly at 125° into quinoline-3-carboxylic acid. The *sodium* ($+2H_2O$), *lead*, *silver*, and *silver hydrogen* salts, $HAg(C_{11}H_5O_4N)$,$0{\cdot}5H_2O$ and $H_3Ag(C_{11}H_5O_4N)_2$,H_2O, are described. *Acridinic anhydride*, m. p. 225°, from the acid and acetic anhydride at 120°, is less reactive than phthalic anhydride. With ethyl and methyl alcohols, it gives *ethyl hydrogen acridinate*, m. p. 170—172°, and *methyl hydrogen acridinate*, sintering at 174—176° (decomp.); with ammonia, *acridinamic acid*, decomp. 174—176°, which is converted by cold 100% sulphuric acid into *acridinimide*, m. p. 314—315°, and with aniline, the *monoanilide*, decomp. 187°, and *dianilide*, sintering at 245° with formation of *acridinphenylimide*, m. p. 319—320°. The last is better prepared from the monoanilide and acetic anhydride at 120°. In the monosubstituted derivatives, the free carboxyl group is probably in the 3-position. *Ethyl acridinate*, m. p. 55—56°, and *methyl acridinate*, m. p. 107—108°, obtained from normal silver acridinate and the requisite alkyl iodide, afford with concentrated ammonia *acridindiamide*, which sinters at 259—270°, forming acridinimide. H. E. F. Notton.

Free organic radicals. V. *peri*-Pyrrolinoanthranolazyls, a new type of nitrogenous, free organic radicals. R. Scholl [with H. Semp and E. Stix] (Ber., 1927, **60**, [*B*], 1236—1253).—The arylpyrrolinoanthranolazyls are nitrogenous, free organic radicals characterised by absence of all tendency to dimerisation, and resembling in stability towards air, acids, and alkalis the common dyes with normal valency. They are unstable towards light, being rapidly decolorised in solution by sunlight. They are decolorised by nitric oxide at the ordinary temperature. They form dark violet-blue crystals and yield red solutions with vivid fluorescence in solvents such as light petroleum or benzene, but blue solutions in phenol, glacial acetic acid, or alcohol, which are either non-fluorescent or fluoresce only in ultra-violet light. In such very dilute solutions, their absorption spectrum exhibits well-marked bands.



They are derived from the (unknown in pure condition) *meso*aminoanthranols containing bivalent nitrogen and

a pyrrolidine ring attached in the *peri*-position (I), to which they probably owe their great stability. The compounds (II), obtained by addition of a hydrogen atom, are readily converted by atmospheric air into the radicals, which are also readily obtained by autoreduction from the products of oxidation (III). Their most remarkable property consists in the absorption of 3OH or 3Br when titrated until colourless with permanganate or bromine, respectively; one group is used for saturation of the nitrogen atom, whilst the remaining two groups become attached to the *meso*-carbon atoms. With permanganate, they are converted through several intermediate stages into aryl α-anthraquinonyl ketones. With chromic acid, two equivalents of oxygen are absorbed by each radical molecule. The arylpyrrolinoanthranolazyls are therefore closely allied to the so-called aroyloxanthronylenes. The following compounds are described: m-*xylyl* syn-α-*anthraquinonyl ketoxime*, m. p. 212—213° after softening, converted by concentrated

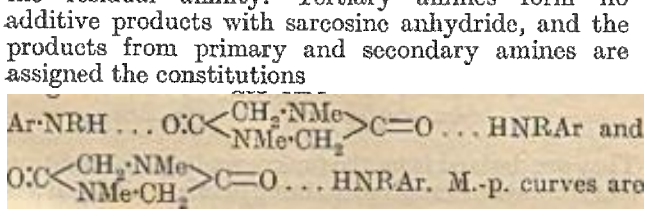


hydrochloric acid at 150° into *anthraquinone*-1-*carboxy*-m-*xylidide*, m. p. 297°, obtained also from anthraquinone-1-carboxyl chloride and *m*-xylidine; 1-m-*xylyl*-1 : 9-*pyrrolinoanthranol*-10-*azyl* (I), decomp. above 290° after softening at 230°; m-*xylyl*-1 : 9-*pyrrolenino*-9-*hydroxy*-10-*anthrone*, m. p. 160° after darkening at 150°; m-*xylyl* α-*anthraquinonyl ketimide*, m. p. above 160° (decomp.); m-*xylyl*-1 : 9-*pyrrolinoanthran*-10-*ol* (II). H. WREN.

Preparation of derivatives of 1-phenyl-2 : 3-dimethyl-5-pyrazolone. I. G. FARBENIND. etc.—See B., 1927, 460.

Fission of 2 : 5-diketopiperazine by acids and alkali hydroxides. I. S. YAITSCHNIKOV (J. Russ. Phys. Chem. Soc., 1926, **58**, 879—881).—2 : 5-Diketopiperazine was hydrolysed with hydrochloric acid at 10° and 100°, and by sodium hydroxide (0·2*N*) at 10°. With the acid, the maximum fission was 69%, with the alkali, 80%. In both cases no unchanged diketopiperazine remains. E. ROTHSTEIN.

Molecular compounds of amino-acids and diketopiperazines. II. P. PFEIFFER, O. ANGERN, and LIU WANG (Z. physiol. Chem., 1927, **164**, 182—206; cf. A., 1925, i, 794).—The anhydrides of glycine and sarcosine form definite molecular compounds with *o*-, *m*-, and *p*-aminobenzoic acids and with tryptophan. Since methyl *p*-aminobenzoate and non-carboxylated arylamines equally combine with sarcosine anhydride, the amino-group must provide the residual affinity. Tertiary amines form no additive products with sarcosine anhydride, and the products from primary and secondary amines are assigned the constitutions



M.-p. curves are given for mixtures of sarcosine anhydride (1 : 4-dimethyl-2 : 5-diketopiperazine) with the following substances: *o*-, *m*-, and *p*-aminobenzoic acids (*compound* with *m*-aminobenzoic acid, 1 : 1, m. p. 118°), methyl *p*-aminobenzoate (1 : 1, m. p. 100°), *p*-methylaminobenzoic acid (1 : 1), *p*-dimethylaminobenzoic acid (no compound), β-naphthylamine (1 : 1, m. p. 98·8°), *o*-phenylenediamine (1 : 2, m. p. 104°), *m*-phenylenediamine (1 : 1, m. p. 101·8°), β-naphthyldibenzylamine (no compound), carbazole (1 : 2), diphenylamine (1 : 2, m. p. 92—93°), tryptophan [1 : 1, +4H$_2$O, syrupy at 223—226°, melted at 232° (decomp.)], 3-methylindole (1 : 2), 2-methylindole (1 : 1, m. p. 85·5—86·5°), indole (1 : 1, m. p. 94—95°), oxindole (1 : 1, m. p. 111—112°), 1 : 2-dimethylindole (no compound), and ethyl 2 : 3 : 5-trimethylpyrrole-4-carboxylate, m. p. 102—103° (no compound). C. HOLLINS.

Compounds of diketopiperazine with amino-acids. E. ABDERHALDEN and E. SCHWAB (Z. physiol. Chem., 1927, **164**, 274—279; cf. A., 1926, 306).—Alanylglycylglycine methyl ester hydrochloride is converted by methyl-alcoholic ammonia into 1-dl-*alanyl*-2 : 5-*diketopiperazine* or 1-*glycyl*-2 : 5-*diketo*-3-*methylpiperazine*, decomp. 260° without melting. In a similar manner, *dl*-leucylglycylglycine methyl ester hydrochloride gives 1-dl-*leucyl*-2 : 5-*diketopiperazine*, decomp. above 240°, which is converted by enzymes into *dl*-leucine and diketopiperazine.

The enolic forms of glycine and alanine anhydrides are more easily adsorbed by animal charcoal than the ketonic forms. The enolic forms of these anhydrides combine with leucylglycine anhydride in aniline at 200° to give molecular *compounds*, decomp. 232—233° and 227°, respectively. C. HOLLINS.

Preparation of a colloidal substance from diglycylglycine methyl ester. E. ABDERHALDEN and E. SCHWAB (Z. physiol. Chem., 1927, **164**, 271—273).—Diglycylglycine is converted into its methyl ester and treated with methyl-alcoholic ammonia. The precipitate first formed redissolves on addition of more ammonia, and after 10—15 min. the liquid becomes filled with a thick precipitate, which after being freed from impurities by dissolution in hot water and reprecipitation on cooling, dissolves only to a colloidal solution. The new *substance* has the empirical formula $C_6H_9O_3N_3$ and gives a *silver* salt, $C_6H_7O_3N_3Ag_2$. It is probably a polymeric glycyl-(glycylglycine anhydride) [1-glycyl-2 : 5-diketopiperazine]. From the original filtrate, glycine anhydride and 1-glycyl-2 : 5-diketopiperazine may be isolated. C. HOLLINS.

Quinazolones from acylated *o*-aminobenzhydrazides. II. [Carbalkoxyl derivatives.] Action of nitrous acid on *o*-aminobenzhydrazide. G. HELLER and A. SILLER (J. pr. Chem., 1927, [ii], **116**, 1—16).—The constitution of *carbomethoxy*-*o*-*aminobenzhydrazide*, NH$_2$·C$_6$H$_4$·CO·NH·NH·CO$_2$Me, m. p. 121·5° [*hydrochloride*, m. p. 230° (decomp.)], which is readily obtained from *o*-aminobenzhydrazide and methyl chloroformate in warm alcohol, follows from its conversion by nitrous acid into 3-*carbomethoxy*-*aminobenzazimide*, m. p. 149°, which is hydrolysed

by sodium hydroxide to *o*-azidobenzoic acid. Like the acyl-*o*-aminobenzhydrazides, the carbomethoxy-derivative undergoes ring-closure with wandering of the carbomethoxyl group when heated at 180—200°, but, instead of the expected 3-amino-2-methoxy-4-quinazolone (cf. A., 1925, i, 1322), 3-aminotetrahydroquinazoline-2 : 4-dione (Kunckell, A., 1910, i, 438) is obtained. With 2 mols. of methyl chloroformate *o*-aminobenzhydrazide gives *carbomethoxy-o-carbomethoxyaminobenzhydrazide*, $CO_2Me{\cdot}NH{\cdot}C_6H_4{\cdot}CO{\cdot}NH{\cdot}NH{\cdot}CO_2Me$, m. p. 154° (decomp.), which passes when recrystallised from water into *3-carbomethoxyaminotetrahydroquinazoline-2 : 4-dione*, m. p. 240°. The latter, like the corresponding ethyl ester, is hydrolysed by sodium hydroxide to 3-aminotetrahydroquinazoline-2 : 4-dione, and converted by heating at 240° into a complex *substance*, m. p. 320° (decomp.). The following are prepared by analogous methods: *carbethoxy-o-aminobenzhydrazide*, m. p. 117° (*hydrochloride*, m. p. 220°); *3-urethanobenzazimide*, m. p. 147°; *carbethoxy-o-urethanobenzhydrazide*, m. p. 138°, and *3-urethanotetrahydroquinazoline-2 : 4-dione*, m. p. 227° (decomp.). On one occasion, *o*-aminobenzhydrazide and ethyl chloroformate in ethyl acetate yielded a *substance*, $C_{10}H_{13}O_3N_3$, m. p. 240·5°, which did not undergo condensation when heated. *Carbethoxy-o-acetamidobenzhydrazide*, m. p. 159° (decomp.), from carbethoxy-*o*-aminobenzhydrazide and acetyl chloride in pyridine, passes on heating at 170° into *3-urethano-2-methyl-4-quinazolone*, m. p. 128° (also $+C_6H_6$, m. p. 105°), which is hydrolysed by 75% sulphuric acid to 3-amino-2-methyl-4-quinazolone. Benzoylation of carbethoxy-*o*-aminobenzhydrazide in pyridine affords *carbethoxy-o-benzamidobenzhydrazide*, m. p. 217° (decomp.), which condenses abnormally at 220° to a *substance*, m. p. 318—319°, and is hydrolysed by hydrochloric acid to *o*-benzamidobenzoic acid. *Acetyl-o-carbomethoxyaminobenzhydrazide*, m. p. 172° (*hydrochloride*, m. p. 215°), and *acetyl-o-urethanobenzhydrazide*, m. p. 174°, from acetyl-*o*-aminobenzhydrazide and the corresponding chloroformic ester in boiling ethyl acetate, are converted by recrystallisation from hot water into 3-acetamidotetrahydroquinazoline-2 : 4-dione, m. p. 240° (Kunckell, *loc. cit.*, gives m. p. 250°).

The primary action of nitrous acid (1 mol.) on *o*-aminobenzhydrazide (cf. Thode, A., 1904, i, 347) is to form a compound, $NH_2{\cdot}C_6H_4{\cdot}CO{\cdot}N(NO){\cdot}NH_2$, which then gives (*a*) in glacial acetic acid equal quantities of *o-aminobenzoylazoimide*, m. p. 82—83° (decomp.), and 3-aminobenzazimide, (*b*) in hydrochloric acid, mainly *o*-aminobenzoylazoimide, and (*c*) on treatment with further nitrous acid (1 mol.), benzazimide. The latter is also formed from *o*-aminobenzhydrazide and gaseous nitrous acid in alcohol. *o*-Aminobenzoylazoimide may be prepared from *o*-aminobenzhydrazide and aqueous *p*-toluenediazonium sulphate. It is hydrolysed by alkali to anthranilic and hydrazoic acids and converted by heat into *o*-phenylenecarbamide, $C_6H_4{<}\overset{NH}{\underset{NH}{>}}CO$. 3-Aminobenzazimide is slowly converted in presence of hydrochloric acid into *o*-aminobenzoylazoimide; on diazotisation it yields a little benzazimide and a diazonium solution, which couples with alkaline β-naphthol with simultaneous hydrolysis to *o*-carboxybenzeneazo-β-naphthol. Similarly, *p*-aminobenzhydrazide and nitrous acid (1 mol.) give *p*-aminobenzoylazoimide, m. p. 85—90° (Curtius, J. pr. Chem., 1916, [ii], **94**, 295; **95**, 337), converted by diazotisation and coupling into *p*-carboxybenzeneazo-β-naphthol. 3-Aminobenzazimide and benzaldehyde condense in warm alcohol to *3-benzylideneaminobenzazimide*, m. p. 174—175°, which is partly transformed by sodium hydroxide into benzaldehyde *o*-carboxyphenylhydrazone. H. E. F. NOTTON.

Isomeric relationships in the pyrazole series. X. Alkyl-, allyl, and chloro-pyrazoles. K. VON AUWERS and K. BAHR (J. pr. Chem., 1927, [ii], **116**, 65—100).—3 : 4-Dimethylpyrazol-5-one is converted by phosphorus oxychloride into 5(3)-*chloro*-3(5) : 4-*dimethylpyrazole*, m. p. 121·5—122·5° (*picrate*, m. p. 150—151°), which with methyl iodide and sodium methoxide gives a mixture of *5-chloro*-1 : 3 : 4-*trimethylpyrazole*, b. p. 68°/13 mm. (*picrate*, m. p. 130°), and *3-chloro*-1 : 4 : 5-*trimethylpyrazole*, b. p. 108°/13 mm., m. p. 30—31° (*picrate*, m. p. 110—111°). The 5-chloro-compound is also obtained by the action of phosphorus oxychloride on 1 : 3 : 4-*trimethylpyrazol-5-one*, m. p. 133—134° (*picrate*, m. p. 148°), the latter being prepared from ethyl methylacetoacetate and methylhydrazine. Addition of methyl iodide to both chlorotrimethyl compounds furnishes *5-chloro*-1 : 2 : 3 : 4-*tetramethylpyrazolium iodide*, m. p. 184—188° (decomp.) (*picrate*, m. p. 124°), which on fission furnishes the 3-chloro-1 : 4 : 5-trimethyl derivative. Addition of benzyl iodide was possible only with the 1 : 3 : 4-derivative, which gave *5-chloro-2-benzyl*-1 : 3 : 4-*trimethylpyrazolium iodide*, m. p. 165°, this on decomposition furnishing the original material together with 5(3)-chloro-3(5) : 4-dimethylpyrazole.

Sulphuryl chloride converts 3 : 5-dimethylpyrazole into *4-chloro*-3 : 5-*dimethylpyrazole*, b. p. 220—222°, m. p. 117·5—118·5° (*picrate*, m. p. 192°; *hydrochloride*, m. p. 160—164°), converted by methyl sulphate into *4-chloro*-1 : 3 : 5-*trimethylpyrazole*, b. p. 85°/15 mm. (*picrate*, m. p. 146—147°). Addition of methyl iodide to this compound yields *4-chloro*-1 : 2 : 3 : 5-*tetramethylpyrazolium iodide*, m. p. 196° (*picrate*, m. p. 127·5—128°).

Chlorination of 3(5)-methylpyrazole with sulphuryl chloride gives *4-chloro*-3(5)-*methylpyrazole*, m. p. 65—66° (*picrate*, m. p. 151·5—152·5°; *acetyl* derivative, b. p. 77·5°/9 mm., m. p. 32—34°; *benzoyl* derivative, m. p. 48—49°; *o-nitrobenzoyl* derivative, m. p. 187—188°). Methylation gives a mixture of *4-chloro*-1 : 3-*dimethylpyrazole*, b. p. 177—178°, 68·5°/10 mm. (*picrate*, m. p. 105°; *hydrochloride*, m. p. 145°), and *4-chloro*-1 : 5-*dimethylpyrazole*, b. p. 184—186° (*picrate*, m. p. 116—117°; *hydrochloride*, m. p. 61°), the structures of which were proved by obtaining them by chlorination of 1 : 3- and 1 : 5-dimethylpyrazoles. Addition of methyl iodide to both compounds yields *5-chloro*-1 : 2 : 3-*trimethylpyrazolium iodide*, m. p. 219—221° (*picrate*, m. p. 129·5—130·5°), which on fission regenerates both the original compounds. Addition of benzyl iodide to the 1 : 3- and 1 : 5-compounds gives *4-chloro-2-benzyl*-1 : 3- and

4-chloro-2-benzyl-1 : 5-dimethylpyrazolium iodide, having m. p. 159° and 129—130°, respectively. The original compounds are regenerated in each case on decomposition of the quaternary salt.

Benzylation of 4-chloro-3(5)-methylpyrazole gives a mixture of *4-chloro-1-benzyl-3-methylpyrazole*, b. p. 281° (*hydrochloride*, m. p. 110—112°; *picrate*, m. p. 94—96°), and *4-chloro-1-benzyl-5-methylpyrazole*, b. p. 288° (*hydrochloride*, m. p. 115—117°; *picrate*, m. p. 101—102°).

Methylation of 4-bromo-3(5)-methylpyrazole furnishes a mixture of *4-bromo-1 : 3-* and *4-bromo-1 : 5-dimethylpyrazole*, having b. p. 76—77°/10 mm., and b. p. 85°/10 mm., m. p. 38°, respectively. From 4-nitro-3(5)-methylpyrazole there were obtained *4-nitro-1 : 3-* and *4-nitro-1 : 5-dimethylpyrazole*, with m. p. 72° and 112°. Both nitro-compounds react with methyl iodide, yielding *4-nitro-1 : 2 : 3-trimethylpyrazolium iodide*, m. p. 168—171°.

Ethyl 3(5)-methylpyrazole-5(3)-carboxylate on allylation gives *ethyl 1-allyl-3-methylpyrazole-5-carboxylate*, b. p. 122°/11 mm. (free *acid*, m. p. 123·5°), together with *ethyl 1-allyl-5-methylpyrazole-3-carboxylate*, b. p. 164°/12 mm. (free *acid*, $+1H_2O$, m. p. 78—80°). Thermal decomposition of the respective acids yields *1-allyl-3-methyl-* and *1-allyl-5-methylpyrazole*, having b. p. 171° (*picrate*, m. p. 77·5—78·5°), and 181—182° (*picrate*, m. p. 113—114°), respectively. These compounds are also obtained by the direct allylation of 3(5)-methylpyrazole in the ratio of 3 : 2, for the above order. Addition of methyl iodide to the 1-allyl-3-compound furnishes *1-allyl-2 : 3-dimethylpyrazolium iodide*, m. p. 79—80°, which on fission gives the original compound (10%) and 1 : 5-dimethylpyrazole (90%).

4-Methylpyrazol-5-one, m. p. 226—227°, is obtained by the action of hydrazine on ethyl α-hydroxymethyleneopropionate.

The optical data for most of the new compounds are tabulated. H. BURTON.

Derivatives of 2 : 4 : 6-trichloropyrimidine. W. WINKELMANN (J. pr. Chem., 1927, [ii], **115**, 292—314).—When 2 : 4 : 6-trichloropyrimidine (cf. Büttner, A., 1903, i, 658) is treated with methylamine, aniline, or sodium ethoxide, the chlorine atoms are successively replaced. Trichloropyrimidine and methylamine in alcohol at the ordinary temperature give a mixture from which *4 : 6-dichloro-2-methylaminopyrimidine*, m. p. 164°, is removed by steam distillation, leaving *2 : 4-dichloro-6-methylaminopyrimidine* (I), m. p. 186°. The former with hot fuming hydriodic acid gives *6-iodo-2-methylamino-4-hydroxypyrimidine*, m. p. 230° (decomp.), and with boiling alcoholic sodium ethoxide *4-chloro-2-methylamino-6-ethoxypyrimidine*, m. p. 95°, which has a celery-like odour. The second isomeride (I) is converted by hydriodic acid into *iodo-6-methylaminopyrimidine*, m. p. 134—135° (*hydriodide*, m. p. 224—225°), which is reduced by zinc dust and water to *6-methylaminopyrimidine*, m. p. 74—75° (*hydrochloride*; *chloroplatinate*). In accordance with the rule of Gabriel and Colman (A., 1901, i, 427), the latter is strongly alkaline. (I) gives with 1 mol. of alcoholic sodium ethoxide at 100° *chloro-6-methylaminoethoxypyrimidine*, m. p. 134, sintering at 130°, and with 2 mols. at 130—140°, *6-methylamino-2 : 4-diethoxypyrimidine*, m. p. 100—102°, which is also formed from 6-chloro-2 : 4-diethoxypyrimidine (see below) and methylamine. When either dichloromethylaminopyrimidine is heated at 100° with alcoholic methylamine *4-chloro-2 : 6-dimethylaminopyrimidine*, m. p. 133° (*hydrochloride*, m. p. 266—268°), reduced by zinc dust and alcohol to *2 : 6-dimethylaminopyrimidine*, m. p. 129—130°, is formed. If excess of methylamine is used at 170—180°, oily *2 : 4 : 6-trimethylaminopyrimidine* (*picrate*, m. p. 232—235°; *hydrochloride*, m. p. 210°) is obtained. *2 : 4-Dichloro-6-anilinopyrimidine*, m. p. 137—138°, from aniline and trichloropyrimidine at the ordinary temperature, is reduced by hydriodic acid to *iodo-6-anilinopyrimidine*, m. p. 166°, which, with zinc dust and alcohol, gives strongly alkaline *6-anilinopyrimidine*, m. p. 142—143° (*hydrochloride*; *chloroplatinate*). At 100°, trichloropyrimidine and aniline give mainly *chlorodianilinopyrimidine hydrochloride*, m. p. 220—222°, from which an oily free *base* was obtained, and at 180—190°, *2 : 4 : 6-trianilinopyrimidine*, m. p. 205°. From trichloropyrimidine and alcoholic sodium ethoxide are formed at 0°, dichloroethoxy-, at the ordinary temperature, chlorodiethoxy-, and at the b. p., *2 : 4 : 6-triethoxypyrimidine*, m. p. 10°, b. p. 255—256°. The constitution of *2 : 4-dichloro-6-ethoxypyrimidine*, m. p. about 25°, b. p. 235°, is confirmed by its conversion by methylamine into 4-chloro-2-methylamino-6-ethoxypyrimidine. *6-Chloro-2 : 4-diethoxypyrimidine*, m. p. 18—20°, b. p. 248°, is reduced by zinc dust and alcohol to oily *2 : 4-diethoxypyrimidine* (*picrate*, m. p. 102°), which is hydrolysed by hydrochloric acid at 100° to uracil (2 : 4-dihydroxypyrimidine).

H. E. F. NOTTON.

Synthesis of 1 : 5-naphthyridine. B. BOBRANSKI and E. SUCHARDA (Ber., 1927, **60**, [*B*], 1081—1084).—The action of glycerol, arsenic and sulphuric acids on 3-aminopyridine leads to the production of *1 : 5-naphthyridine*, m. p. 75°, the constitution of which is established by direct comparison with the compound obtained by Klisiecki and Sucharda (unpublished work). The *hydrochloride*, *anhydrous* and *monohydrated sulphate*, *picrate*, m. p. 200° (decomp.), and *hexahydrated chloroplatinate* are described.

H. WREN.

Dicarbazyls. II. 9 : 9′-Dicarbazyl and its halogen derivatives. J. MCLINTOCK and S. H. TUCKER (J.C.S., 1927, 1214—1221).—Oxidation of 3 : 6-dibromocarbazole (best prepared by the bromination of carbazole in boiling carbon disulphide) either with potassium permanganate in acetone solution or with sodium dichromate in acetic acid, yields *3 : 6 : 3′ : 6′-tetrabromo-9 : 9′-dicarbazoyl*, m. p. 249—250°, which is also synthesised by the action of iodine on the 9-potassium derivative (not isolated) of 3 : 6-dibromocarbazole. This dicarbazyl is stable towards most reducing agents and, unlike the tetra-arylhydrazines, does not undergo dissociation. Concentrated hydrogen iodide at 150° converts it entirely into carbazole. By similar processes is obtained *3 : 6 : 3′ : 6′-tetraiodo-9 : 9′-dicarbazyl*, m. p. 269—270°. Dicarbazyl *A*, m. p. 220° (Perkin and Tucker, J.C.S., 1921, **119**, 216), on reduction with hydriodic acid yields only carbazole, and by direct bromination or

iodination yields 3 : 6 : 3′ : 6′-tetrabromo(or iodo)-9 : 9′-dicarbazyl, identical with the synthetic specimens, and it is therefore 9 : 9′-dicarbazyl. All attempts to synthesise the latter failed, and it could not be converted (by a change of the benzidine type) into 3 : 3′-dicarbazyl. 1 : 3 : 6 : 8-Tetrabromocarbazole, which is not acetylated by the usual methods and does not yield a nitroso-derivative, is not oxidised by potassium permanganate in acetone, and with sodium dichromate in boiling glacial acetic acid it yields only a minute quantity of a crystalline *substance*, m. p. above 300°. Oxidation of 3 : 6-dihalogenocarbazoles in acid solution in an attempt to obtain 1 : 1′-dicarbazyls, yielded only the 9 : 9′-compounds. Dicarbazyl *B*, m. p. 265° (Perkin and Tucker, *loc. cit.*), on reduction with hydriodic acid yields an amorphous *substance*, m. p. 100—110°. When similarly treated, the amorphous dicarbazyl *C* yields carbazole and an amorphous *substance*, m. p. 300—310°, whilst on distillation (bath at 300°) it yields carbazole and a *substance*, m. p. about 320°. J. W. Baker.

Triazines. Action of Grignard reagents on carbonyl azides. A. Bertho (J. pr. Chem., 1927, [ii], **116**, 101—117).—The reaction between carbonyl azides and magnesium phenyl bromide, forming substituted triazines, can be represented: $R{\cdot}CO{\cdot}N_3 + PhMgBr \rightarrow R{\cdot}CO{\cdot}N(MgBr){\cdot}N{:}NPh \rightarrow R{\cdot}CO{\cdot}NH{\cdot}N{:}NPh$. Thus carbamyl azide reacts with magnesium phenyl bromide, yielding *phenyltriazinecarboxylamide* (*benzeneazocarbamide*), m. p. 157° (decomp.). This compound when treated with alcoholic silver nitrate solution gives a *silver* derivative, and is hydrolysed by acids to phenol, nitrogen, carbon dioxide, and ammonia. The formation of these substances is explained by the intermediate production of benzenediazonium chloride and carbamide, the last being isolated as the nitrate when hydrolysis is carried out with nitric acid. Phenylcarbamyl azide and magnesium phenyl bromide yield benzanilide, the formation of which is explained thus: $NHPh{\cdot}CO{\cdot}N_3 + PhMgBr \rightarrow NHPh{\cdot}COPh + N_3MgBr$. Hydrazodicarbonazide together with carbonyl azide, both substances being prepared by the interaction of sodium nitrite and carbohydrazide hydrochloride, gives the sec.-*hydrazide* of *phenyltriazinecarboxylic acid*, $(NPh{:}N{\cdot}NH{\cdot}CO{\cdot}NH{\cdot})_2$, m. p. 162° (decomp.) (*tri-silver* derivative, $C_{14}H_{11}O_2N_8Ag_3$); the carbonyl azide is completely decomposed. Methyl azidoformate yields *methyl phenyltriazinecarboxylate*, isolated as the *silver* derivative together with *methyl aniline*-NN-*dicarboxylate*, $NPh(CO_2Me)_2$, m. p. 142—143°. From the residue of the preparation of the above silver salt a red oil, b. p. 100—110°/0·5 mm., was obtained which after treatment with magnesium methyl iodide and subsequent decomposition gave azobenzene, diphenyl, and diphenylcarbinol. Ethyl azidoformate gives *ethyl phenyltriazinecarboxylate*, *monosilver* derivative), together with products similar to those obtained from the methyl ester. The constitution of the triazine ester was proved by treating with phenylcarbimide, and hydrolysing the compound formed with hydrogen chloride. There were benzenediazonium chloride and α-phenyl-β-carbethoxycarbamide. Benzoyl azide is converted into *benzoylphenyltriazine*, NPh.N·NHBz, m. p. 84° (decomp.) (*silver* derivative). H. Burton.

Chemical mechanism of porphyrin formation and constitution of hæmin. Criticism of H. Fischer's views. W. Küster (Z. physiol. Chem., 1927, **163**, 267—283; cf. Küster and Heess, A., 1925, i, 992).—Methyl-β-bromo-α-methoxyethylmaleinimide (*loc. cit.*) is converted by 66% hydrobromic acid in a sealed tube at 100° into a *dilactone* of methyl-αβ-dihydroxyethylfumaric acid, $\begin{matrix}CMe{=}C{\cdot}CO{\cdot}O\\ CO{\cdot}O{\cdot}CH{-}CH_2\end{matrix}$, decomposing above 200° without melting. The structure of the imide and the nature of the linking of the side-chains in hæmin are thus confirmed. By the action of hydrobromic–acetic acid on dichlorodimethyl-(chloro)hæmin, there is obtained chlorobromohæmatoporphyrin dimethyl ether, $C_{36}H_{40}O_6N_4ClBr$, the formation of which is represented thus:

$$R{\cdot}C{:}CH_2 \\ R{\cdot}CH{:}CH \end{matrix} \rightarrow \begin{matrix} R{\cdot}C{-}CH_2Cl \\ R{\cdot}CHCl{\cdot}CH \end{matrix} \rightarrow$$

$$R{\cdot}CHBr{\cdot}CH_2Cl \\ R{\cdot}CHCl{\cdot}CH_2Br \end{matrix} \rightarrow \begin{matrix} R{\cdot}CH(OMe){\cdot}CH_2Cl \\ R{\cdot}CH(OMe){\cdot}CH_2Br \end{matrix}$$

The same dimethyl ether was prepared, together with a green by-product, from pentachlorodimethyl (chloro)hæmin by Küster and Zimmermann (A., 1926, 748), the hydrobromic–acetic acid having here a reducing action.

The remainder is polemical against H. Fischer, and new formulæ for hæmin (from glacial acetic acid), hæmin dimethyl ester, and hæmochromogen are put forward. C. Hollins.

Thiazoles. XII. Synthesis of isomerides of dehydrothio-*p*-toluidine and of some related compounds. Constitution and tinctorial properties in the thioflavine and chloroamine-yellow groups. M. T. Bogert and R. W. Allen (J. Amer. Chem. Soc., 1927, **49**, 1315—1323; cf. A., 1926, 743).—3-*Nitro*-2-*thiocyano*-, m. p. 45·5°, 2-*nitro*-3-*thiocyano*-, m. p. 86°, and 3-nitro-4-thiocyano-toluene, m. p. 125°, were prepared from the corresponding nitroamines by the method of Korczyński (A., 1920, i, 643). 3 : 3′-*Dinitrodi*-o-*tolyl disulphide*, m. p. 149°, and 3 : 3′-dinitrodi-*p*-tolyl disulphide, m. p. 175°, were prepared from the corresponding nitrothiocyano-derivatives by hydrolysis to the thiophenol and subsequent atmospheric oxidation. 2 : 2′-Dinitrodi-*m*-tolyl disulphide could not be obtained analogously, nor from the corresponding nitroiodo- and nitroamino-toluenes. The *zinc* salt of 3-*aminothio*-o-*cresol*, and 3 : 3′-*diamino*-*di*-o-*tolyl disulphide*, m. p. 127°, are described. Treatment of the zinc salt of 3-aminothio-*p*-cresol with *o*-nitrobenzaldehyde and hydrogen sulphide in glacial acetic acid affords 2-o-*nitrophenyl*-5-*methylbenzthiazole*, m. p. 91—92°, 2-o-*nitrophenyl*-7-*methylbenzthiazole*, m. p. 108·5°, being obtained similarly. 2-m-*Nitrophenyl*-5-*methylbenzthiazole*, m. p. 185°, is obtained by heating the zinc salt of 3-aminothio-*p*-cresol with *m*-nitrobenzoyl chloride at 100°, 2-m-*nitrophenyl*-7-*methylbenzthiazole*, m. p. 181°, being obtained analogously, whilst *p*-nitrobenzoyl chloride affords similarly 2-p-*nitrophenyl*-7-*methylbenzthiazole*,

m. p. 209°. The following amino-derivatives are obtained by reduction of the above corresponding nitro-compounds: 2-o-*aminophenyl-5-methyl-*, m. p. 154°; 2-m-*aminophenyl-5-methyl-*, m. p. 179° (*dehydrothio-*m-*toluidine*); 2-o-*aminophenyl-7-methyl-*, m. p. 83°; 2-m-*aminophenyl-7-methyl-*, m. p. 132°; and 2-p-*aminophenyl-7-methylbenzthiazole*, m. p. 171°. These, as well as 2-*p*-aminophenyl-5-methylbenzthiazole, were converted into the corresponding *thioflavines* by methylation under pressure (cf. Cassella, G.P. 51,738). The *p*-amino-derivatives dyed silk in fluorescent, greenish-yellow shades, the depth of shade decreasing slightly as the methyl group passes through positions 5, 6, and 7. The *o*-amino-derivatives gave paler and duller shades, with little fluorescence, whilst with the *m*-amino-derivatives the green tint was replaced by a red one, the shades being still pale and dull. Sulphonation of 2-*p*-aminophenyl-7-methylbenzthiazole, followed by hypochlorite oxidation, affords an *isomeride* of chloramine-yellow, from which it is scarcely distinguishable. Treatment of the zinc salt of 3-aminothio-*p*-cresol with *p*-hydroxybenzaldehyde and hydrogen sulphide in glacial acetic acid yields 2-p-*hydroxyphenyl-5-methylbenzthiazole*, m. p. 281°, 2-p-*hydroxyphenyl-7-methylbenzthiazole*, m. p. 232°, being obtained similarly. F. G. Wilson.

Thiazoles. XIII. Synthesis of 6-dimethylamino-2-arylbenzthiazoles from 2-amino-5-dimethylanilinethiosulphuric acid and aromatic aldehydes. M. T. Bogert and I. A. Updike (J. Amer. Chem. Soc., 1927, **49**, 1373—1382; cf. preceding abstract).—Condensation of 2-amino-5-dimethylanilinethiosulphuric acid (cf. Heller, Quast, and Blanc, A., 1925, i, 313) with benzaldehyde in boiling glacial acetic acid affords 6-dimethylamino-2-phenylbenzthiazole, m. p. 135° [not 185°, as previously recorded in error (A., 1922, i, 576)]. The nitrobenzaldehydes yield analogously 2-o-*nitrophenyl-*, golden-brown, m. p. 146·8°, 2-m-*nitrophenyl-*, red, m. p. 176°, and 2-p-*nitrophenyl-6-dimethylaminobenzthiazole*, dark red, m. p. 246°, which, on reduction, afford 2-o-*amino-*, yellow, m. p. 130·8°, 2-m-*amino-*, yellow, m. p. 173·5°, and 2-p-*amino-phenyl-6-dimethylaminobenzthiazole*, greenish-yellow, m. p. 221°, respectively. Treatment of the last-named compound with fuming sulphuric acid, followed by oxidation with hypochlorite, yields a brownish-red, amorphous *dye*. Condensation of 2-amino-5-dimethylanilinethiosulphuric acid with *p*-dimethylaminobenzaldehyde in glacial acetic acid affords 2-(p-*dimethylaminobenzylideneamino*)-5-*dimethylanilinethiosulphuric acid*, red, m. p. 210—215°, together with 2-(p-*dimethylaminophenyl*)-6-*dimethylaminobenzthiazole*, olive-green, m. p. 230°, the latter being obtained from the former by continued boiling with glacial acetic acid. 2-o-*Hydroxy-*, greenish-yellow, m. p. 183°, and 2-p-*hydroxy-phenyl-6-dimethylaminobenzthiazole*, yellow, m. p. 290°, are obtained as above from the corresponding hydroxybenzaldehydes. 2-m-*Hydroxyphenyl-6-dimethylaminobenzthiazole*, orange-red, m. p. 227—228°, was prepared from the corresponding amino-derivative through the diazo-compound, which was also converted into 2-*phenyl-6-dimethylaminobenzthiazole-3'-arsinic acid*, brick-red, m. p. above 300°, and -4'-*arsinic acid*, red, m. p. similar. The corresponding -2'-arsinic acid could not be obtained in this way. F. G. Willson.

Aminobenzthiazoles. VIII. Effect of polar substituents on the formation and stability of nuclear-substituted 1-aminobenzthiazole bromides. G. M. Dyson, R. F. Hunter, and R. W. Morris (J.C.S., 1927, 1186—1192).—The effect of various substituent groups in the 5-position on the stability of the bromides of 1-aminobenzthiazole is studied, the order of decreasing stability being $(CN,CO_2Et) > Br,Cl > OEt,OMe$. The following are described: 1-*amino-5-cyano-*, m. p. 196° (*tetrabromide*, m. p. 236°; *hexabromide*, charring at 290°); 1-*amino-5-carbethoxy-*, m. p. 242° [*dibromide*, m. p. 125° (decomp.); *tribromide*, m. p. 247° (decomp.)]; 5-*chloro-1-amino-*, m. p. 199° (*dibromide*, charring at 215°; *tetrabromide*, m. p. 82—83°; *hexabromide*, not melting below 270°; *acetyl* derivative, m. p. 225°; *tetrabromide of acetyl derivative*, m. p. 215°); 1-*amino-5-ethoxy-*, m. p. 174° (*tetrabromide hydrobromide*, charring at 200°); 1-*amino-5-methoxy-*, m. p. 147° (*dibromide*, charring at 240°); 1-amino-5-methyl- [*tribromide*, m. p. 295° (decomp.); *tetrabromide*, not melting below 275°] *benzthiazoles*. Bromine and *p*-acetylphenylthiocarbamide yield a bromo-additive *compound*, m. p. 137—140°, converted by sulphurous acid into a sulphur-free *substance*, not melting below 300°. Treatment with bromine of *o*-nitrophenylthiocarbamide and reduction of the mixed tri- and tetra-bromides produced yields 3-*nitro-1-aminobenzthiazole*, charring at 232°, whilst *o*-bromophenylthiocarbamide and bromine afford the *tribromide*, m. p. 155° (decomp.) of 3-bromo-1-aminobenzthiazole. J. W. Baker.

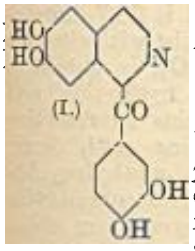
Aminobenzthiazoles. IX. The unsaturation of aminobenzthiazoles containing a static triad system, and the synthesis of some 1-dimethylaminobenzthiazoles. R. F. Hunter and E. R. Styles (J.C.S., 1927, 1209—1213).—The bromine additive products of various (static) 1-dimethylaminobenzthiazoles are more stable than those of the corresponding unalkylated (mobile) derivatives (cf. preceding abstract). The following are described: s-o-*tolyl-*, m. p. 138°; s-p-*methoxyphenyl-*, m. p. 125°; s-p-*ethoxyphenyl-*, m. p. 163°; s-p-*tolyl-*, m. p. 169°; s-p-*chlorophenyl-*, m. p. 152°; s-α-*naphthyl-*, m. p. 162°, *dimethylthiocarbamides*. By the action of bromine on these are obtained: 1-*dimethylamino-*, m. p. 86° [*dibromide*, m. p. 91—93° (decomp.); *tetrabromide hydrobromide*, m. p. 101° (decomp.); *hexabromide*, m. p. 211° (decomp.)]; 1-*dimethylamino-5-methoxy-*, m. p. 144° [*tetrabromide*, m. p. (decomp.)]; 1-*dimethylamino-5-ethoxy-*, m. p. 118° [*tetrabromide*, m. p. 190° (decomp.)]; 1-*dimethylamino-5-methyl-*, m. p. 86° [*tetrabromide hydrobromide*, m. p. 95° (decomp.); *hexabromide*, m. p. 188° (decomp.)]; 5-*chloro-1-dimethylamino-*, m. p. 99° [*dibromide hydrobromide*, m. p. 264° (decomp.)], *benzthiazoles*; 2-*dimethylamino-β-naphthathiazole*, m. p. 138° [*tetrabromide*, m. p. 225° (decomp.)]. J. W. Baker.

Application of the ionic theory of acidity to practical alkalimetry, with special reference to nicotine. R. Dubrisay (Ann. Falsif., 1927, 20,

197—204).—The p_H of a solution of nicotine during neutralisation by strong acid has been followed by means of the hydrogen electrode. A point of inflexion in the curve occurs at p_H 5·45, showing that at the point of equivalence the solution is still acid. Indicators showing a colour change in the region p_H 5·0—6·0 were tested, bromocresol-purple being selected as the most suitable, as it is violet at p_H 6·0, olive-green at p_H 5·6, and yellow at p_H 4·95. Two buffer solutions were prepared of p_H 5·4 and 6·0, respectively, and after addition of the same volume of indicator to each, the nicotine solution was titrated to a colour intermediate between those of the two buffer solutions. The results given by this method for determining the nicotine content of tobacco were in good agreement with those obtained when using the litmus method, and the judgment of the correct end-point in the former case required far less skill.

H. J. DOWDEN.

Hydrolysis of alkoxyl groups in alkaloids by means of aluminium chloride. M. OBERLIN (Arch. Pharm., 1927, **265**, 256—273).—Alkoxy*iso*quinolyl phenyl ketones are converted by means of anhydrous aluminium chloride, not into benzanthrone derivatives, but into the corresponding hydroxy-ketones. When papaveraldine is heated with aluminium chloride at 140—150° and the product treated with dilute sulphuric acid, *papaveraldoline sulphate* is formed (84% yield). *Papaveraldoline* (I) is very unstable, but furnishes characteristic yellowish-green to yellowish-brown salts (*hydrochloride*, *nitrate*, *picrate*, and *picrolonate*) and a *benzoyl* derivative, m. p. 209°. Diazomethane converts papaveraldoline sulphate into papaveraldine. Papaverine and aluminium chloride at 170—175° furnish papaveraline sulphate in 90% yield, which is converted by methylation and subsequent reduction into laudanosine. Similarly, bromopapaverine (picrate, m. p. 168—169°) is converted into bromopaveroline, (*picrate*, decomp. 241—242°), which affords *N*-methylbromo*iso*papaverine on methylation, whilst laudanosine is dealkylated to *laudanosoline* (*sulphate*), m. p. 230°, the latter furnishing laudanomethine on methylation.



Quinine and hydroquinine react with aluminium chloride in nitrobenzene solution, giving good yields of *apo*quinine ($[\alpha]_D^{20}$ —208·2° in alcohol) and hydrocupreine (hydrochloride, $[\alpha]_D^{20}$ —150·0° in absolute alcohol), respectively. Berberine hydrochloride under the action of aluminium chloride loses both its methylenedioxy- and methoxyl groups and affords impure *berberoline*, which gives palmatine on methylation, whilst cotarnine hydrochloride furnishes *cotarnoline sulphate* (decomp. 265—270°). The quality of the aluminium chloride greatly affects the results obtained.

S. COFFEY.

Condensations with methylhydrastinine [and cotarnine]. M. OBERLIN (Arch. Pharm., 1927, 274—288).—The carbinol-base form of methylhydrastinine condenses with substances containing mobile hydrogen to form derivatives of 1-hydromethylhydrastinine. In absence of a condensing agent, acetone forms 1-(*acetonyl*)*hydromethylhydrastinine*, m. p. 119—120°, ethyl phenylacetate, *ethyl* αα-1-*hydromethylhydrastinylphenylacetate*, m. p. 111—112°, ethyl 2 : 4-dinitrophenyl acetate, and a black condensation product analogous to that isolated from cotarnine by Hope and Robinson (J.C.S., 1911, **99**, 2132). 1-(*o-Nitrobenzyl*)*hydromethylhydrastinine*, orange-yellow needles, m. p. 121—122°, from *o*-nitrotoluene, and the corresponding 2′-*nitro*-5′-*methoxybenzyl*- (m. p. 154—155°), 6′-*nitrohomoveratryl*- (m. p. 159—160°), and 6′-*nitrohomopiperonyl*- (m. p. 178—179°) derivatives are obtained by condensation in presence of sodium ethoxide. Similarly, *iso*quinoline methiodide affords 1-(6′-*nitrohomopiperonyl*)-*N*-*methyl*-1 : 2-*dihydro*isoquinoline, ruby-red, m. p. 101—102°. 6-Nitrobenzylcreosol furnishes 1-(3′-*methoxy*-4′-*benzyloxy*-6′-*nitrobenzyl*)*hydromethylhydrastinine*, yellow, m. p. 113—114°, turning blue-black in sunlight, and forming very sparingly soluble salts, whilst 2 : 4 : 6-trinitrotoluene affords 1-(2′ : 4′ : 6′-*trinitrobenzyl*)-*hydromethylhydrastinine* (explodes at 145°). Aldehydes also condense with methylhydrastinine; the 6′-*nitrohomopiperonoyl*-, 6′-*nitrohomoveratroyl*-, 2′-*nitrohomoveratroyl*-, and 2-*nitrobenzoyl*-*hydromethylhydrastinines* all decompose without melting, and, unlike the nitrobenzyl compounds, are not sensitive to light, whilst they react with phenylhydrazine to give the phenylhydrazone of the original aldehyde and methylhydrastinine. 6-Nitrosafrole and methylhydrastinine react in presence of methyl-alcoholic potassium hydroxide, furnishing 1-[α-(6-*nitropiperonyl*)*allyl*]*hydromethylhydrastinine*, m. p. 132—133°; sparingly soluble *sulphate* and *hydrochloride*. 6-Nitroeugenol methyl ether and 1-phenyl-3-methyl-5-pyrazolone afford 1-[α-(6′-*nitroveratryl*)*allyl*]*hydromethylhydrastinine*, m. p. 157—158°, and 1-*phenyl*-3-*methyl*-4-(1-*hydromethylhydrastinyl*)-5-*pyrazolone*, decomp. 130—135°. In the same way, cotarnine affords 1-[α-(6′-nitroveratryl)allyl]hydrocotarnine, m. p. 136—137°, and 1-*phenyl*-3-*methyl*-4-(1-*hydrocotarnyl*)-5-*pyrazolone*. The majority of the nitro-compounds described can be reduced to well-defined amino-bases, which may be diazotised and coupled to form dyes. The *oxime*, m. p. 153—154°, and *anil*, m. p. 106—107°, of methylhydrastine are also described.

S. COFFEY.

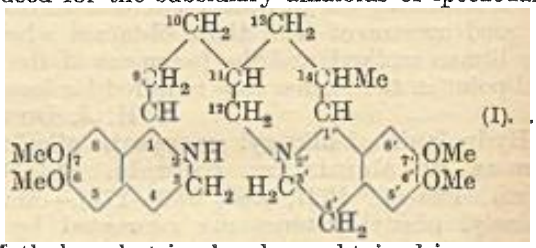
Yohimba alkaloids. II. K. WARNAT (Ber., 1927, **60**, [*B*], 1118—1122; cf. A., 1926, 1263).—Analyses of the ethyl and propyl esters of yohimboaic acid indicate the formula $C_{21}H_{28}O_3N_2$ for yohimbine, in agreement with Field (J.C.S., 1923, **123**, 3003; this vol., 579) and with Hahn and Brandenberg (this vol., 471); contrast Spiegel (this vol., 163). Hahn's nomenclature "*allo*yohimbine" for the author's "dihydroyohimbine" is accepted. The identity of *iso*- with *meso*-yohimbine is maintained, but that of these substances with coryanthine is regarded as erroneous. Treatment of yohimboaic acid with potassium hydroxide and methyl sulphate affords a substance, $C_{21}H_{28}O_4N_2,4H_2O$, m. p. 255°, which has no basic or acidic properties and cannot be esterified (cf. Spiegel, A., 1916, i, 286); it is converted by ethyl alcohol or dilute hydrochloric acid into a substance, m. p. 298°. Since neither substance adds methyl iodide, there is no opportunity for effect-

ing the Hofmann degradation. Potassium yohimboate, when heated above its m. p., gives an amorphous *substance*, $C_{19}H_{21}ON_2$, m. p. 122°. Distillation of yohimboaic acid affords a dimethylindole, m. p. 55° (picrate, m. p. 157°), identical with that obtained by Barger (J.C.S., 1914, **107**, 1025), which is not the 2 : 3-derivative (contrast Barger, *loc. cit.*) or the 1 : 2-compound. Bases resembling quinoline are obtained only in small amount. The most notable product is a *base*, $C_{13}H_{12}N_2$, m. p. 230—232° (*hydrochloride*, decomp. above 270°; *picrate*, m. p. 258—260°), which appears closely allied to phenanthridine. Its relative abundance indicates that it is not formed during the distillation. It is obtained in larger quantity by the distillation of *allo*yohimboaic acid and in small amount when yohimboaic acid is treated with molten potassium hydroxide. H. WREN.

Preparation of physostigmine [eserine]. F. CHEMNITIUS (J. pr. Chem., 1927, [ii], **116**, 59—64; cf. Stedman and Barger, A., 1925, i, 292, where further references are given).—A detailed account of apparatus and methods suitable for the extraction of physostigmine from quantities of 500 kg. of Calabar beans, the monthly output of base being 4 kg., representing 0·3% of the raw material. The preparation is carried out in complete absence of traces of ammonia, which colours the product red, and as rapidly as possible, to avoid premature crystallisation of the base. The coarsely-powdered material is impregnated with sodium hydrogen carbonate, dried, and extracted with ether. The alkaloid is dissolved from the concentrated extract by warm 3% sulphuric acid and, after addition of a little sulphurous acid, regenerated from the cold solution by sodium hydrogen carbonate. The product, crystallised from ether, may usually be directly converted into the pure sulphate or salicylate; inferior material is first purified through the latter salt. H. E. F. NOTTON.

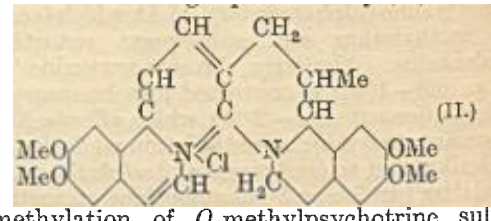
Harmaline and harmine. V. HASENFRATZ (Ann. Chim., 1927, [x], **7**, 151—226).—A detailed account of investigations already published (cf. A., 1912, i, 209, 383, 577, 797; 1926, 531, 1264).—The alkaloids are extracted from *Peganum harmala* with acetic acid, precipitated from this solution as hydrochlorides by addition of sodium chloride, and separated by gradual addition of a solution of ammonia, which first precipitates all the harmine, the process being controlled by microscopical examination of the precipitate. The yields are harmine 1%, and harmaline 1·5%, calculated on the weight of the seeds. Harmine hydrochloride, fluorescent at the ordinary temperature, becomes phosphorescent at the temperature of liquid air. The following data appear to be new: *iso*bromoharmine heated with dilute hydrochloric acid in a sealed tube at 160° for 8 hrs. is converted into bromoharmine, the change being irreversible. *apo*Harmine brominated in acetic acid yields *bromo*apo*harmine hydrobromide*, which with alkali yields the free *base*, m. p. 229°. Reduction of iodo*apo*harmine with zinc and hydrochloric acid yields *apo*harmine. The following compounds appear to be new: the *hydriodides* of bromoharmaline, *bromomethylharmaline*, bromomethylharmine (*base*, m. p. 252°), dibromomethylharmine (*base*, m. p. 148°); *hydrochlorides* of bromoharmine, dibromoharmine, bromoharmalol, *iso*bromoharmol, bromoharmol, iodomethyl*apo*harmine, $+2H_2O$; *hydrobromide* of bromomethyl*apo*harmine; *chloroplatinates* of bromoharmine, dibromoharmine, $+2H_2O$, bromoharmalol, bromoharmol, $+2H_2O$, iodomethyl*apo*harmine. Methyl*apo*harmine, $+2H_2O$, has m. p. 64°, anhydrous, m. p. 183° (Fischer, A., 1898, 160, gives 77—78°). J. W. BAKER.

Alkaloids of ipecacuanha. IV. W. H. BRINDLEY and F. L. PYMAN (J.C.S., 1927, 1067—1077).—The formula (I) for emetine, a modification of that suggested by Robinson on phytochemical grounds, is proposed, and enables intelligible formulæ to be deduced for the subsidiary alkaloids of ipecacuanha.



(I.)

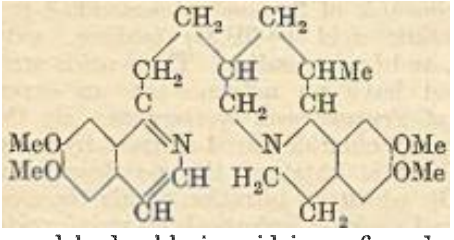
O-Methylpsychotrine has been obtained in a crystalline form, m. p. 123—124° (corr.), $[\alpha]_D$ +43·2° [*picrate*, softening at 142° and gradually melting up to 175° (corr.)]. On oxidation with potassium permanganate, the only crystalline product isolated is 6 : 7-dimethoxy*iso*quinoline-1-carboxylic acid, whilst with chromic acid a substance, $C_{29}H_{38}O_4N_2,H_2Cr_2O_7$, is obtained, which when treated with sodium hydroxide and acidified with hydrochloric acid yields rubremetine hydrochloride. Oxidation of emetine with ferric chloride, bromine, or iodine, or of *O*-methylpsychotrine with bromine or iodine also yields rubremetine salts, the loss of basicity of one nitrogen atom which occurs being attributed to amidine formation, rubremetinium chloride being represented by (II).



(II.)

Demethylation of *O*-methylpsychotrine sulphate heptahydrate, using 1 mol. of hydrochloric acid for 6 hrs. at 170°, yields 54% of psychotrine [*hydrogen oxalate*, m. p. 145° (decomp.) (corr.), $+4·5H_2O$ and anhydrous] identical in all respects with the natural alkaloid, preferential hydrolysis of the 6-methoxy-group in the *para*-position to the vinyl double linking [between C(1) and C(9)] being assumed. This is confirmed by the formation (along with emetine and *iso*emetine) of demethoxyemetine and demethoxy*iso*emetine (base *C*, Pyman, J.C.S., 1917, 419) by the reduction of *O*-methylpsychotrine. Pure emetamine has m. p. 153—154° (corr.), $[\alpha]_D$ −6·3° (anhydrous) (Pyman, *loc. cit.*, gave m. p. 155—156°, $[\alpha]_D$ −6·0), and m. p. 138—139° (corr.) $[\alpha]_D$ +13·6° (+0·5 mol. ether) [*dihydrochloride*, $+8·5H_2O$, m. p. 77·80°, anhydrous, m. p. 218—223° (corr.) (decomp.); *hydriodide*, softens 208°, effervesces up to 274°; *nitrate*, $+2H_2O$, m. p. 165—166° (corr.), $[\alpha]_D$ −7·3°, and

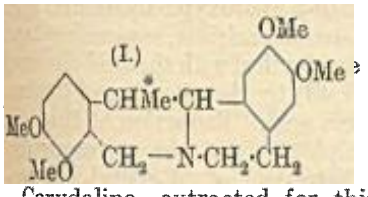
anhydrous; *picrate*, softening 147° and gradually melting with decomp. up to 173° (corr.); *dimethiodide* ($+H_2O$), decomp. 238° (corr.)]. The action of bromine on emetamine yields a *substance*, m. p. 185—190°. The formation of *iso*emetine by the reduction of emetamine either with sodium and alcohol or



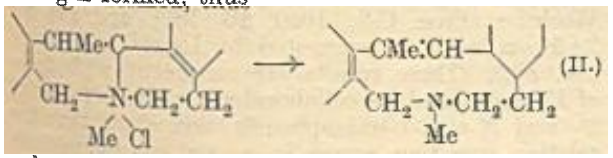
(III.)

with tin and hydrochloric acid is confirmed. Emetamine is represented by (III). Cephæline contains a hydroxyl group in place of one of the methoxyl groups in emetine, and previously recorded observations are explained on this formula. J. W. Baker.

Corydaline and *iso*corybulbine. F. von Bruchhausen and H. Stippler (Arch. Pharm., 1927, **265**, 152—166).—The position of the methyl group* in corydaline is still doubtful, although Gadamer (*ibid.*, 1921, **259**, 246; see also A., 1922, i, 675) regards the formula (I) as that which agrees best with the facts (cf. also Spath and collaborators, A., 1922, i, 168, etc.).



Corydaline, extracted for this investigation from *Corydalis cava*, was obtained in two fractions, viz., a purer form of m. p. 135°, which gave no crystalline hydrochloride, and an apparently impure form, m. p. 126—127°, which readily gave a crystalline hydrochloride. An attempt was made, without success, to identify tetrahydropalmatine (cf. Spath, Mosettig, and Trothandl, A., 1923, i, 593) as the impurity present. Corydaline yields two *methiodides*: the one is crystalline, m. p. 238—240° (decomp.), $[\alpha]_D$ +137·4°; the other is amorphous, m. p. 64—70°, $[\alpha]_D$ +110·4°. It likewise yields two *methosulphates*, p. 225—227°, $[\alpha]^{20}$ +140°, and m. p. 93—96°, $[\alpha]_D^{20}$ +114°, respectively. Either methiodide, when converted into the methochloride and boiled with methyl-alcoholic potassium hydroxide, yields optically inactive *de*-N-*methylcorydaline*, m. p. 111—112° (the methylcorydaline of Freund and Josephi, A., 1894, i, 100). The disappearance of optical activity is satisfactorily accounted for only by supposing that a 10-ring is formed, thus



(II.)

and such a formulation is possible only when the methyl group * in formula (I) has the position given. *N*-methylcorydaline is converted by boiling with aqueous ethyl alcohol into inactive methylcorydalin-hydroxide, identified as inactive corydaline methochloride, m. p. 187—189°. De-*N*-methylcorydaline methiodide, m. p. 195—197°, converted into the methosulphate, and reduced with sodium amalgam, yields *dihydrode*-N-*dimethylcorydaline*, m. p. 53—54° (the *bromide*, *chloroaurate*, and *chloroplatinate*, decomp. 160—170°, are described). This compound is still unsaturated, as it readily takes up bromine. It is reduced further by hydrogen and palladised charcoal to *tetrahydrode*-N-*dimethylcorydaline*, m. p. 137°. When this compound is oxidised in cold aqueous solution, as the sulphate, by potassium permanganate, methylacetoveratrone (3 : 4-dimethoxy-2-methylacetophenone) is obtained, whereas when the oxidation is carried out in ethyl acetate using ozone, both methylacetoveratrone and an aminocarboxylic acid are isolated. This aminocarboxylic acid was obtained in very small quantity, but its properties (the *chloroplatinate* is described) indicate that it is the expected 4 : 5-*dimethoxy*-2-*dimethylaminomethylbenzoic acid*. The formula (I) for corydaline is confirmed by these results.

In *iso*corybulbine, the position of the phenolic hydroxyl was unknown until Spath and Dobrowsky (A., 1925, i, 1085) published their conclusions. An attempt to elucidate this point led to the following incomplete results. *iso*Corybulbine yields a *methiodide*, m. p. 218—221°, $[\alpha]_D^{20}$ +129·6°; when treated with ethyl iodide and sodium hydroxide, this is converted into the ethyl ether, *ethyl*isocorybulbine *methiodide* (the corresponding *chloroaurate* is described). From this by boiling with methyl-alcoholic potassium hydroxide optically inactive *de*-N-*methylethyl*isocorybulbine, m. p. 105—107°, is obtained, but the yield is meagre because the product is converted into the quaternary ammonium base even by moist ether. When the ethereal solution is directly treated with methyl iodide, *de*-N-*methylethyl*isocorybulbine *methiodide* is satisfactorily obtained (the *chloroaurate* is described); the corresponding *chloride*, when reduced with sodium amalgam, should give the dihydro-compound like its analogue described above, but actually, chiefly because of lack of sufficient material, no identifiable product was obtained.

An attempt to demethylate dehydrocorydalinium chloride by heating with carbamide (cf. Frerichs, Arch. Pharm., 1910, 248, 280) failed to give the expected product. W. A. Silvester.

Separation of alkaloids, particularly of morphine, from visceral extracts. R. Marcille (Ann. Chim. Anal., 1927, [ii], **9**, 129—132).—The acid extract is treated with light petroleum, followed by chloroform; again with light petroleum to eliminate any dissolved chloroform; made alkaline with sodium hydrogen carbonate; extracted with light petroleum and then chloroform, and after addition of alcohol to 45% of the total volume, by chloroform again. D. G. Hewer.

Use of alkaloid reagents in presence of sulphuric acid. R. Marcille (Ann. Chim. Anal., 1927, [ii], **9**, 132—135).—Reagents which are unstable on keeping, such as Wasicky's *p*-dimethylaminobenzaldehyde reagent, may best be used in the solid form. The alkaloid residue and particles of the reagent are placed separately on a watch-glass, 2 or 3 drops of sulphuric acid dropped on to the latter, and the whole is mixed, or for small

quantities of alkaloid the reagent may be allowed to flow on to the alkaloid, when the colour reaction will become apparent. Formaldehyde is the best reagent for the detection of morphine in toxicological specimens. D. G. HEWER.

Microchemical reactions for thebaïne. M. WAGENAAR (Pharm. Weekblad, 1927, **64**, 472—474).—The properties and common reactions of the alkaloid are described. S. I. LEVY.

Preparation of thebaïne derivatives. C. H. BOEHRINGER SOHN, CHEM. FABR. ETC.—See B., 1927, 460.

Reinecke's salt as a microchemical reagent for alkaloids. L. ROSENTHALER (Arch. Pharm., 1927, **265**, 319—323).—Reinecke's salt (tetrathiocyanatodiamminochromiammonium), prepared from ammonium thiocyanate and dichromate, gives characteristic microcrystalline precipitates with atropine, berberine, quinine, coniine, hydrastinine, morphine, narceine, pilocarpine, piperine, strychnine, stovaine, tutocaine, novocaine, cocaine, tropacocaine, and alypine. S. COFFEY.

Ephedrine: its isolation and detection from the toxicological point of view. K. TSIANG and E. D. BROWN (J. Amer. Pharm. Assoc., 1927, **16**, 294—296).—Ephedrine gives no colour reaction with sulphuric, nitric, or hydrochloric acid, sulphuric acid with sugar, or with potassium dichromate, Froehde's reagent, or ferric chloride solution. It may be identified by the characteristic form of the four crystalline precipitates produced with Millon's reagent, which produces star or leaf-like crystals at a minimum dilution of 1%; with gold chloride, fine needles, some in the form of rosettes, at 0·04%; with platinic chloride, branching acicular crystals, at 0·01%; and with Kraut's reagent, needles with marked tendency to branch, at 0·1%. In all four cases, the formation of crystals occurs slowly. Adrenaline and tyramine give crystals which are similar in appearance, especially with Kraut's reagent, but they can be distinguished from ephedrine by their colour reactions with ferric chloride. Caffeine gives similar precipitates with gold chloride and Kraut's reagent, but not with platinic chloride or Millon's reagent. The tests are suitable for the detection of ephedrine when mixed with animal tissue. W. J. POWELL.

Acylamidohydroxyphenylarsenious oxides. I. G. FARBENIND. ETC.—See B., 1927, 460.

Trypanocidal action and chemical constitution. VI. Amphoteric s-carbamidoarylarsinic acids. H. KING (J.C.S., 1927, 1049—1060).—A number of *s*-carbamidoarylarsinic acids which retain a free basic centre have been prepared either (1) by the action of carbonyl chloride on aminoarylarsinic acids containing a second basic centre unattacked by carbonyl chloride, or (2) by nitration and reduction of *s*-carbamidoarylarsinic acids. The action of piperidine on 4-chloro-3-nitrophenylarsinic acid yields 3-*nitro*-4-*piperidinophenylarsinic acid* (*calcium* and *barium* salts), which on reduction yields the corresponding 3-*amino-acid*, $+H_2O$ (I) (*monohydrochloride*, *calcium*, *magnesium*, and *barium* salts), from which are obtained the corresponding 3-*acetamido-* and 3-m-*nitrobenzamido-* (*calcium* and *barium* salts) *acids*. The latter, on reduction, yields 3-m-*aminobenzamido*-4-*piperidinophenylarsinic acid* (II) (*magnesium* and *barium* salts). The action of carbonyl chloride on (I) yields the s-*carbamide* of 3-*amino*-4-*piperidinophenylarsinic aci* ($+H_2O$) (*magnesium* salt) and on (II) yields, similarly, the s-*carbamide* of 3-m-*aminobenzamido*-4-*piperidinophenylarsinic acid* ($+3H_2O$) (*sodium*, *magnesium*, *calcium*, and *barium* salts). These acids are toxic to mice and have no influence on an experimental culture of *Trypanosoma equiperdum*. By the action of carbonyl chloride on 4-amino-2-hydroxyphenylarsinic acid is obtained the s-*carbamido*-derivative ($+2H_2O$), which on nitration yields the s-*carbamide* of 5-*nitro*-4-*amino*-2-*hydroxyphenylarsinic acid* ($+2H_2O$ and anhydrous) (*magnesium*, *calcium*, *barium*, *sodium*, and *tetra-ammonium* salts), which on reduction yields the s-*carbamide* of 4 : 5-*diamino*-2-*hydroxyphenylarsinic acid*. Potassium cyanate converts 4-amino-2-hydroxyphenylarsinic acid into 2-*hydroxy*-4-*carbamidophenylarsinic acid* ($+0·5H_2O$) (*magnesium*, *calcium*, and *barium* salts). The curative dose of these acids is the same as the tolerated dose, a relapse occurring in each case. Diazotisation of picramic acid and treatment with arsenious oxide in 2*N*-sodium hydroxide yields 3 : 5-dinitro-2-hydroxyphenylarsinic acid, m. p. 244—246° (*ammonium*, *calcium*, *magnesium*, and *barium* salts), probably identical with the acid obtained by Benda (A., 1912, i, 61) by the nitration of 5-nitro-2-hydroxyphenylarsinic acid. Reduction of this acid with sodium hyposulphite yields the corresponding 3 : 5-*diamino-acid*. Nitration of *N*-acetyl-2-aminophenol with nitric acid (*d* 1·5) in acetic anhydride yields the 4- and 6-nitro-compounds (*o* and *p* to the hydroxyl group). Nitration of *ON*-diacetyl-*o*-aminophenol with nitric acid under the conditions described by Meldola, Woolcott, and Wray (J.C.S., 1896, **69**, 1330) and Ingold and Ingold (A., 1926, 833) yields *N*-acetylpicramic acid (which, boiled with acetic anhydride and pyridine, yields ON-*diacetylpicramic acid*, m. p. 190—191°). With nitric and sulphuric acids it yields mainly picramic acid together with 4-nitro-2-aminophenol, the *O*-acetyl group being hydrolysed prior to nitration (hydrolysis is complete with sulphuric acid at 10—15° for 1 hr.), whilst in acetic anhydride the results of Ingold and Ingold (*loc. cit.*) are confirmed, the products being *ON*-diacetyl, 3-nitro-2-aminophenol (hydrolysing to 3-*nitro*-2-*aminophenol*, m. p. 216—217°) and *ON*-diacetyl-5-nitro-2-aminophenol (*op* to the *O*-acetyl group). The dinitro-product obtained in the nitration of *ON*-diacetyl-2-aminophenol is therefore the 4 : 6-dinitro-2-aminophenol, as stated by Meldola and Wechsler (Proc. C.S., 1900, **16**, 180), and not the 3 : 5-compound, as suggested by Ingold and Ingold (*loc. cit.*). These results are consistent with those of Reverdin and his collaborators on the nitration of *O*- and *N*-acyl-4-aminophenols, and show that the relative orienting power in *o*- and *p*-aminophenols is in the order OH>NHAc>OAc. J. W. BAKER.

Preparation of organic arsenic compounds [acetophenonearsinic acids]. DEUTSCHE GOLD- U. SILBER-SCHEIDEANSTALT VORM. ROESSLER. See B., 1927, 429.

Hydrargyrum salicylicum. [Derivatives of *o*- and *p*-anhydrohydroxymercurisalicylic acids.] E. RUPP and H. GERSCH (Arch. Pharm., 1927, 265, 323—331).—"Mercurisalicylic acid" as usually prepared (cf. Dimroth, A., 1902, i, 851; Lajoux and Grandval, A., 1893, i, 642; Buroni, A., 1903, i, 256) is always impure. The pure product, consisting of a mixture of *o*- and *p*-anhydrohydroxymercurisalicylic acids, is prepared from mercuric sulphate and salicylic acid. The *para*-compound furnishes p-*thiocyanomercurisalicylic acid* (soluble *potassium salt*) when treated with potassium or ammonium thiocyanates, whilst the *ortho*-derivative affords potassium mercury thiocyanate and salicylic acid. Use has been made of this reaction to determine the composition of various samples of mercurisalicylic acid, commercial samples containing 46·8—53·0% of *p*-mercurisalicylic acid, that from mercuric acetate 52·7% and that from mercuric sulphate only 13·9%. Similarly, sodium sulphite reacts with *p*-hydroxymercurisalicylic acid to give *sodium* p-*sodiumsulphitomercurisalicylate*, whilst the *o*-hydroxymercuri-group is eliminated by this treatment. S. COFFEY.

Mercurated derivatives of furan and of pyrrole. R. CIUSA and G. GRILLO (Gazzetta, 1927, 57, 322—329).—Furan reacts with mercuric acetate to form a *tetramercuriacetate*, decomp. 226—228° (converted by potassium hydroxide into a grey substance, impure *furan tetramercurihydroxide*, which explodes at 210°), which with sodium chloride gives the *tetramercurichloride*, decomp. 235°. This on treatment with iodine and potassium iodide gives tetraiodofuran, new m. p. 165° (cf. A., 1922, i, 1057). Pyromucic acid treated with mercuric acetate evolves carbon dioxide, forming also a grey precipitate from which tetraiodofuran can be obtained as above, and which on treatment with potassium hydroxide yields the tetramercurihydroxide. In one experiment, not reproducible, a *furan monomercuriacetate* was obtained, which gave with sodium chloride the corresponding *mercurichloride*.

Pyrrole (cf. Fischer, this vol., 75) gives a *tetramercuriacetate*, from which the *tetramercurichloride* is obtained. Both these substances carbonise before melting; the latter is converted by iodine and potassium iodide into tetraiodopyrrole.

E. W. WIGNALL.

Mercuri-derivatives of *N*-methylthiodiphenylamine. C. FINZI (Giorn. Chim. Ind. Appl., 1927, 9, 176—177).—Treatment of an acetic acid or alcoholic solution of thiodiphenylamine with mercuric acetate yields, not a mercuri-derivative of thiodiphenylamine, but *o*-dithiotetraphenylhydrazine (cf. Pesci, A., 1916, i, 289). Under similar conditions, *N*-methylthiodiphenylamine gives a mixture of the *monomercuriacetate* derivative, m. p. 165°, and the *dimercuriacetate*, which browns, without melting, at 300°.

T. H. POPE.

Phenylmethylstannanes. R. H. BULLARD and ROBINSON (J. Amer. Chem. Soc., 1927, 49, —1373).—Tin tetraphenyl reacts with iodine h formation of diphenyltin di-iodide (di-iodoiphenylstannane), m. p. 71—72°, b. p. 176—182°/2 mm. (cf. Aronheim, A., 1879, 249). Treatment of sodium triphenylstannide with methyl iodide in liquid ammonia affords triphenylmethylstannane. Disodium dimethylstannide and bromobenzene in liquid ammonia yield, apparently, a nitrogen compound which reacts with water to form dimethyltin oxide, but *diphenyldimethylstannane*, m. p. not above —55°, b. p. 127—140°/3 mm. (decomp.), is obtained in 84% yield by treating disodium diphenylstannide with methyl iodide in liquid ammonia. Treatment of sodium trimethylstannide with bromobenzene in liquid ammonia yields mainly *tri*(*trimethylstannyl*)-*amine*, according to the scheme $3NaSnMe_3+3PhBr+NH_3=(SnMe_3)_3N+3C_6H_6+3NaBr$, together with some *phenyltrimethylstannane*, b. p. 203—208°, which can be obtained by Grignard reaction from tin trimethyl bromide and bromobenzene. Bromine converts phenyltrimethylstannane into tin trimethyl bromide (bromotrimethylstannane) and bromobenzene.

F. G. WILLSON.

Organo-metallic oxonium salts. T. HARADA (Bull. Chem. Soc. Japan, 1927, 2, 105—109).—The formation of the substance $(Me_3Sn)_2O,Me_3SnI,H_2O$ (Kraus and Harada, A., 1925, i, 1254) by the action of sunlight on tin trimethyl iodide (trimethyliodostannane) does not take place unless tin tetramethyl is present. Its aqueous solution deposits crystals of a *compound*, $(Me_3Sn)_2O.HI,H_2O$, m. p. 221°, which can also be prepared by the action of tin trimethyl hydroxide on hydriodic acid in hot alcoholic solution. By the action of sodium on the compound $(Me_3Sn)_2O,Me_3SnI,H_2O$ in liquid ammonia, tin trimethyl and its oxide, $(Me_3Sn)_2O$, are obtained.

W. J. POWELL.

α-Hæmatin, the iron-porphyratin of plants, and the corresponding porphyrins. O. SCHUMM [with E. MERTENS] (Z. physiol. Chem., 1927, **166**, 1—20).—Both α-hæmatin and the iron-porphyratin of plants, when boiled for only 15 min. with methyl-alcoholic hydrogen chloride, undergo change, probably involving saturation of unsaturated linkings. Long boiling must therefore be avoided when iron-porphyratins of plant or animal origin are esterified. Prolonged action of hot methyl-alcoholic hydrogen chloride converts the porphyratins into a substance from which, by hydrolysis and removal of iron by means of hydrazine hydrate and acetic acid, there is obtained a new porphyrin. This differs completely from hæmateric acid, but resembles Nencki's hæmatoporphyrin, from which it is easily separable by Willstätter's method of fractionation. The hydrochloric acid number is reduced approximately to that of Nencki's hæmatoporphyrin when the porphyrin is boiled with 25% hydrochloric acid, and the solubility in chloroform is largely lost. It is probably a methyl ether of Nencki's hæmatoporphyrin. Most of the iron is removed from α-hæmatin by long boiling with 3% methyl-alcoholic hydrogen chloride, but cold esterification yields a product which on addition of a little hydrazine hydrate gives a spectrum agreeing with that of the iron complex compound of the new porphyrin. The correspondence between α-hæmatin and the plant porphyratin shows itself in the production of spectroscopically identical porphyrins by electrochemical reduction of hæmateric acid and of the porphyratin after removal of iron by means of

hydrazine and acetic acid; and further by the conversion of the porphyratin by boiling 1% methyl-alcoholic hydrogen chloride, followed by alkaline hydrolysis and the removal of iron, into a chloroform-soluble porphyrin having the same properties as that similarly obtained from α-hæmatin. A method is described for the preparation from yeast of a crude porphyratin which is stable for at least a week.

C. Hollins.

Reaction of iodine with lecithin. M. Romieu (Compt. rend., 1927, **184**, 1206—1208).—Lecithin is stained greenish-brown with iodine solution. The colour is more readily produced after preliminary treatment of lecithin with dilute hydrochloric acid, hot water, or other agent promoting its decomposition. The effect is distinguished from that of iodine on glycogen, since heating in alcoholic solution does not destroy the colour. The reaction is considered to be due to the formation of an unstable iodocholine derivative in solid solution in lecithin. The possibility of confusing the lecithin and glycogen reactions is emphasised. M. Clark.

Nitrogenous groups of nucleic acid. H. O. Calvery and W. Jones (J. Biol. Chem., 1927, **73**, 73—76).—After hydrolysis of yeast-nucleic acid with ammonia at the ordinary temperature, there were isolated guanine, adenine, cytosine, and uracil nucleotides; the supposition that yeast-nucleic acid contains two purine and two pyrimidine groups is thus confirmed. Previous failures to obtain uracil nucleotide were due to the solubility of the lead salt of this compound in presence of sodium acetate.

C. R. Harington.

Structure of silk fibroin. I. Structure of peptone prepared from silk. E. Abderhalden and E. Schnitzler (Z. physiol. Chem., 1927, **164**, 159—181).—Silk peptone is treated at various temperatures with *N*-alkali, the changes being followed by means of the optical behaviour of the copper salts, and comparisons are made with glycyl-*d*-alanine anhydride and glycyl-*l*-tyrosine anhydride similarly treated. The action of enzymes is also investigated.

The copper salt of silk peptone ($[\alpha]^{20}$ −19°), prepared by heating the aqueous solution with freshly-precipitated, neutral copper oxide at 100° for 1 hr., is dextrorotatory; and if the peptone is previously hydrolysed with *N*-alkali, a copper salt of still higher rotatory power is obtained, carboxyl groups being liberated by hydrolysis of anhydride groupings. As the duration and temperature of the alkaline hydrolysis of the peptone are increased, the copper content of the copper salt obtained increases, and the rotatory power curve exhibits distinct inflexions corresponding with (i) fission of glycyl-*d*-alanine anhydride (increase), (ii) fission of glycyl-*l*-tyrosine anhydride (increase), and (iii) formation of amino-acids (decrease). Similar behaviour is observed with a mixture of the two anhydrides.

The fermentation of silk peptone by trypsin and erepsin also results in increased copper content of the copper salt; the rotatory power of the copper salt first increases and then decreases. Treatment of the fermented peptone with alkali has little effect on the composition or optical properties of the copper salt. In a mixture of glycyl-*d*-alanine, glycyl-*l*-tyrosine, and the two corresponding anhydrides the glycyl-*d*-alanine anhydride is hydrolysed by a mixture of trypsin and erepsin, glycyl-*l*-tyrosine anhydride only by alkali, but in the latter case fission by alkali is much easier after pre-treatment with the enzymes.

C. Hollins.

Structure of silk fibroin. R. O. Herzog (Z. physiol. Chem., 1927, **166**, 120; cf. preceding abstract).—The suggestion is made that silk fibroin may be composed of associated compounds of the dipeptide and anhydride type. C. Hollins.

Blood pigments. V. Relation of hæmatin to hæmochromogen. F. Haurowitz (Z. physiol. Chem., 1927, **164**, 255—261).—In the reduction of hæmatin, dimethylhæmatin, *meso*hæmatin, or hæmatohæmatin by excess of hydrazine hydrate under a variety of conditions, for each atom of iron present 0·25 atom of nitrogen is developed, corresponding with 1 atom of hydrogen used up. No catalytic decomposition of the hydrazine occurs. For quantitative reduction of the hæmatin, at least 40 equivalents of hydrazine must be used. Since esterification of the carboxyl group in hæmin, hydrogenation of the side-chain (to *meso*hæmatin), and treatment of hæmin with pyridine or sodium cyanide make no difference to the reaction with hydrazine hydrate, the reduction must take place at the oxygen atom attached to the iron or to a carbon or nitrogen atom of the porphin residue. C. Hollins.

Hydrolysis of elastin by acids and alkali hydroxides. I. S. Yaitschnikov (J Russ. Phys. Chem. Soc., 1926, **58**, 877—878; cf. A., 1925, i, 320).—Elastin was hydrolysed by 0·2*N*-hydrochloric acid at 10°, 37°, 70°, and 100°, and by sodium hydroxide at 10° and 100°. No hydrolysis took place at 10° or 37° with the acid. In the other cases the rates of hydrolysis agreed with the formula $R_t = x/t^{\frac{1}{3}}$.

E. Rothstein.

Proteins. III. Action of superheated water on proteins. II. S. Komatsu and C. Okinaka (Mem. Coll. Sci. Kyoto, 1927, **10**, 241—247).—See A., 1926, 1163.

Proteins. IV. Action of superheated water on proteins. III. S. Komatsu and C. Okinaka (Mem. Coll. Sci. Kyoto, 1927, **10**, 249—254).—From the study of the amide- and diamino-nitrogen contents of the products obtained by digesting edestin, gliadin, and casein, with water at 120° (A., 1926, 853, 1163), it is concluded that hydrolysis of the protein takes place, yielding metaprotein, peptone, subpeptone, proteose, polypeptides, and amino-acids. The yield of the least complex products is increased by prolonged heating. H. Burton.

Combination between acid dyes and proteins. L. M. Chapman, D. M. Greenberg, and C. L. A. Schmidt (J. Biol. Chem., 1927, **72**, 707—729).—The combination of proteins such as gelatin with acidic dyes which form insoluble precipitates with the protein was determined by titrating the protein solution with the dye until the latter tinted the filtrate, or by adding excess of dye and determining the excess in the filtrate. The combination is not

an adsorption phenomenon, but occurs in stoicheiometric proportions; the amount of dye bound increases with the acidity, and is determined by the histidine, arginine, and lysine of the protein. The combining power of proteins for dyes is slightly greater than that for acids. The fact that combination can take place at, and even on the alkaline side of, the isoelectric point of the protein, indicates that the latter must be, to some extent, dissociated in this region. C. R. HARINGTON.

Determination of amino-acids and polypeptides in the products of protein digestion. R. MARTENS (Bull. Soc. Chim. biol., 1927, 9, 454—482).—The titration of an amino-acid in 80% alcoholic solution with sodium hydroxide to a blue colour with thymolphthalein gives a very accurate determination of the carboxyl groups, and has certain advantages over the methods of Foreman and Sorensen. A back-titration of the resulting solution with hydrochloric acid to a red colour with methyl-red determines the amount of amino-compounds in the solution, and the double titration indicates the relationship between the amino- and carboxyl groups. For the direct examination of protein digests, the solution is decolorised, where necessary, by the formation of a precipitate of silver chloride, and neutralised to p_H 6·8. A portion of the solution, after the addition of alcohol to give 80%, is titrated with aqueous 0·2*N*- or 0·1*N*-sodium hydroxide to thymolphthalein (*A*), a few drops of methyl-red are added, and the solution is titrated with 0·2*N*- or 0·1*N*-hydrochloric acid to a standard red colour (*B*). A separate portion of the neutralised solution, to which alcohol has been added to give 50%, is titrated with 0·2*N*- or 0·1*N*-sodium hydroxide to phenolphthalein (*C*), and the use of the formula $100(A-C)/71$ enables the respective importance of the amino-acids and the polypeptides to be measured. A. WORMALL.

Determination of carbon in organic substances by oxidation in solution. B. LUSTIG (Biochem. Z., 1927, 184, 67—84).—The determination of carbon in a large number of organic substances has been effected by boiling with acid permanganate for a long time and measuring the carbon dioxide produced. The time of boiling can be considerably decreased by increasing the concentrations of acid and permanganate, by using platinum gauze as catalyst, with proteins by a pre-treatment with alkaline hydrogen peroxide, and with chlorinated substances by addition of silver nitrate to the permanganate during boiling. P. W. CLUTTERBUCK.

Destruction of organic matter for toxicological analysis. A. P. SEMENCOV and V. Z. PAVLOV (J. Russ. Phys. Chem. Soc., 1926, 58, 903—908).—The popular Fresenius–Babo method for the destruction of organic matter takes 8—10 hrs., and mercury and arsenic are lost during the oxidation. A solution of the organic matter in half its weight of sodium hydroxide is submitted to a rapid stream of chlorine. Towards the end of the reaction, the liquid is warmed. When absorption is complete, the yellow liquid deposits a precipitate, which, however, does not contain arsenic. On acidification, fatty acids are precipitated, which are also free from mineral matter. After filtering, the liquid is ready for analysis. The oxidation of 100—200 g. of organic material occupies less than 1 hr. E. ROTHSTEIN.

Determination of methyl alcohol in presence of ethyl alcohol. F. S. MORTIMER (Ind. Eng. Chem., 1927, 19, 635—636; cf. Leach and Lythgoe, A., 1905, ii, 655).—The refractivities of mixtures of water and ethyl and methyl alcohols at 20° have been determined by means of the Zeiss immersion refractometer, and with the aid of the ternary diagram thus obtained the amounts of the two alcohols present in a given mixture can be calculated from the refractive index, provided that the total alcohol content is known. Since equal weight concentrations of the two alcohols in water have nearly the same density, the total alcohol content can readily be found from the specific gravity. The refractivities of mixtures containing less than 40% of total alcohols are more regular than those which contain more than this amount, hence only this portion of the system has been investigated. W. J. POWELL.

Comparison of sensitivities of various tests for methyl alcohol. L. O. WRIGHT (Ind. Eng. Chem., 1927, 19, 750—752).—A survey of the various methods proposed for the detection of methyl alcohol in presence of ethyl alcohol. The method recommended—oxidation with potassium permanganate and detection of the formaldehyde formed by means of rosaniline–sulphurous acid reagent—can be used for quantitative work, and a suitable standardised procedure is described. Glycerol and pectin, which give a similar colour reaction, may be eliminated by distillation. W. J. POWELL.

Mercurimetry. A. IONESCO-MATIU (Ann. sci. Univ. Jassy, 1927, 14, 363—373).—Acetone may be determined by precipitating as a complex salt with mercuric sulphate, as described by Denigès, then dissolving this compound in a mixture of nitric and sulphuric acids and titrating the mercuric salt liberated with sodium chloride, according to Votoček and Kašpárek's method (A., 1923, ii, 184). R. CUTHILL.

Determination of dihydroxyacetone. Measurement of time of reactions. H. SCHMALFUSS (Ber., 1927, 60, [*B*], 1045—1047).—Dihydroxyacetone may be determined in solution by comparison of the time required for incipient reduction of Fehling's solution under standard conditions with that necessary for dihydroxyacetone solutions of known concentration. The process is applicable in presence of substances which do not reduce cold Fehling's solution; dextrose appears to delay reduction. H. WREN.

Micro-determination of pentose in yeast-nucleic acid and its derivatives. W. S. HOFFMAN (J. Biol. Chem., 1927, 73, 15—25).—Xylose and the *d*-ribose of purine nucleotides are quantitatively converted into furfuraldehyde by distillation with 20% hydrochloric acid for 3 hrs. The conversion of arabinose into furfuraldehyde is much slower. Owing to their resistance to acid hydrolysis, the pyrimidine nucleotides yield small amounts only of furfuraldehyde under these conditions. On treat-

ment of yeast-nucleic acid in this manner, a little more than half the pentose is obtained as furfuraldehyde, which supports the hypothesis that yeast-nucleic acid contains an equal number of purine and pyrimidine nucleotide elements. C. R. HARINGTON.

Detection of methylpentoses as methylfurfuraldehyde. E. VOTOCEK and F. RÁC (Chem. Listy, 1927, 6, 231—233).—A substance giving the reactions of methylfurfuraldehyde is produced by the distillation of ketorhamnose with 12% hydrochloric acid, indicating that the furfuraldehyde reaction is given by both ketonic and aldehydic methylpentoses. R. TRUSZKOWSKI.

Phenol tests. III. The indophenol test. H. D. GIBBS (J. Biol. Chem., 1927, 72, 649—664).—The blue colour due to indophenol formation obtained by the action of 2 : 6-dibromobenzoquinonechloroimide on phenol serves for the detection of the latter in a concentration of 1 : 20,000,000; by spectrophotometric observation of the colour development, the reaction can be utilised for the quantitative determination of amounts of phenol of this order of magnitude. The reaction proceeds best at p_H 9—10. Absorption curves are given for 2 : 6-dibromo- and 2 : 6-dichloroindophenol. C. R. HARINGTON.

Reactions of dyes with nitrous acid. J. V. DUBSKY and A. OKAC (Rec. trav. chim., 1927, 46, 296—302).—When a dye such as magenta is used as a reagent for nitrous acid, it has the advantage that a subsequent coupling reaction will produce a change of colour, instead of a mere production of colour. Benzidine, with β-naphthol as coupling agent, is not so sensitive as is claimed by Eegriwe (A., 1925, ii, 156). α-Naphthol, α-naphthylamine, and H-acid (8-amino-α-naphthol-3 : 6-disulphonic acid) are preferable to β-naphthol, and in general an α-derivative is about ten times as sensitive as the β-derivative. Since α-naphthol gives an intense yellow colour with nitrous acid of concentration 10^{-7}, this must be taken into account in considering subsequent colour changes. More than 600 dyes have been tested for their sensitivity to nitrous acid when followed by a coupling agent, and the results with some of these are tabulated. Magenta is the most sensitive; with nitrous acid of concentration 10^{-7}, it gives a yellow colour on adding phenol and a red colour on adding α-naphthol; with nitrous acid of concentration 10^{-8}, a violet colour on adding α-naphthylamine. E. W. WIGNALL.

Determination of tyrosine by means of Millon's reaction. D. ZUVERKALOV (Z. physiol. Chem., 1927, **163**, 185—192).—To 1 c.c. of protein solution (1% casein, egg-albumin, peptone, or globulin) in 5% sodium hydroxide, 3 c.c. of glacial acetic acid are added, then 2 c.c. of 10% mercuric sulphate in 5% sulphuric acid and 1 drop of 0·5% sodium nitrate; the whole is heated just to the b. p. over a free flame, and, after cooling, the coloration is compared with a standard made from 1 c.c. of 0·04% tyrosine solution. Under these conditions, tryptophan, unless excess is present, produces no coloration. The acetic acid must be glacial, and excess of nitrite or prolonged heating must be avoided. The colour reaches its maximum in 15—20 min. and persists for 2—3 hrs. C. HOLLINS.

Determination of minute amounts of *l*-α-amino-β-3 : 4-dihydroxyphenylpropionic acid and tyrosine in presence of one another. H. SCHMALFUSS and H. LINDEMANN (Biochem. Z., 1927, **184**, 10—18).—*l*-α-Amino-β-3 : 4-dihydroxyphenylpropionic acid in very dilute solution (*M*/2000—*M*/333,000 is converted into melanin without flocculation occurring, and the reaction can therefore be used for colorimetric determination of the amino-acid, the best dilution being *M*/2000—*M*/30,000. In mixtures of this acid with tyrosine, the former may be determined colorimetrically, and the latter by difference from the total amino-acid. P. W. CLUTTERBUCK.

Biochemistry.

Blood as a physico-chemical system. IV. D. B. DILL, C. VAN CAULAERT, L. M. HURXTHAL, J. L. STODDARD, A. V. BOCK, and L. J. HENDERSON (J. Biol. Chem., 1927, 73, 251—262).—A nomographic representation of the data obtained on the blood of a normal man is compared with a similar nomogram previously constructed for a man (A., 1924, i, 780) and with that representing the horse (cf. Van Slyke and others, A., 1923, i, 1249). The two human bloods are almost identical, whilst that of the horse shows certain differences, particularly a higher concentration of hæmoglobin in the red corpuscles. C. R. HARINGTON.

Visible and ultra-violet spectrum of blood and of its constituents. R. SUHRMANN and W. KOLLATH (Biochem. Z., 1927, **184**, 216—230).—The validity of Beer's law is investigated and confirmed, using 0·1—0·5% solutions of blood, in respect to both the visible and the ultra-violet spectra. Quantitative determination of the absorption curves for blood, for plasma, and corpuscles from 578 to 230 μμ shows that the absorptions due to the constituents are combined in the whole blood additively. From the values obtained for the absorption constant are calculated the percentage of the radiation absorbed in the visible and ultra-violet spectrum by a layer of corpuscles 7·8 μ thick, and also the depth of penetration of waves of different wave-lengths when absorption is 99%. P. W. CLUTTERBUCK.

Denaturation of proteins. III. Denaturation of hæmoglobin. H. WU and K. H. LIN (Chinese J. Physiol., 1927, **1**, 219—234).—When hæmoglobin is treated with acid, alkali, alcohol, or heat, both a reversible and an irreversible change take place. The former is described as ψ-denaturation. In the case of acid, the reversible process is much the more rapid, but with the other reagents the two changes overlap. Reduced hæmoglobin, methæmoglobin, and carboxyhæmoglobin may, after treatment with dilute

id, be completely reconstituted by making alkaline. 'hen oxyhæmoglobin is treated in this way, only a rt is re-formed, and this appears as methæmoglobin. e amount of methæmoglobin so formed is of an der to explain the observation of Roaf and Smart id of Quagliariello, that acid liberates from oxyhæmo- obin only half as much oxygen as does potassium rricyanide. R. K. CANNAN.

Reduction of hæmatin and methæmoglobin. . HILL and H. F. HOLDEN (Biochem. J., 1927, **21**, 35—631).—The reduction of methæmoglobin to æmoglobin requires one equivalent of hydrogen per tom of iron. The reduction of hæmatin to reduced æmatin or to pyridine-hæmochromogen requires also ne equivalent of hydrogen per atom of iron. The ıethæmoglobin was prepared by oxidising oxyhæmo- lobin with ferric tartrate in acid solution. On ıaking such solution alkaline, the ferrous salt formed educed some of the methæmoglobin. In the case f the reduction of hæmatin, advantage was taken f the fact that both reduced hæmatin and pyridine- ıæmochromogen are insoluble. S. S. ZILVA.

Hæmocyanin. IV. Dependence of shape of oxygen dissociation curve on state of ionisation of the protein. (MRS.) E. STEDMAN and E. STED- MAN (Biochem. J., 1927, **21**, 533—543).—The iso- electric points of the hæmocyanins from *Cancer* and *Homarus* are at p_H 4·7, that of hæmocyanin from the snail (*Helix pomatia*) is at p_H 5·3. The viscosity of solutions of hæmocyanin from *Cancer* passes through a maximum at p_H 7·3; at the same p_H, the affinity of the pigment for oxygen passes through a minimum. A similar relationship seems to hold in the case of the hæmocyanin from *Homarus*. S. S. ZILVA.

Urea content of capillary and venous blood. E. SVENSGAARD (Biochem. J., 1927, **21**, 522—529).— There is usually a higher concentration of urea in capillary than in venous blood in the course of the day. This was found to be the case with fasting normal individuals, with patients suffering from diabetes, nephritis, or icterus, and with subjects after ingestion of protein, urea, a diet poor in protein, fat, starch, and dextrose. S. S. ZILVA.

Iron in the blood-serum of different animal species. V. HENRIQUES and A. ROCHE (Bull. Soc. Chim. biol., 1927, **9**, 501—504).—The total and the hæmoglobin-iron have been determined in the sera of the rabbit, cat, dog, horse, pig, and ox, and the differences, varying from 1·5 to 2·5 mg. of iron per litre of serum, indicate the constant presence of non- pigmentary iron in the serum of the species examined. This finding is opposed to the statement of Abder- halden that serum contains no iron. The nature of the substances containing this iron and the physio- logical significance are not known. A. WORMALL.

Glycolysis. VII. Distribution of phosphorus in blood. P. RONA and K. IWASAKI (Biochem. ., 1927, **184**, 318—340).—The diffusible hydrolysable phosphoric ester of the blood is contained only in the ormed elements of the blood. The increase in the morganic phosphorus when blood or a suspension of corpuscles is kept is related to the concentration of re cing sugar present. Addition of dextrose, lævulose, or mannose (and, to a less degree, of galactose) diminishes the hydrolysis of the ester, indicating an equilibrium reaction. The disac- charides and lactic and pyruvic acids are inactive. Displacement of the equilibrium towards synthesis of the ester is favoured in solutions alkaline to p_H 7·3. Hæmolysis and fluoride inhibit synthesis.

R. K. CANNAN.

Action of external stimuli on the refractive index of blood-serum. S. BALACHOVSKY and W. TURBABA (Biochem. Z., 1927, **182**, 233—235).— Evidence is adduced of supposed variations in the refractive index of human, rabbit's, and dog's blood serum following painful stimuli. J. PRYDE.

Determination of catalase in blood. P. J. GOBZOW and W. D. JANKOWSKY (Biochem. Z., 1927, **185**, 63—69).—The method of Bach and Subkowa (A., 1922, i, 392) for the determination of blood catalase is criticised on the ground that insufficient excess of hydrogen peroxide was employed; to obtain accurate results, 40—60 mg. of hydrogen peroxide must be used for 0·001 c.c. of blood. The spontaneous inactivation of catalase which takes place in diluted blood at the ordinary temperature may be prevented by addition of alcohol to make 1 : 5000 concentration. C. R. HARINGTON.

Determination of blood-chlorides. J. J. SHORT and A. D. GELLIS (J. Biol. Chem., 1927, **73**, 219—222). —The iodometric method of McLean and Van Slyke (A., 1915, ii, 573) is more satisfactory for the deter- mination of blood-chlorides than the adaptation of the Volhard method employed by Whitehorn (A., 1921, ii, 272). A modification of the former method is described. C. R. HARINGTON.

Determination of oxalic acid in blood, urine, and body-fluids. J. KHOURI (Bull. Soc. chim., 1927, [iv], **41**, 394—396).—Oxalic acid in blood or biological fluids is determined as follows: 5 c.c. (at least) of the serum are freed from proteins by treat- ment with an equal volume of 20% trichloroacetic acid. The mixture is centrifuged, and the clear liquid is treated with lead acetate solution to complete precipitation, centrifuged again, the residue digested successively with 4 c.c. and 2 c.c. of 10% sulphuric acid, centrifuged, and the clear liquids are united. The mixture is extracted with 2 volumes of ether con- taining 10% of alcohol. The residue from the ethereal extract is treated with an alcoholic solution of carbamide as previously described (A., 1923, ii, 795). Determination of oxalic acid in urine by direct extraction with ether is unsatisfactory. The sample of urine (10—20 c.c.) should be treated with a very slight excess of Sarvonat's phosphotungstic acid solution (1½—2 volumes), filtered, and the precipitate washed with water. After neutralisation with ammonia and slight acidification with dilute sulphuric acid, the solution is evaporated to 10 c.c. and extracted with twice its volume of ether containing 10% alcohol. The subsequent procedure is as described above. R. BRIGHTMAN.

Colorimetric determination of proteins of plasma, cerebrospinal fluid, and urine. H. WU and S. M. LING (Chinese J. Physiol., 1927, **1**, 161— 168).—The colorimetric method for the determin-

ation of proteins in plasma by means of their reaction with phosphomolybditungstic acid (phenol reagent) (Wu, A., 1922, ii, 406) has been modified and extended to the determination of the proteins of cerebrospinal fluid and urine. The chief modification consists in the use of sodium hydroxide instead of sodium carbonate for developing the blue colour. The colour develops more rapidly under these conditions, is more intense, and shows no tendency to become turbid. R. K. CANNAN.

Determination of small quantities of dextrose [in blood]. M. J. SCHULTE (Pharm. Weekblad, 1927, **64**, 485—497).—The existing methods of determining dextrose in blood have been re-examined, using blank solutions made up with the purest dextrose obtainable, and found to contain 98·2—98·3% of dextrose. The reduction of cupric salts is not proportional to the amount of dextrose present; hence all determinations based on addition of known quantities of dextrose to the test solution are unsuitable. The Cohen–Tervaert and the Schaffer–Hartmann methods are accurate, if account be taken of this; new tables are given, from which the percentages of dextrose in blood may be read directly from the titration results. The latter method is unsuitable for dextrose content below 0·2%, the former for quantities below 0·1%. S. I. LEVY.

Micro-determination of reducing sugars [in solutions and] in blood. G. FONTES and L. THIVOLLE (Bull. Soc. Chim. biol., 1927, **9**, 353—445).—A critical comparison has been made of the principal methods available for the micro-determination of dextrose in solution. The method finally adopted involves the use of a modified alkaline copper solution and of a special apparatus for the filtration of the cuprous oxide formed. The precipitate obtained is dissolved in a phosphomolybdic acid reagent and the blue solution titrated with standard potassium permanganate solution until there is no colour left. In the application to blood samples, sodium fluoride, soaked in solution on blotting-paper in amounts not greater than 2 mg. per c.c., is added, to prevent clotting, and tungstic acid is used as a precipitant. Determinations of the "immediately reducing blood-sugar" (as dextrose) have been made in whole blood, plasma, and the corpuscles of different animal species and normal and pathological human subjects, and the effects on these values of the anticoagulants in general use determined. The conflicting results of previous authors are discussed in the light of the results, and it is found that in no case are the corpuscles free from reducing sugars, although they never contain more than the plasma. With the goose, rabbit, and dog, plasma always contains more reducing sugars than the corpuscles, and this is independent of the value for "immediately reducing blood-sugar." With normal human blood, the values for plasma and corpuscles are sometimes identical, but in many cases there is a distribution which favours the plasma; the differences which are observed, however, are less than those for the other species examined. Sodium fluoride is recommended in quantities of 2 parts per 1000 as the best anticoagulant. A. WORMALL.

Formation of fibrinogen. F. FALUDI (Biochem Z., 1927, **184**, 245—256).—The increase in bilirubin formation in dogs having a gall-bladder fistula, o administration of a cholagogue, is not accompanie by any increase in fibrinogen, but actually by a decrease, caused by the hydræmia which results fro the action of, *e.g.*, phenylquinolinecarboxylic aci or dehydrocholic acid. Hydræmia lasts usuall about 8 hrs. It appears, therefore, that fibrinoge arises independently of bilirubin in the reticulo-endothelial cells. P. W. CLUTTERBUCK.

Chemical changes underlying the coagulatio of the blood. A. WADSWORTH, F. MALTANER, an E. MALTANER (Amer. J. Physiol., 1927, **80**, 502—521).—Solutions of thrombinogen (serozyme) prepare by Bordet's method are not, as Bordet believed, free from fibrinogen. Failure of plasma to clot after treatment with tricalcium phosphate is due not to the removal of thrombinogen, but to the liberation of alkali through dissolution of some of the phosphate. A lipoid corresponding in elementary analysis with a phosphatide without its nitrogenous base has been isolated from tissues. It possessed coagulative properties and formed a calcium compound with calcium ions. Fibrinogen and the proteins of serum form insoluble complexes with this lipoid in slightly acid solution. It is suggested that coagulation is the formation of such a complex when the lipoid, fibrinogen, and calcium ions are suitably concentrated at active surfaces. R. K. CANNAN.

Destruction of lactic acid by blood-cells. J. WARKANY (Biochem. Z., 1927, **184**, 480—483).—The lactic acid produced during glycolysis in defibrinated blood was slightly in excess of the sugar (determined by Bang's method) simultaneously disappearing. The question of the destruction of lactic acid by blood-cells is thus confused by the fact that lactic acid may arise from carbohydrates in the blood which are not determined by the method of Bang. R. K. CANNAN.

Mineral components of organised matter. M. COPISAROW (Chem. News, 1927, **134**, 323—326, 338—340).—Data concerning the distribution of iron, copper, zinc, manganese, aluminium, lead, alkali and alkaline-earth metals, magnesium, radium, and water in different organs of higher and lower animals have been collected. The available knowledge on the mineral matter of vegetables has also been summarised. Analysis of the ash of bacteria discloses variations depending on the nature of the culture medium. The occurrence of arsenic, tellurium, and selenium in the plant world is discussed. The data on the composition of the ash of different plants and different parts of the same plant indicate a definite correlation between biochemical requirements and the quantitative as well as qualitative aspects of the mineral content of plants. R. A. MORTON.

Proteolytic enzymes in river crayfish. P. KRUGER and E. GRAETZ (Z. physiol. Chem., 1927, **166**, 128—134; cf. Ringer and Grütterink, A., 1926, 977).—The optimum p_H for the fermentation of peptone, fibrin, and leucylglycine by intestinal juices of river crayfish is found to be 6—8, as against Ringer and Grutterink's higher values. The juices contain,

in addition to the tryptic and peptic enzymes (optimum p_H 7·5—8·5), a pepsinase (optimum p_H 2·7) which hydrolyses fibrin but not blood- or egg-albumin. C. HOLLINS.

Analysis of the sea-slug, *Stichopus japonicus*, Selenka (Hai-shen). K. H. LIN and C. C. CHEN (Chinese J. Physiol., 1927, **1**, 169—174).—Determination has been made of the distribution of nitrogen in the body-wall of this sea-slug, which is a common article of diet in China. The protein may be regarded as of fair nutritional value. 5·05% of carbohydrate is present in an insoluble form. R. K. CANNAN.

Micro-determination of the relative distribution of glutathione in insects. D. E. FINK (Science, 1927, **65**, 143—145).—The insect is dissected in a saturated solution of ammonium sulphate (5 c.c.), to which is then added sodium nitroprusside (5% solution, 4—6 drops) and ammonia solution (1 c.c.). The distribution of glutathione is estimated by microscopical observation of the deep magenta colour developed in the tissues and organs. Normal insects give reactions in the stomach, in the sex organs during development, and in the muscles of the thorax, head, legs, and alimentary tract. Feeding or injection with arsenicals largely reduces the amount of reaction. A. A. ELDRIDGE.

Absence of a cellulase in *Limnoria*. C. M. YONGE (Nature, 1927, **119**, 855).—The wood-borers *Lemnoria lignorum* and *Chelura terebrans* do not contain a cellulase. A. A. ELDRIDGE.

Biochemistry of "mutton bird" oil. C. L. CARTER and J. MALCOLM (Biochem. J., 1927, **21**, 484—493).—The oil obtained from the stomach of the mutton bird is hydrolysed by mammalian pancreatic lipase *in vitro* and is digested, absorbed, and utilised by the mammal. When cetyl alcohol is fed to the rat, only a small proportion is excreted in the fæces. The oil contains vitamin-*A*, although the degree of potency varies markedly in different samples. It also gives the sulphuric acid, trichloroacetic acid, and phosphorus pentoxide tests. There is preliminary evidence that vitamin-*A* comes over on distillation of the unsaponifiable fraction of the oil at 180—200°/4 mm. pressure. The cetyl, oleyl, and other alcohols are changed during or after absorption of the oil, since they can no longer be detected. On subcutaneous and intraperitoneal injection, the oil appears to be taken up in undissociated form by the leucocytes, and to travel by the lymphatics. S. S. ZILVA.

Cholesterol content of hair, wool, and feathers. H. C. ECKSTEIN (J. Biol. Chem., 1927, **73**, 363—369).—The hair of human adults contains 0·1—0·2%, and that of children 0·3—0·45% of cholesterol; that of the cat, dog, rabbit, and rat contains about 0·6%; in the rabbit and dog, the cholesterol forms 30—40% of the total lipins of the hair, whilst in no other mammalian species does it amount to more than 13·3% of the total lipins. Wool contains about ·1% of cholesterol, which is 5—12% of the total lipins. Feathers contain 0·26—0·29% of cholesterol, but the relationship of this to the total lipins is variable. C. R. HARINGTON.

Isolation from tissues of certain pentose derivatives. L. B. WINTER (Biochem. J., 1927, **21**, 467—478).—Two pentose derivatives were isolated from the muscle and liver of the goat. One of these contains *d*-ribose, and is probably an alkylriboside. The other derivative, which has not been identified, is unstable. The stable methylated derivative of this compound hydrolyses at the same rate as trimethyl-β-methylarabinoside, from which, however, it differs in its specific rotation (+17·6°). S. S. ZILVA.

Chemistry of the adrenal cortex. A. VON SZENT-GYORGYI (Nature, 1927, **119**, 782—783).—The reducing agent, "C_{xiii}," present in extracts of the adrenal cortex has been purified; it has m. p. 175°. The C_{xiii} content of the adrenal gland of the cow is approximately 0·1%. A. A. ELDRIDGE.

Cerebrosides of brain. E. KLENK (Z. physiol. Chem., 1927, **166**, 268—286).—Dried brain tissue, after extraction with cold acetone and with light petroleum, still contains the larger part of the cerebrosides. These may be dissolved out by continuous extraction for several days with hot acetone, the solvent being renewed at intervals during this period. In this way, the extracted material is divided up into four fractions, each of which has been investigated separately. The percentage of galactose in the crude extract diminishes with successive fractions. The iodine value of the cerebroside fatty acids is highest in the first extracted fractions, which contain much nervonic acid. By far the greater proportion of the fatty acid in the last two fractions is cerebronic acid. Methods used in the separation of the fatty acids are described. Further evidence is adduced that lignoceric acid and hydrogenated nervonic acid are identical. An unsaturated hydroxy-fatty *acid*, $C_{24}H_{48}O_3$, has been isolated. H. D. KAY.

Nervonic acid. E. KLENK (Z. physiol. Chem., 1927, **166**, 287—293).—The position of the double linking in nervonic acid has been ascertained by the ozonisation method of Harries. As the hydrolysis products of ozonised nervonic acid, normal nonoic acid, together with a straight-chain *dicarboxylic acid*, $C_{15}H_{28}O_4$, m. p. 111—111·5°, are obtained. The structure $CH_3{\cdot}[CH_2]_7{\cdot}CH{:}CH{\cdot}[CH_2]_{13}{\cdot}CO_2H$ is assigned to nervonic acid. H. D. KAY.

Presence of kerasin in ox-spleen. E. WALZ (Z. physiol. Chem., 1927, **166**, 210—222).—This galactolipin is present in normal ox-spleen. Accompanying it is a substance which gives a violet-red coloration with orcinol and hydrochloric acid in presence of ferric chloride, contains phosphorus, 22·4% of galactose, and agrees in its properties with a substance separated by Thierfelder from brain. H. D. KAY.

Diaminomonophosphatide from ox-spleen. E. WALZ (Z. physiol. Chem., 1927, **166**, 223—226).—A substance corresponding analytically with sphingomyelin, but of lower dextrorotatory power, has been isolated from ox-spleen. H. D. KAY.

***X*-Ray investigation of spiders' silk.** R. O. HERZOG and W. JANCKE (Z. physiol. Chem., 1927, **164**, 306—307).—The *X*-ray diagram for the threads of the Madagascar spider very closely approximates

to that for true silk. The two fibres hence contain the same crystalline constituents. C. HOLLINS.

Composition of the aqueous humour. T. IKEBATA (Biochem. Z., 1927, **182**, 236—244).—The aqueous humour contains very little diastase, but variations in the diastase value of the blood are reflected in similar variations in the aqueous humour. Alterations in the albumin : globulin ratio and in the sugar of the blood also affect the values of these components of the aqueous humour. The aqueous humour of the rabbit contains lipase and a proteolytic enzyme. J. PRYDE.

Secretion of bile. IV. E. NEUBAUER (Biochem. Z., 1927, **184**, 231—233).—In continuation of previous work (A., 1924, i, 909; 1926, 1056), lithocholic acid is shown to have no cholagogic properties. P. W. CLUTTERBUCK.

Magnesium content of the cerebrospinal and other body-fluids. H. COHEN (Quart. J. Med., 1927, **20**, 173—186).—A method for determining magnesium in 2 c.c. of fluid is described. In 18 normal and pathological cases, the average magnesium content (3·28 mg. per 100 c.c.) is greater than that of the contemporary blood-serum (2·56 mg. per 100 c.c.); the excess is less marked in meningitis, and becomes a deficiency in pleural and peritoneal effusions. *Post mortem*, the serum contains more magnesium than does the cerebrospinal fluid, although there is an increase in both. The magnesium content of cerebrospinal fluid is independent of age, sex, cell or protein content, and Wassermann reaction. CHEMICAL ABSTRACTS.

Human milk. I. Technique. II. Determination of vitamin-*A*. III. Determination of vitamin-*B*. I. G. MACY, J. OUTHOUSE, A. GRAHAM, and M. L. LONG. **IV. Vitamin-*A* and -*B* content of cows' milk.** J. OUTHOUSE, I. G. MACY, V. BREKKE, and A. GRAHAM (J. Biol. Chem., 1927, **73**, 153—174, 175—188, 189—201, 203—208).—I. A description of nutritional technique.

II. Good growth was obtained in young rats on addition of 2·5—3·0 c.c. of mixed human milk *per diem* to a diet otherwise free from vitamin-*A*.

III. Human milk is very low in content of vitamin-*B*; whilst normal growth was obtained by daily administration of about 20 c.c. of milk as the sole source of vitamin-*B*, even 35 c.c. *per diem* did not supply sufficient vitamin-*B* for the period of lactation in the rat.

IV. 3 C.c. of cow's milk *per diem* forms an adequate source of vitamin-*A*, and 20—25 c.c. *per diem* supplies sufficient vitamin-*B* for normal growth in rats. C. R. HARINGTON.

Substances extracted from cows' milk. N. F. TOLKATCHEVSKAYA (J. Russ. Phys. Chem. Soc., 1926, **58**, 888—891).—By examining the successive precipitates obtained by treatment of cows' milk with mercuric sulphate, alcohol, mercuric acetate, sodium carbonate, and, finally, after treatment with picric acid and phosphotungstic acid, respectively, it is shown that carnosine is not present. Choline chloroplatinate was isolated. E. ROTHSTEIN.

Urea content of camel's urine. J. PETRI (Z. physiol. Chem., 1927, **166**, 125—127; cf. Read, A., 1925, i, 1204).—Read's statement that camel's urine contains only very slight traces of urea is unfounded. 100 C.c. of the urine are shown to contain 2·27 g. of total nitrogen, 1·705 g. being present as urea, 0·001 g. as ammonia, 0·043 g. as uric acid and purine bases. From 200 c.c., 2·92 g. of crystalline urea are obtained. C. HOLLINS.

Determination of lactic acid in urine. J. WARKANY (Biochem. Z., 1927, **184**, 474—479).—The urine is treated with phosphotungstic acid and filtered. An aliquot portion of the filtrate is treated with copper sulphate and lime to remove sugars and other interfering substances, and the lactic acid in the filtrate determined by the method of Von Furth and Charnass. The lactic acid contents of normal and pathological urines are recorded. R. K. CANNAN.

Influence of mineral salts on metabolism. O. KAUFFMANN-COSLA and W. ZORKENDÖRFER (Biochem. Z., 1927, **184**, 19—27).—Administration of Marienbad sodium sulphate waters to slight and mild diabetics causes an increased oxidative power of the cell. Loss of fat by patients under similar treatment is probably also caused by increased oxidation. P. W. CLUTTERBUCK.

Effect of protein in the diet in diabetes mellitus. A. LYALL (Quart. J. Med., 1927, **20**, 115—122).—Nitrogen-equilibrium is possible on a low protein diet. Protein up to 2 g. per kg. has no deleterious effect on sugar tolerance. Protein does not increase ketosis. CHEMICAL ABSTRACTS.

Iodine metabolism. III. T. VON FELLENBERG (Biochem. Z., 1927, **184**, 85—89).—The general result that urinary iodine excretion is greater in the inhabitants of non-goitrous than in those of goitrous districts is further borne out by determination of the iodine content of the urine of Norwegian subjects. The iodine content of various types of fish, which form the staple diet of such subjects, was also determined (cf. A., 1924, i, 114; 1926, 1056). P. W. CLUTTERBUCK.

Iodine content of some rocks and its relation to the chemical part of the goitre problem. E. WILKE-DORFURT.—See this vol., 642.

p_H of the gastro-intestinal tract of certain rodents used in feeding experiments and its possible significance in rickets. T. REDMAN, S. G. WILLIMOTT, and F. WOKES (Biochem. J., 1927, 21, 589—605).—In the guinea-pig, the following average p_H results were obtained : stomach 2·8—4·3, average 3·8; duodenum 4·8—5·3, average 5·1; jejunum 5·1—7·1; ileum 7·0—7·9, average 7·4; cæcum and large intestine 5·2—6·9, average about 6·4. In normal adult rats, the average figures were : stomach 4·0, duodenum 5·5, jejunum 6·0, ileum 6·8, cæcum and large intestine 6·5. In rats 1—3 months old, the average figures were : jejunum 6·8, ileum 7·0, cæcum and large intestine 6·7. The reaction in the gastro-intestinal tract of the white mouse on a diet of bread and milk is similar to that of the rat, or perhaps more acid; the highest p_H recorded was less than 6·0. The results obtained with a young rabbit were similar to those registered in the case of the guinea-pig. Rats on a rachitic diet developed alkalinity

throughout the intestinal tract, especially in the cæcum and large intestine. The administration of cod-liver oil or irradiated cholesterol restored the acidity. S. S. ZILVA.

Conditions of formation of malignant tumours. IV. Lactic acid, cytochrome, and glutathione contents of normal and cancer tissues. R. BIERICH, A. ROSENBOHM, and K. KALLE (Z. physiol. Chem., 1927, **164**, 207—216; cf. A., 1926, 860, 1169).—Cytochrome has been shown to be a regular constituent of all normal epithelial tissue in warm-blooded animals. The cytochrome content in cancers is now shown to increase in proportion to the cancer cells present, and the same applies to the lactic acid and glutathione content. Since cytochrome is an intercellular pigment, it is not present in disintegrated cancer tissue. C. HOLLINS.

Distribution of electrolytes in dogs following ligation of both ureters. D. W. ATCHLEY and E. M. BENEDICT (J. Biol. Chem., 1927, **73**, 1—14).—In acute uræmia, produced, in dogs, by ligation of both ureters, the total base of the blood showed no significant variation. The phosphates and sulphates of the blood showed an increase which was balanced by an almost equivalent decrease in chlorides and carbonates. Parallel changes were observed in the chloride content of the tissues. C. R. HARINGTON.

I. Fate of dihydroxyacetone in the animal. II. Metabolism of dihydroxyacetone in pancreatic diabetes. J. MARKOWITZ and W. R. CAMPBELL (Amer. J. Physiol., 1927, **80**, 548—560, 561—575).—Dihydroxyacetone is converted into dextrose by the liver. When the liver is absent, this substance still disappears in part from the blood when it is injected, but is probably stored in the tissues, for a considerable part of that lost from the blood was recovered unchanged from the muscles. These results provide further evidence for the view that dihydroxyacetone is not an intermediate in the catabolism of carbohydrate.

II. When dihydroxyacetone is administered to depancreatised dogs, its concentration in the blood steadily falls, whilst the concentration of dextrose rises, and the substance is ultimately quantitatively excreted as dextrose in the urine. It is not oxidised, and has no antiketogenic action. R. K. CANNAN.

Carbohydrate metabolism. III. Influence of dihydroxyacetone on the respiratory metabolism and on the inorganic phosphate of the blood. C. G. LAMBIE and F. A. REDHEAD (Biochem. J., 1927, **21**, 549—559).—Dihydroxyacetone produces, both in diabetics and normals, a more rapid and more marked rise in the respiratory quotient, the oxygen consumption, and the total metabolism than does dextrose, whether administered intravenously or orally. These changes produced in diabetics are comparable with those obtained in normal persons. There is also a fall in the inorganic phosphate of the blood in both diabetics and normals, which is more rapid and marked than after the administration of dextrose. The curves of inorganic blood-phosphate follow closely those of the respiratory metabolism. Lævulose produces effects intermediate between those of dextrose and dihydroxyacetone, but more closely approximating to those of the former when small doses are employed. Respiratory quotients above unity are obtained after oral administration of 50 g. of dihydroxyacetone in normals. S. S. ZILVA.

Formation of succinic acid in the body. I. Determination of succinic acid and its formation in muscle and liver pulp. P. W. CLUTTERBUCK (Biochem. J., 1927, **21**, 512—520).—Rabbit liver, weight for weight, is about eight times as active as rabbit muscle in the conversion of both succinic and fumaric acids into malic acid. The velocity of the first reaction is much less than that of the second. The succinic acid reaction with muscle does not attain quite the same equilibrium as the fumaric acid reaction. Cyanide inhibits the change from succinic to fumaric acid, but has no action on the conversion of fumaric into malic acid. No production of succinic acid in presence of minced organs could be established by using the following possible precursors: acetone, sodium acetate, acetoacetate, α-ketoglutarate, δ-ketohexoate, and diacetylsuccinate. The conversion of succinic acid into fumaric and malic acids was followed polarimetrically, the method being based on the greatly enhanced rotation of *l*-malic acid in presence of uranium acetate. S. S. ZILVA.

Degradation of acetoacetic acid in the kidney. I. SNAPPER and A. GRUNBAUM (Biochem. Z., 1927, **185**, 223—228).—Perfusion through the surviving kidney of blood containing acetoacetic acid leads to disappearance of 45—73% of the latter, less than 10% being reduced to β-hydroxybutyric acid. The kidney thus behaves quite differently from the liver (this vol., 374). It is pointed out also that experiments *in vitro* with minced kidney tissue lead to different results (cf. Von Lagermark, A., 1913, i, 1271) and that, for experiments of this type to have physiological significance, the method of perfusion of the surviving organ should be adopted. C. R. HARINGTON.

Stimulation of sugar-regulating mechanism as shown by duplicate blood-sugar curves. W. G. LENNOX and M. BELLINGER (J. Biol. Chem., 1927, **73**, 237—249).—The total hyperglycæmic reaction following administration of dextrose was determined by measuring the area enclosed by the curve of the blood-sugar variation and the base line of the normal sugar concentration. When two successive doses of dextrose were given by mouth at intervals of 20 min. to 2 hrs., the magnitude of the second reaction was inversely proportional to the dose of sugar; when the latter was administered intravenously, the absolute magnitude of the first reaction, and both the absolute and relative magnitudes of the second reaction, were much greater. C. R. HARINGTON.

Acid rigor of glycogen-containing and alkaline (exhaustion) rigor of glycogen-poor muscles. L. WACKER (Biochem. Z., 1927, **184**, 192—215).—The state of nutrition of the muscles at the moment of death determines the processes causing rigor, muscles rich in glycogen yielding an acid rigor, due to the formation of considerable amounts of lactic acid, and muscle poor in glycogen an alkaline rigor. Alkaline rigor can be produced by first removing glycogen

by hunger, insulin, or by repeated small doses of strychnine. The different behaviour of red and white muscle is confirmed, white muscle, which possesses greater buffering power, yielding, 24 hrs. after death, 0·7% of lactic acid, and red only 0·53%. In the most extreme case of alkaline rigor, white muscle gave only 0·043%, and red 0·046% of lactic acid. Exhaustion rigor appears in rabbits within a few minutes and acid rigor after several hours. Considerable amounts of ionised protein remain during alkaline rigor (6—7%), but in acid rigor there is but little remaining. P. W. CLUTTERBUCK.

Effect of hydrogen-ion concentration on smooth muscle. B. A. MCSWINEY and W. H. NEWTON (J. Physiol., 1927, **63**, 51—60).—Increasing the hydrogen-ion concentration from p_H 7·5 leads to relaxation of smooth muscle followed by contraction beyond about p_H 5·9 and by relaxation again about p_H 2·1. Increasing alkalinity causes contraction, succeeded, at p_H 11·5, by relaxation. R. K. CANNAN.

Hydrogen-ion concentration of muscles of the cat. K. FURUSAWA and P. M. T. KERRIDGE (J. Physiol., 1927, **63**, 33—41).—The glass electrode has been employed to determine the p_H of skeletal, cardiac, and uterine muscle of the cat under nearly resting conditions, and that of skeletal and cardiac muscle after electrical stimulation and in rigor mortis. Titration curves of minced skeletal and cardiac muscle are reported. R. K. CANNAN.

Ammonia in muscle and its relation to function. I. J. K. PARNAS and W. MOZOLOWSKI (Biochem. Z., 1927, **184**, 399—441).—Maceration of vertebrate muscle in water or physiological salt solution leads to the traumatic formation of about 5 mg. of ammonia per 100 g. of muscle. A borate solution at p_H 9·3 prevents this. A method is described for the determination of ammonia in muscle- and other tissues. This traumatic production of ammonia is most prominent in skeletal muscle, less in cardiac muscle, and is not found in gland-tissues. In frog muscle, it is complete in 90 sec. By extraction with the alkaline borate solution, the ammonia precursor and some enzyme are removed, and may be activated by neutralisation. Most of the enzyme is left behind in the residue. The process is unaffected by absence of oxygen. Heat, caffeine, and chloroform rigors have a similar effect to the mechanical disintegration of the tissue. Ammonia accumulates in the intact muscle after isolation from the animal. This is more intense in the muscle of warm- than of cold-blooded animals. The process does not depend on the presence or absence of oxygen, but fatigue (electrical stimulation or strychnine) produces ammonia in the intact muscle. The urea of the muscle does not change with the ammonia. The formation of ammonia in muscle is connected with muscular activity. R. K. CANNAN.

Effect of products of hydrolysis of protein on metabolism. I. Fraction extracted by and precipitated in butyl alcohol. II. Effects of individual amino-acids. D. RAPPORT and H. H. BEARD (J. Biol. Chem., 1927, **73**, 285—298, 299—319).—I. The fraction of the amino-acids, resulting from the acid hydrolysis of gelatin and caseinogen, which is extracted by butyl alcohol and separates spontaneously from the solvent (cf. Dakin, A., 1919, i, 150), has a specific dynamic effect which is proportional to the amount injected, and is greater, per g. of nitrogen, than that of the original protein, this difference being more marked in the case of caseinogen. Administration of the amino-acid fraction together with the protein results in an additive specific dynamic action; the amino-acid fraction does not neutralise the specific dynamic effect of glycine administered simultaneously, thus differing from the proteins themselves and the complete mixture of hydrolytic products (this vol., 170).

II. The specific dynamic action of valine is nil; that of phenylalanine is greater than that of glycine, whilst tyrosine is approximately equivalent to alanine; the sum of the effects of the glycine, alanine, leucine, tyrosine, and phenylalanine accounts for the whole of the effect of the above-described amino-acid fraction from gelatin and caseinogen, the greater effect of the caseinogen fraction being due to its high content of phenylalanine. The specific dynamic effects of other proteins, however, cannot be calculated from their content of these amino-acids. From the above results, it appears that the specific dynamic effect of an amino-acid is proportional neither to its nitrogen content nor to its power of raising the amino-nitrogen concentration in the blood.

C. R. HARINGTON.

Nitrogenous metabolism in the puerperium. V. J. HARDING and R. C. MONTGOMERY (J. *Biol.* Chem., 1927, **73**, 27—40).—All attempts to check the process of involution of the uterus, by administration of high-calorie, high-carbohydrate diets during the puerperium, failed. Negative nitrogen balances, despite the adequate nitrogen intake, were observed in all cases save one, in which lactation was suppressed. It is thought, therefore, that the loss of nitrogen which occurs in the normal puerperium is associated with the initiation of lactation rather than with involution of the uterus. This conclusion is supported by observations of the creatine excretion, which is very much greater in the lactating than in the non-lactating puerperium. C. R. HARINGTON.

Chemistry of menstruation. K. KLAUS (Biochem. Z., 1927, **185**, 3—10).—Whilst choline could not be isolated from menstrual blood, trimethylamine and possibly traces of methylamine were obtained from this source. It is thought, therefore, that the choline previously shown to be present in the blood of women during menstruation (A., 1926, 195) is excreted through the uterus and broken down by the action of the vaginal flora. C. R. HARINGTON.

Fate of anthranilic acid in the animal body. K. MITSUBA and K. ICHIHARA (Z. physiol. Chem., 1927, **164**, 244—254).—No kynurenic acid is observed in the urine of animals injected subcutaneously with anthranilic acid, the latter being converted to a small extent into *o*-carbaminobenzoic acid. The urine of the treated animals is strongly lævorotatory and has reducing properties, both being probably due to a new conjugated glycuronic acid. *m*- and *p*-Aminobenzoic acids do not couple with glycuronic acid in the animal body. C. HOLLINS.

Formation of hippuric acid in the animal organism. M. SEKINE (Z. physiol. Chem., 1927, **164**, 226—235).—It is shown that, contrary to general belief, the formation of hippuric acid from phenylalanine is not exclusively due to protein fermentation in the intestine, but can take place in the tissues without participation by the intestinal bacteria. The conversion also takes place in the surviving kidney. Hippuric acid formation is not observed after subcutaneous injection of phenylpyruvic or phenyl-lactic acid, nor by perfusion of dog's kidney with phenylpyruvic acid. It is suggested that hippuric acid is formed by way of cinnamic acid and benzoic acid.

C. HOLLINS.

Fat and lipin metabolism. I. Alimentary lipæmia. II. Alimentary cholesterolæmia. III. Alimentary lecithinæmia. S. LEITES (Biochem. Z., 1927, **184**, 273—299, 300—309, 310—317).—I. Changes in the concentrations in the blood of neutral fat, cholesterol, and phosphatides have been determined at intervals after the oral administration of olive oil and oleic acid to dogs. Emphasis is laid on the increase in cholesterol. From comparisons of the arterial and venous blood of various organs, it is concluded that cholesterol is concerned with the functions of the liver, spleen, and lungs in fat metabolism.

II. When cholesterol is fed with olive oil, the changes in the blood and bile are similar to those when olive oil is alone fed. The cholesterol is withdrawn from circulation chiefly by the lungs.

III. The increase in phosphatides of the blood and the differences between the arterial and venous blood of various organs after feeding lecithin are no greater than when olive oil, oleic acid, or cholesterol is fed. An increase in cholesterol and in neutral fat occurs. The results confirm the conclusion that the lungs have a function in the preliminary metabolism of fats and cholesterol.

R. K. CANNAN.

Physicochemical explanation of normal bone formation, production of crystalline deposits in illness, and of influence of alkalis on assimilation. N. R. DHAR (Z. anorg. Chem., 1927, **162**, 243—250; cf. A., 1926, 426).—It is suggested that normal bone formation is effected by the adsorption and coagulation of colloidal calcium phosphate and carbonate present in the body-fluids by the same salts already present in the cartilage in the semi-solid state, the process going on continuously. In old age, the bones become thin and porous, probably because the hydrogen-ion concentration of the body-fluids increases, and also the amount of water decreases, so that the concentration of the peptising agents present is increased. Dead tissue and foreign substances may act as nuclei for the adsorption and coagulation of sols of various less soluble substances, such as uric acid. The initial formation of such deposits may be ascribed to the dilution of the peptising agents present by excess of water. Alkalis promote assimilation, and may therefore be of use in remedying certain states due to defective assimilation. e stabilising action of the citrate ion on milk and oo is probably to be attributed to its increasing charge of the colloid particles.

R. CUTHILL.

Lactose and calcium–phosphorus balance in dogs. E. G. GROSS (Amer. J. Physiol., 1927, **80**, 661—667).—A lactose diet reduced the ammonia excretion and increased the calcium excretion of normal dogs. In parathyroidectomised dogs, lactose prevented the retention of phosphorus and calcium.

R. K. CANNAN.

Diet and calcium assimilation. X. Influence of ultra-violet light on calcium and phosphorus metabolism in milking cows. E. B. HART, H. STEENBOCK, H. SCOTT, and G. C. HUMPHREY (J. Biol. Chem., 1927, **73**, 59—68).—Neither the calcium and phosphorus metabolism nor the production of milk in milking cows is significantly affected by exposure of the animals to ultra-violet light. The difference between this result and that previously obtained for goats (A., 1925, i, 108) is ascribed to the fact that the cow obtains most of its vitamin-*D* from the food.

C. R. HARINGTON.

Influence of renal function on concentration of sulphur compounds in blood. Effect of administration of sulphur on concentration of sulphur compounds in blood and urine. W. DENIS and L. REED (J. Biol. Chem., 1927, **73**, 41—50, 51—57).—The effect of uranium nephritis on the sulphur compounds of the blood varies with the nature of the renal lesion produced. When diuresis results, whether or not the non-protein nitrogen be increased, the total sulphates are markedly and the neutral sulphur slightly reduced; when anuria results from large doses of uranium, the concentration of all sulphur compounds in the blood rises. Oral administration of 0·5 g. of sulphur per kg. to dogs resulted in an increase in all sulphur compounds of blood and urine, which, however, accounted for only 10% of the sulphur ingested. The increase was most marked in the inorganic sulphates. It is probable, therefore, that the sulphur was absorbed in the form of hydrogen sulphide, produced by bacterial action in the intestine, and that this was largely oxidised in the body to sulphate.

C. R. HARINGTON.

Sulphur metabolism of the dog. V. Toxic action of mercapturic acids. E. H. CALLOW and T. S. HELE (Biochem. J., 1927, **21**, 606—610).—*p*-Bromo- and *p*-chloro-phenylmercapturic acids, whether given by the mouth or subcutaneously, cause transient hæmoglobinuria in the dog. There is a minimum dose required to produce this effect. There is no evidence of any conversion of mercapturic acids into ethereal sulphates in the dog.

S. S. ZILVA.

Sulphur metabolism of the dog. VI. Metabolism of the pig and dog compared. H. I. COOMBS and T. S. HELE (Biochem. J., 1927, **21**, 611—622).—Ethereal sulphates are less readily formed in the pig than in the dog on the administration of phenolic substances. The balance of the phenols is probably excreted in combination with glycuronic acid. As in the dog, there is also no rise in the neutral sulphur. No mercapturic acids could be isolated after the administration of monohalogenbenzenes to the pig, nor was there any evidence of conversion of mercapturic acids into ethereal sulphates. Mercapturic acids in doses three times the toxic dose for the dog

per kg. body-weight do not produce hæmoglobinuria in the pig (see preceding abstract). S. S. Zilva.

Sulphur metabolism of the dog. VII. Effect of fluorobenzene on sulphur metabolism. H. I. Coombs (Biochem. J., 1927, **21**, 623—624).—Oral administration of fluorobenzene raises the output of neutral sulphur in the dog only to a small extent. The administration of benzene produces an increase of the same order. S. S. Zilva.

Micrurgical studies in cell physiology. III. Action of carbon dioxide and some salts of sodium, calcium, and potassium on the protoplasm of *Amœba dubia*. P. Reznikoff and R. Chambers (J. Gen. Physiol., 1927, **10**, 731—738).—The toxicity of various salts to *Amœba dubia* is primarily determined by their cations, but modifying effects of the anions have been detected by the micrurgical technique. W. O. Kermack.

Micrurgical studies in cell physiology. IV. Colorimetric determination of the nuclear and cytoplasmic p_H in the starfish egg. R. Chambers and H. Pollack (J. Gen. Physiol., 1927, **10**, 739—755).—Normal cytoplasm of living echinoderm eggs has p_H between 6·6 and 6·8, but after injury it becomes more acid. The intranuclear p_H of the immature *Asterias* egg is 7·5+0·1. W. O. Kermack.

Effect of salt concentration of the medium on the rate of osmosis of water through the membrane of living cells. B. Lucke and M. McCutcheon (J. Gen. Physiol., 1927, **10**, 665—670).—Experiments on the rate of diffusion of water through the membrane of the unfertilised egg of the sea urchin (*Arbacia*) in solutions of sea-water of various strengths, indicate that the permeability of the membrane to water is greater when the osmotic pressure of the medium is high than when it is low. W. O. Kermack.

Activation of starfish eggs by acids. II. Action of substituted benzoic acids and of benzoic and salicylic acids as influenced by their salts. R. S. Lillie (J. Gen. Physiol., 1927, **10**, 703—723).—The activation of unfertilised starfish eggs by a suitable organic acid is greater in presence of the sodium salt of that acid, although in an unbuffered medium the effect is usually dependent on the p_H alone. The experimental facts are consistent with the view that the cell membrane is permeable only to the undissociated acid, which after penetration dissociates and thus activates the cell. W. O. Kermack.

Preparation of sepiamelanin from sepiamelanic acid. O. Adler (Biochem. Z., 1927, **185**, 169—172).—Sepiamelanic acid had similar physiological effects to those described for tyrosine-melanic acid (A., 1923, i, 1218), but was more powerful in its action. On heating for 2 hrs. at 270°, it was converted into sepiamelanin. C. R. Harington.

Physiology of the spleen. K. Mitsuba (Z. physiol. Chem., 1927, **164**, 236—243).—For at least some time after extirpation of the spleen the quantity of conjugated sulphuric and glycuronic acids in the urine increases. The increase bears no relation to the anæmia which follows the operation. It is probable that the spleen has a destructive action on various poisons. It also plays an important role in the formation of urochrome pigments from tryptophan in the animal organism. C. Hollins.

Action of choline on the animal organism and its relation to creatine. E. Abderhalden and S. Buadze (Z. physiol. Chem., 1927, **164**, 280—305).—Choline may be administered to animals *per os* or subcutaneously in considerable doses (up to one third of the lethal dose) without serious effects. It is shown that this is not due to destruction of the base in the intestinal canal nor to deficient resorption. The increased creatinine excretion in the urine of dogs treated with choline (Riesser, A., 1914, i, 632) is confirmed. Riesser's view, that choline after partial demethylation combines with carbamide to form creatine, is supported by the increase in creatine or creatinine in brain or muscle preparations treated with liver preparation, containing arginase, after addition of arginine, and choline. It is possible that creatine is a stage in the metabolism of choline, and especially that muscle- and probably nerve-tissues remove choline by conversion into creatine. The process may be reversible. The conversion of serine into creatine by way of hydroxyethylamine and choline seems probable. C. Hollins.

Preparation and pharmacological action of triacetylpyrogallol-*o*-carboxylic acid. S. Frankel (Biochem. Z., 1927, **184**, 383—384).—Pyrogallol was converted into its carboxylic *acid* by heating with sodium hydrogen carbonate and water, and acidifying the solution; by treatment with acetic anhydride, this was converted into *triacetylpyrogallol-o-carboxylic acid*, m. p. 164°. The antipyretic and narcotic actions of this substance were less than those of aspirin. R. K. Cannan.

Preparation of the sodium salts of the higher unsaturated acids of cod-liver oil. B. I. Slovzov and P. P. Astanin (Arch. biol. nauk, 1924, **24**, 73—75).—The calcium soaps of the acids of cod-liver oil were pressed, mixed with plaster of Paris, and extracted for several days at 10° with benzene containing 5% of ethyl alcohol, in which calcium oleate is relatively insoluble. These soaps yielded fats of high iodine value (150—183) which may be used therapeutically as substitutes for chaulmoogra oil derivatives. Chemical Abstracts.

Nomenclature of ferments. I. A. Smorodincev (J. Russ. Phys. Chem. Soc., 1926, **58**, 897—902).—The author proposes to use the term "ferment" only, since there is now no distinction made between organised ferments and unorganised ferments. The following reactions due to ferments are recognised, and names are proposed for each kind of ferment. *A*. Hydrolyses: (i) of ethers and carbohydrates—gycidase: (ii) of esters—lipidase: (iii) Protein ferments—protedase. *B*. Oxidative and reducing ferments. *C*. Coagulating ferments. *D*. Ferments which hydrolyse with evolution of carbon dioxide. E. Rothstein.

Enzyme specificity. H. von Euler and K. Josephson (Z. physiol. Chem., 1927, **166**, 294—317).—Mainly theoretical. The presence of a third sub-

stance besides enzyme and substrate may partly inhibit enzymic activity in two ways: (*a*) there may be combination between the enzyme and the inhibitory substance which leads to a diminution in the amount of the active enzyme, (*b*) the rate of breakdown of the enzyme–substrate complex to the final products of hydrolysis may be slowed. The criteria for the existence of these two types of inhibition are discussed in the light of recent work of Euler, Josephson, Kuhn and Munch, and others on the hydrolysis of sucrose and raffinose by invertase. The experimental results when α-glucose is the inhibitory substance appear to be due to the superposition of two kinds of inhibition phenomena.

It is suggested that in the hydrolysis of sucrose two successive intermediate invertase–sucrose complexes occur. In the first, the combination between enzyme and substrate is through the lævulose half of the sucrose molecule, whilst in the second, and extremely labile, complex both halves of the disaccharide molecule are bound to the enzyme. The affinity of intestinal ereptase for glycine and glycylglycine is through the amino-group in each case. Enolisation and the formation of a second linking between the peptidase molecule and the substrate may precede actual hydrolysis of the dipeptide.

A comparison is made between the relative hydrolytic activity of pure invertase and of hydrochloric acid toward sucrose. H. D. Kay.

Influence of starch injection on blood amylase. M. Magaram and W. Engelhardt (Biochem. Z., 1927, **182**, 215—219).—The amylase content of normal rabbit's blood varies during the day and from day to day in a manner which bears no relationship to the nutritive conditions. Following single or repeated starch injections, no regular variations in the amylase value are observed either on the day of injection or on subsequent days. J. Pryde.

Activation of pancreatic lipase. K. M. Buikov and D. S. Fursikov (Arkh. Biol. Naouk, 1925, **25**, 21—26).—Bile has no effect on the digestion of olive or cod-liver oil by lipase. The activity of the lipase is enhanced by the addition of ethyl alcohol, or, to a smaller extent, by ethyl ether, chloroform, acetone, or carbon disulphide. The effect is not universal, and it is hence considered that the activating agent must react with the enzyme as well as with the substrate. It is not necessary to assume the existence of specific lipases. Lanolin, which is not attacked by pancreatic lipase, is digested on addition of carbon disulphide; acetone entirely inhibits the decomposition of lanolin. Chemical Abstracts.

Enzymes of hexose fission and their range of action. I. H. von Euler, R. Nilsson, and T. Lovgren (Z. physiol. Chem., 1927, **166**, 91—102).—The enzymic action of extracts of rabbit muscle, alone and with addition of insulin, adrenaline, and co-zymase, is followed by determinations of glycogen, dextrose, and lactic acid, and of methylene-blue reduction. The differences between glycogen lost and the sum of the dextrose and lactic acid formed (calculated as glycogen) are noted. C. Hollins.

Enzymic formation of lactic acid in muscle extract. IV. Hexosemonophosphates. O. Meyerhof and K. Lohmann (Biochem. Z., 1927, **185**, 113—164).—In their chemical behaviour, the hexosemonophosphates at present known fall into two groups: the compounds obtained from natural sources (cf. Robison, A., 1923, i, 86; Neuberg, A., 1918, i, 423) and those obtained synthetically (cf. Nodzu, A., 1925, i, 515; Neuberg and Hatano, A., 1926, 941). The natural compounds have a greater reducing value (approximately equivalent to that of dextrose), and are much more readily spontaneously oxidised in phosphate solution than the synthetic compounds. The hexosephosphate of Robison shows a higher aldose value by the method of Willstatter and Schudel (A., 1918, ii, 337), and is less readily oxidised in phosphate solution than that of Neuberg; it probably contains, therefore, a higher proportion of dextrose than the latter. The compound of Robison has pk_1 0·94, pk_2 6·11; that of Neuberg pk_1 0·97, pk_2 6·11; the synthetic hexosephosphate of Hatano, pk_1 0·61, pk_2 5·83; that of Nodzu, pk_1 0·84, pk_2 5·67. Muscle extract is almost without effect on the synthetic hexosephosphates; the natural compounds, however, undergo a transformation similar to that observed for the polysaccharides and fermentable hexoses (this vol., 75), there being at first a rapid formation of lactic acid and equivalent disappearance of inorganic phosphate, followed by slower production of lactic acid parallel with reappearance of phosphate. The reaction demands the presence of co-ferment and exhibits the same relationships to fluorides and arsenate as in the previous cases. Similar results were again obtained on submitting the natural hexosemonophosphates to yeast fermentation. It is therefore very probable that a hexosemonophosphate is an intermediate stage in the enzymic degradation of carbohydrate by muscle extract or by yeast. C. R. Harington.

Co-zymase. X. H. von Euler, R. Nilsson, and B. Jansson (Z. physiol. Chem., 1927, **163**, 202—218; cf. this vol., 77. 279).—Experiments on the decolorisation of methylene-blue by preparations of washed and unwashed, fresh and dried frog and rat muscle, in presence or absence of added sodium succinate or zymophosphate, show that drying usually activates the reductase, and in every case the washed muscle preparations are activated both by sodium succinate and by zymophosphate. The extract made by rubbing muscle with sand and water reduces methylene-blue when similarly activated; it both produces and consumes lactic acid, and exchange of phosphorus occurs. The ratio of co-zymase in blood to that in muscle is found to be 1 : 15.

Washed dried bottom-yeast is unable to ferment zymophosphate in the absence of added co-zymase.

The identity of co-zymase with co-reductase (Batelli and Stern's "pnein," Meyerhof's "respiratory body") is confirmed, and the ratio of the co-zymase contents of muscle extract and yeast extract is found to be about 0·04 : 1.

The bearing of these results on the mode of action of insulin is discussed. C. Hollins.

Effect of *X*-rays on autolysis and proteolysis. R. Herzger (Biochem. Z., 1927, **184**, 341—358).—The autolysis of the liver and lungs of *X*-irradiated

guinea-pigs is 50—60% greater than that of the tissues of normal animals, although direct irradiation of the minced organs *in vitro* is without effect. Increased proteolysis of peptone by the tissues of the irradiated animals is also observed.

R. K. CANNAN.

Characterisation of pepsin action. III. H. STEUDEL and J. ELLINGHAUS (Z. physiol. Chem., 1927, **166**, 84—90; cf. A., 1926, 866; Waldschmidt-Leitz and Simons, A., 1926, 1049).—Repetition of fermentation experiments with caseinogen, edestin, and gelatin confirms results previously reported; the ratio of new carboxyl groups to new amino-groups liberated during the action of the enzyme is not 1 : 1 (Waldschmidt-Leitz and Simons), but varies from 2 : 1 to 6 : 1, and in the case of gelatin reaches 48 : 1 in 2 hrs., becoming 5·3 : 1 in 4 hrs. and 5·5 : 1 in 24 hrs. No measurable quantity of new carboxyl groups results from the action of pepsin on histone, although new amino-groups are liberated.

C. HOLLINS.

Effect of halogen salts on peptic digestion. W. M. CLIFFORD (Biochem. J., 1927, **21**, 544—548).—Clotting of milk by pepsin is hastened by sodium, potassium, and ammonium chlorides and bromides, the optimum concentration lying between 0·07 and 0·018*M*. The ammonium salts have the strongest effect. The iodides and fluorides of the above cations either retard or inhibit the clotting action of the enzyme. This retarding action of the salts is also a function of concentration. The effect of ammonium iodide is very weak compared with that of sodium iodide. The ammonium radical favours coagulation by pepsin. In presence of magnesium, calcium, and barium halides, there is a great increase in the rate of coagulation of milk by pepsin. The action is weakest with magnesium salts.

S. S. ZILVA.

Trypsin and enterokinase. E. WALDSCHMIDT-LEITZ and K. LINDERSTROM-LANG (Z. physiol. Chem., 1927, **166**, 227—240).—The adsorption relationships of the three substances concerned—trypsin (=trypsinogen), enterokinase, and trypsin-kinase—have been studied. Trypsin and trypsin-kinase adsorbed on aluminium hydroxide are still enzymically active. Enterokinase, on the other hand, loses its activity by adsorption on the same agent, *i.e.*, is rendered incapable of combining with, and so activating, trypsin. Trypsin and trypsin-kinase are adsorbed in a quantitatively similar way by the same concentration of aluminium hydroxide. The specificity of the two enzymes remains the same after adsorption, since the enterokinase portion of the activated trypsin molecule which is responsible for the difference in the specific action of the two proteases, *i.e.*, has to do with the formation of the trypsin–substrate complex, is not concerned directly in the adsorption linking. When enterokinase itself is adsorbed, as on aluminium hydroxide or on caseinogen, either the specific trypsin- or the protein-binding group of the activator is taken up by the adsorbent, so that the adsorption complex cannot be other than inactive.

H. D. KAY.

Preparation of trypsin free from enterokinase. E. WALDSCHMIDT-LEITZ and K. LINDERSTRÖM-LANG (Z. physiol. Chem., 1927, **166**, 241—246).—Trypsin-kinase, but not (inactive) trypsin, is specifically adsorbed by caseinogen. A pure trypsin preparation may be obtained from the extract of dried pancreas (which contains erepsin and activated trypsin in addition to trypsin itself) by adding a solution of caseinogen to the extract and precipitating the protein, together with adsorbed trypsin-kinase, by adding a suitable quantity of acetic acid. The same process is repeated twice on the filtrate, to ensure quantitative removal of the activated enzyme. The trypsin in the final filtrate is then freed from erepsin by the method of Waldschmidt-Leitz and Harteneck (A., 1925, i, 1360).

H. D. KAY.

Enzymic activity of pancreatic and intestinal secretions. E. WALDSCHMIDT-LEITZ and J. WALDSCHMIDT-GRASER (Z. physiol. Chem., 1927, **166**, 247—261).—Most of the recent work on the specificity of the pancreatic enzymes has been carried out on extracts of dried pancreas. The present work deals with the enzymes in normal pancreatic juice (fistula dogs). Pancreatic juice is, enzymically, qualitatively similar to extracts of the dried gland, but the enzyme concentration in the secretion is about one fifth to one tenth that in the extract. Moreover, the ratio enzymic : non-enzymic material is less in the secretion than in the extract for lipase, amylase, and erepsin, but greater for trypsin. For purposes of investigation, the extract of the dried gland is more useful, on the whole, than the natural secretion.

Pancreatic and intestinal erepsin are identical. The secretion of an isolated loop of small intestine, months after the operation, still contains appreciable quantities of erepsin, although neither trypsin nor enterokinase is present. After pancreatectomy, the enterokinase content of the intestinal mucosa diminishes in a few days to a very low figure. The presence of enterokinase depends on the supply of pancreatic juice. The juice contains the inactive precursor, which is transformed into the active "kinase" in the cells of the gut wall.

H. D. KAY.

Enzymic hydrolysis of protamines. E. WALDSCHMIDT-LEITZ and T. KOLLMAN (Z. physiol. Chem., 1927, **166**, 262—267).—The hydrolysability of the four protamines clupeine, salmine, scombrine, and sturine by the purified proteases trypsin (=trypsinogen), trypsin-kinase (=activated trypsin), erepsin, papain, and papain–hydrogen cyanide has been studied. Trypsin-kinase is most active, then papain–hydrogen cyanide, both enzymes attacking all four protamines. Erepsin and papain are entirely without action, but trypsin brings about partial hydrolysis of the first three proteins. Clupeine and salmine succumb very similarly to enzymic attack, scombrine is intermediate, whilst sturine is the most resistant. There is a correlation in this group of proteins between decreasing ease of hydrolysis and decreasing proline content.

H. D. KAY.

Tryptic digestion. IV. R. EHRENBERG (Biochem. Z., 1927, **184**, 90—104).—The method of free diffusion from tryptic digests is used to study the course of proteolysis and of the changes in activity of the enzyme. Using trypsin and a 1—2% solution of caseinogen there is at first an apparent increase in concentration of enzyme. The diffusibility of the

enzyme decreases initially, then increases, and finally exceeds the original value. With higher concentration of caseinogen, the changes are the same, but are relatively smaller, owing to increased formation of inhibiting material from the substrate (cf. A., 1925, i, 103, 202; 1926, 203). P. W. CLUTTERBUCK.

Trypsin. S. KOLODZIEJSKA and C. FUNK (Biochem. Z., 1927, **182**, 264—272).—Treatment of trypsin solutions with picric acid yields active precipitates from which the trypsin may be regenerated by means of nitron. The picric acid precipitate may be fractionated with acetone or by conversion into the sodium or barium salt. Crystalline fractions are obtained which show a definite tryptic activity. Estimated on an activity basis, the picric acid precipitation gives a trypsin preparation some 50—80 times as pure as the original. J. PRYDE.

Inhibitory action of fatty acids, particularly the unsaturated acids, on enzymic action. L. VELLUZ (Bull. Soc. Chim. biol., 1927, **9**, 483—500).—The formation of a film of fatty acid on the surface of pepsin or urease diminishes the activity of the enzyme, but a film of soap has no influence on the action of trypsin or urease. If the fatty acids are adsorbed on some other colloid, such as gum-arabic, or if acids soluble in water are used, no inhibition of the action of pepsin occurs. With low concentrations of fatty acid relative to the amount of pepsin or urease, the inhibition increases with increasing concentration of fatty acid, and the unsaturated acids have a more marked effect than the corresponding saturated acids. With large amounts of fatty acid, there is no difference between the inhibitory effects of saturated and unsaturated acids on the activity of pepsin; with urease, the saturated acids have the greater effect, this being attributed to the greater complexity of the mechanism of urease action. The factors concerned in this case are the spreading power of the fatty acid, which partly determines the thickness of the film, and the osmotic pressure of the external solution. It is suggested that similar complexes of enzymes with soaps or fatty acids may be concerned in the *in vivo* regulation of enzymic reactions, and that activation or inhibition results when the p_H becomes greater or less than 7, respectively. A. WORMALL.

Oxidations by hydrogen peroxide in presence of sulphydryl compounds. D. C. HARRISON (Biochem J., 1927, **21**, 507—511).—The presence of sulphydryl compounds does not prevent the oxidation of sodium nitrite when hydrogen peroxide is slowly added in presence of peroxydase (cf. Szent-Gyorgyi, this vol., 76). S. S. ZILVA.

Preparation and properties of plant perhydridases. D. MICHLIN (Biochem. Z., 1927, **185**, 222).—By extraction of potatoes with water and treatment of the filtered extract with acetone, the perhydridase is precipitated; the precipitate may be filtered off, freed from water by washing with acetone, and preserved in the anhydrous condition under light petroleum. The activity of the preparation is determined by its capacity to reduce nitrate to nitrite in presence of aldehydes. Purine bases cannot take the place of the aldehyde as oxygen acceptor, nor can the enzyme reduce methylene-blue in presence of aldehydes or purines; it is therefore apparently not identical with the Schardinger enzyme of milk. C. R. HARINGTON.

Possible significance of hexosephosphoric esters in ossification. VII. Bone phosphatase. M. MARTLAND and R. ROBISON (Biochem. J., 1927, **21**, 665—674; cf. A., 1924, i, 462).—The activity of the bone phosphatase increases with the alkalinity up to p_H 9·4, but above 8·4 this is offset by the gradual inactivation of the enzyme. In the body, the optimum p_H may therefore be about 8·4. The activity–p_H curve has the form of the dissociation curve of a weak acid, p_K about 8·2, or the dissociation-residue curve of a weak base. Variations in the concentration of the substrate between 0·003 and 0·3 *M* do not affect the initial rate of hydrolysis. The rate of hydrolysis of glycerophosphoric ester is greatly retarded by inorganic phosphate even in low concentrations, but is not appreciably affected by similar concentrations of the second hydrolysis product—glycerol. In high concentrations of glycerol and in presence of inorganic phosphate, synthesis of phosphoric ester takes place, as much as 25% of the inorganic phosphate being esterified under certain conditions. The synthetic action of the enzyme has likewise been demonstrated with mannitol, glycol, dextrose, and lævulose. No effect on the rate of hydrolysis or the optimum p_H of the enzyme has been detected as a result of adding adrenaline, pituitrin, or thyroid. S. S. ZILVA.

Tannase. II. K. FREUDENBERG, F. BLUMMEL, and T. FRANK (Z. physical. Chem., 1927, **164**, 262—270; cf. Freudenberg and Vollbrecht, A., 1922, i, 285).—An improved method of preparing tannase is described. The hydrolysis of methyl gallate by tannase, using strontium gallate as buffer salt, is followed by electrometric determinations of p_H, and is shown to proceed more quickly in the less acid solutions. C. HOLLINS.

Iodometric determination of tyrosinase. H. HAEHN and J. STERN (Biochem. Z., 1927, **184**, 182—186).—The method of Raper and Wormall (A., 1923, i, 1146) for the determination of tyrosinase is modified, the pigments being precipitated by use of barium chloride in alkaline solution (instead of by keeping for 2 days in acid solution), the tryosine in the clear filtrate being determined as in the original method. The method is then very much quicker, and gives the same results. P. W. CLUTTERBUCK.

Uricase. H. O. CALVERY (J. Biol. Chem., 1927. **73**, 77—80).—The author agrees with Spiers (A., 1915, i, 1028) in being unable to confirm the results of Ascoli and Izar (A., 1909, ii, 909) on the anaerobic synthesis of uric acid by uricase. The enzyme is destroyed by exposure to high concentrations of carbon dioxide for some days. C. R. HARINGTON.

Growth of yeast. IV. Nephelometric method of counting yeast suspensions. G. L. PESKETT (Biochem. J., 1927, **21**, 460—466).—The method is based on the principle of comparing the suspensions of the yeast against standard suspensions of barium sulphate; the tubes receive equal illumination and

are compared against a dark background. There is a direct relationship between the number of cells present per c.c. and the concentration of the barium sulphate suspension, and the number of cells can therefore be calculated from a graph. Such graphs are given for two species of yeast. In one case, the maximum error of any single observation is 17%, whilst over the greater part of the graph the error is only about 3%. The corresponding figures for the other species are 21% and 7%, respectively. Determinations in growing cultures can be made by this method without risk of contamination. S. S. ZILVA.

Utilisation of pentoses by yeasts, and the composition of plant gums. O. D. ABBOTT (Missouri Agric. Exp. Sta. Res. Bull., 1926, **85**, 1—29).—Various yeasts and related organisms destroy pentoses in mineral nutrient solutions; media more acid than p_H 5·0 interfere with the process. Traces of carbon dioxide, alcohol, a non-volatile acid, and, in some cases, probably glyceraldehyde or glycollaldehyde are formed. Galactose is as resistant as the pentoses to the yeasts in Fleischmann's yeast-cake. Orange gum, $(C_{30}H_{44}O_{22})n$, is completely hydrolysed by taka-diastase. CHEMICAL ABSTRACTS.

Fermentative transformation of benzoylmethylcarbinol by yeast. C. NEUBERG and W. KOMAREVSKY (Biochem. Z., 1927, **182**, 285—290).—Inactive benzoylmethylcarbinol is converted in presence of top yeasts and sugar into lævorotatory β-phenyl-α-methyl ethylene glycol. J. PRYDE.

Hexosemonophosphoric acid obtained from yeast fermentation. C. NEUBERG and J. LEIBOWITZ (Biochem. Z., 1927, **184**, 489—507).—Robison's method of isolation has been modified. The brew is neutralised to phenolphthalein and the proteins are coagulated by heat. After filtration, calcium or barium acetate is added to remove all the hexosediphosphoric ester, and the filtrate precipitated with basic lead acetate. Further purification involves alternate precipitation as the barium and the lead salt. From a fermentation of 200 g. of sucrose, 60 g. of the barium salt were obtained. A crystalline brucine salt is formed from which the barium salt may be recovered unchanged in rotation ($[\alpha]_D$ +24·2—24·7° for the free acid). The copper-reducing power of the free acid is 60—68% of that of dextrose. After hydrolysis of the ester with taka-diastase, determination of the reducing power by the iodine method gave results 15% below those of the copper method. The polarimetric findings, however, did not allow this discrepancy to be explained by assuming the presence of a mixture of 85% dextrose and 15% lævulose. Robison's monophosphoric acid is thought to consist of 80—90% of a homogeneous substance which cannot be hydrolysed without secondary changes occurring in the sugar residue. R. K. CANNAN.

Symmetric and asymmetric cleavage of racemic tyrosine in yeast fermentation and the influence of vitamin-like substances on it. F. EHRLICH (Biochem. Z., 1927, **182**, 245—263).—Yeast in presence of sugar and inorganic salts converts *dl*-tyrosine into tyrosol, the residual tyrosine being optically inactive. On the other hand, if a small amount of malt germ or yeast autolysate be added to the fermentation mixture, the process proceeds asymmetrically, and *d*-tyrosine may be isolated from the residue. Importance is attached to the observation in relation to the possible occurrence of " bios "-like substances in yeast and other plant extracts. J. PRYDE.

Influence of fatty acids and hydroxy-acids and their salts on alcoholic fermentation by living yeast. II. Propionic, butyric, *iso*butyric, glycollic, lactic, hydroxy*iso*butyric, α- and β-hydroxybutyric acids and their sodium salts. H. KATAGIRI (Biochem. J., 1927, **21**, 494—506).—Fermentation by living yeast was observed with various concentrations of these compounds. The simple fatty acids have an inhibiting effect on the rate of fermentation, a hyperbolic relation existing between the rate of fermentation and the concentration of free acid. The specific effect, which is probably due in great measure to the chemical nature of the acid, is nearly as great as that of acetic acid, but very much less than that of formic acid. No specific effect of the hydroxy-acids on the rate of fermentation, as compared with phosphate buffer solutions, was observed, except in the case of glycollic acid, which had a slight inhibiting action, similar to that of the simple fatty acids. Curves showing an optimum p_H value with phosphate buffer solutions of various concentrations are given. As in the case of enzyme action in general, the rates of fermentation at constant concentration of buffer solutions are principally controlled by the p_H value. The optimum p_H and its sharpness depend on the concentration of the phosphate buffer solution. As the concentration diminished, the optimum p_H moved to the alkaline side. The effect of buffer solutions of sodium hydrogen carbonate and carbonic acid is very similar to that of phosphate buffers, the rate of fermentation, however, being more exclusively controlled by the p_H. S. S. ZILVA.

Lactic fermentation. IV. A. I. VIRTANEN, E. WICHMANN, and B. LINDSTROM (Z. physiol. Chem., 1927, **166**, 21—38).—*Str. lactis* and *Bacillus casei* ε convert 94—97% of sucrose into lactic acid, the former (optimum temperature for growth 30°) giving *d*-lactic acid, the latter (optimum 40°) the inactive acid. The effect of variations in p_H, phosphate concentration, and temperature on the fermentation and of p_H temperature on the bacterial growth are investigated. The optimum p_H for the fermentation is about 6·2 for both bacteria. Addition of phosphate up to 1% in both cases greatly accelerates lactic acid formation. The fermentation proceeds most rapidly at 50—51 for *B. casei* ε, and at 30° for *Str. lactis*, the temperature curves being quite different in the two cases. *B. casei* ε does not grow appreciably at 50—51°, and not at all at p_H 7·2, although the rate of fermentation is then 75% of the maximal rate. C. HOLLINS.

Origin of the products of dehydration and polymerisation of β-hydroxybutyric acid. Hydroxybutyric fermentation. M. LEMOIGNE (Bull. Soc. Chim. biol., 1927, **9**, 446—453; cf. A., 1926, 1178).—Fermentation by *Bacillus M*, which appears to be closely related to *B. megatherium* (cf. Ann. Inst.

Pasteur, 1925, 39, 144), results in the production of small quantities of β-hydroxybutyric acid, considerable amounts of a derivative formed by dehydration and polymerisation of this acid, and traces of acetone. These products are obtained at the expense of dextrose, or to a less extent at the expense of proteins, the latter being deaminised in the process. In the autolysis of certain bacteria, the β-hydroxybutyric acid formed is derived from the intracellular reserve of the polymeride, $(C_4H_6O_2)_n$.

A. WORMALL.

Fermentation of sugar by bacilli of the coli-aerogenes group. I. A. I. VIRTANEN and P. E. SIMOLA (Z. physiol. Chem., 1927, **163**, 284—297).—Anaerobic fermentations of dextrose carried out with a variety of *Bacillus coli* from fæces yielded at 20° about 40% of lactic acid and 14% of volatile fatty acids, whilst aerobic fermentations produced about 33% of lactic acid and 21% of volatile acids. The difference between the anaerobic and aerobic results is due, at least partly, to oxidation of previously formed lactic acid in the latter case. A variety of *B. coli* from water gave results showing similar differences between the aerobic and anaerobic fermentations, but the quantities of lactic acid produced were much smaller and those of volatile acids greater. *B. coli* contains co-zymase.

C. HOLLINS.

Precipitation of calcium by micro-organisms. C. NAESLUND (Biochem. Z., 1927, **184**, 1—9).—The precipitation of calcium and the formation of concretions in cultures of living micro-organisms proceed along with the growth of the organisms, and are probably due to decrease in hydrogen-ion concentration.

P. W. CLUTTERBUCK.

Decomposition of illuminating gas and carbon monoxide by bacteria. W. HASEMANN (Biochem. Z., 1927, **184**, 147—171).—Illuminating gas and carbon dioxide are oxidised by bacteria of moist earth containing humus, carbon dioxide being formed. Different types of bacteria specifically attack the different constituents of the coal gas (hydrogen, methane, carbon monoxide). From coal-gas cultures, four strains of bacteria are isolated: first, *Bacillus oligocarbophilus*, Beijerinck and van Delden, which oxidises hydrogen and carbon monoxide, the optimum temperature being 30°; second, *B. methanicus*, Sohngen, which oxidises only methane; third, *B. pantothrophus*, Kaserer, and fourth *B. X* (unknown), which oxidise only hydrogen. The micro-organisms which anaerobically oxidise carbon monoxide to carbon dioxide derive the necessary oxygen by reduction of sulphates.

P. W. CLUTTERBUCK.

Crystalline insulin. J. J. ABEL, E. M. K. GEILING, C. A. ROUILLER, F. K. BELL, and O. WINTERSTEINER (J. Pharm. Exp. Ther., 1927, **31**, 65—85).—When pyridine is added to an acid solution of pure insulin containing brucine acetate, no separation of insulin takes place until the p_H is between 5·55 and 5·65, when the insulin separates in a crystalline condition. With commercial preparations of insulin and similar conditions, the addition of the pyridine causes marked precipitation at p_H less than 5·5, and is precipitate consists mainly of impurities, and contains very little active material. The insulin is not precipitated until the solution is brought to the isoelectric point of insulin—that is, between p_H 5·55 and 5·65—by the addition either of more pyridine or, better, of ammonia, when the insulin gradually separates in a crystalline condition. This observation forms the basis of a simple method for the preparation of crystalline insulin. By working up the pyridine precipitate and the mother-liquors there was obtained, in all, 0·4848 g. of crystalline insulin from 2·001 g. of commercial insulin powder (containing 13 international units per mg.). The role of brucine acetate has not been precisely determined, but it is conjectured that a brucine–insulin complex is formed which remains in solution until the isoelectric point of insulin is reached, when insulin itself separates by virtue of its low solubility at this point. The possibility that the crystals obtained are not really insulin itself, but an inactive compound containing a very small quantity of highly active material adsorbed on their surface is considered and dismissed. The crystalline insulin has an activity probably exceeding 40 international units per mg. It gives the biuret, Pauly, Millon, and ninhydrin reactions, and no tryptophan was detected by colour reactions. The simplest formula corresponding with the analyses is $C_{45}H_{69}O_{14}N_{11}S,3H_2O$ (the water being lost at 105—120°), but the actual formula may be a multiple of this. Solutions of the compound are lævorotatory, but the rotation is dependent on the exact conditions of observation. Crystallographic observations suggest that insulin is dimorphous.

W. O. KERMACK.

Purification and properties of insulin. F. DICKENS, E. C. DODDS, W. LAWSON, and N. F. MACLAGAN (Biochem. J., 1927, **21**, 560—571).—The crude insulin is precipitated with 2% trichloroacetic acid. The precipitate is dissolved in 0·1*N*-hydrochloric acid and brought down again with saturated sodium chloride. After being taken up in water at p_H 4, the solution is run into *M*/8-potassium oxalate and the active principle is finally precipitated. Starting with 10 g. of crude insulin containing 85,000 units, a residue weighing 3·304 g. containing 73,000 units is obtained by this process of fractionation. Qualitative tests on the purified product are described. Analytical results on specimens of insulin of varying degrees of purity are also given.

S. S. ZILVA.

Is insulin inactivated by dextrose? V. DU VIGNEAUD (J. Biol. Chem., 1927, **73**, 275—283).—No definite evidence could be obtained of the destruction of insulin on incubation with dextrose at 39° either in slightly acid or slightly alkaline solution; the addition of traces of iron salts was without effect.

C. R. HARINGTON.

Influence of hexosediphosphoric acid and hexosemonophosphoric acid on insulin hypoglycæmia. H. P. MARKS and W. T. J. MORGAN (Biochem. J., 1927, **21**, 530—532).—These two compounds cannot replace dextrose in the relief of insulin hypoglycæmia.

S. S. ZILVA.

Glycogen content of frog's muscle after injection of insulin and its relation to contraction. J. M. D. OLMSTED and J. M. HARVEY (Amer. J. Physiol., 1927, **80**, 643—648).—Prolonged insulin

convulsions render the muscles of frogs practically free from glycogen (less than 0·02%). Such muscles, on maximal stimulation in the intact animal, contract for hours as effectively as do normal muscles.

R. K. CANNAN.

Lead. XV. Effect of the parathyroid hormone on the excretion of lead and calcium in lead poisoning. D. HUNTER and J. C. AUB (Quart. J. Med., 1927, **20**, 123—140).—There is parallelism between the storage and excretion of calcium and lead. Administration of parathyroid extract caused considerable excretion of calcium and lead from the bones. The blood-calcium showed a variable increase. Calcium lactate in the diet increased the action of parathyroid. Increased excretion of calcium was more marked in the urine than in the fæces.

CHEMICAL ABSTRACTS.

Posterior pituitary extract and cholesterol metabolism. R. C. MOEHLIG and H. B. AINSLEE (Amer. J. Physiol., 1927, **80**, 649—651).—Posterior pituitary extract injected into rabbits for 10 days increased the concentration of cholesterol in the blood.

R. K. CANNAN.

Physiological role of vitamin-*B*. III. Vitamin-*B* deficiency in pigeons. S. K. KON and J. C. DRUMMOND (Biochem. J., 1927, **21**, 632—651).—Many of the characteristic symptoms such as green fæces, ruffled feathers, etc., observed in pigeons fed on diets deficient in vitamin-*B* are due to failure to consume sufficient food to maintain the body-weight. The lack of appetite and the occurrence of acute nervous symptoms are characteristic of vitamin-*B* deficiency. There is no relation between the nervous symptoms and degenerative changes in the nerves. The gradual fall of the body temperature in deficient pigeons is due to partial starvation. The blood-sugar level, the adrenaline content of the adrenals, and the amylopsin activity from the pancreas and intestines are not affected by the vitamin deficiency, nor is there any difference in the utilisation of the ingested food. Vitamin-*B* does not seem to control carbohydrate metabolism.

S. S. ZILVA.

Physiological role of vitamin-*B*. IV. Relation of certain dietary factors in yeast to growth of rats on diets rich in proteins. A. HASSAN and J. C. DRUMMOND (Biochem. J., 1927, **21**, 653—661).—By studying the distribution of the chief nitrogenous constituents in the urine of rats subsisting on a diet with a high protein content, but the usual quantity of vitamin-*B*, no abnormal course of protein metabolism could be detected. The subnormal rate of growth on such a diet is not due to any inorganic deficiency in the diet or to a disturbed acid–base exchange. The restoration of a normal rate of growth can be achieved by the addition to the above diet of extra yeast extract untreated or previously treated with hot alkalis. Such a treated extract without the presence of any untreated vitamin-*B* extract did not promote growth on the high-protein diet. A composite nature of vitamin-*B* is suggested.

S. S. ZILVA.

Composite nature of the water-soluble *B*-vitamin. H. CHICK and M. H. ROSCOE (Biochem. J., 1927, **21**, 698—711).—Confirmatory evidence is produced that the water-soluble *B*-vitamin of McCollum and Kennedy contains at least two constituents (cf. preceding abstract): (1) an antineuritic vitamin which prevents or cures the collapse, accompanied in some cases by symptoms of paralysis in rats and polyneuritis in birds, and (2) the pellagra-preventive or P-P factor of Goldberger and his colleagues (U.S. Public Health Rep., 1924, **39**, 87; 1925, **40**, 54; 1926, **41**, 297, 1025), which prevents or cures the marasmus accompanied by severe skin lesions developing in young rats after 6—8 weeks on a deficient diet containing the antineuritic vitamin. Yeast is a rich source of both vitamins; pure wheat embryo is rich in the antineuritic factor, but comparatively poor in the P-P factor. A preparation practically free from the antineuritic vitamin can be obtained by heating yeast in an autoclave at 120° for 4—5 hrs. The strongly antineuritic material prepared from yeast by Peters' method (A., 1924, i, 1388) was found to be devoid of the P-P factor. It is suggested that the latter principle be designated vitamin-*B*, in contradistinction to the antineuritic vitamin with which it is so closely associated.

S. S. ZILVA.

Solubilities of vitamin-*C* in lemon juice. E. B. VEDDER and W. E. LAWSON (J. Biol. Chem., 1927, **73**, 215—218).—Lemon juice was neutralised with calcium carbonate and evaporated to dryness. The vitamin-*C* was most effectively extracted from the resulting material with alcohol. The substance contained in the alcoholic extract could be freed from sulphur and phosphorus, without loss of physiological activity, by treatment of its aqueous solution with lead acetate.

C. R. HARINGTON.

Antiscorbutic fraction of lemon juice. V. S. S. ZILVA (Biochem. J., 1927, **21**, 689—697).—Decitrated lemon juice and active fractions derived from that source reduce phenolindophenol to its leuco-compound. In this way, the reducing capacity of such solutions can be determined. If insufficient of the indicator to destroy the reducing property of such solutions be added, the reduced compound is re-oxidised in the air and is further reduced by the active solution. This alternate reduction and oxidation proceeds until the reducing power of the medium is destroyed. The reducing agency, like the antiscorbutic factor, is destroyed in alkaline medium in presence of air, on aerating the active solution, and on storage. On fractionating decitrated lemon juice, it is, however, found in as high quantities in inactive as in active fractions. On adding phenolindophenol to decitrated lemon juice until the indicator is no longer reduced, and testing the treated solution immediately, no very great loss in the antiscorbutic activity is observed. On heating decitrated lemon juice in a neutral or an acid medium in an autoclave at a pressure of 1 atm. for 1 hr., no very great destruction of the antiscorbutic activity or of the reducing capacity of the solution takes place. On storing, however, both functions deteriorate very much more quickly than in untreated decitrated lemon juice.

S. S. ZILVA.

Quantitative differentiation of vitamins-*A* and -*D*. H. C. SHERMAN and M. C. HESSLER (J. Biol.

Chem., 1927, **73**, 113—120).—In the authors' previous experiments, in which young rats were kept on diets containing limited amounts of vitamin-*A*, the results were not appreciably affected by irradiation of the animals except when the food was carrot, which contains little vitamin-*D* in relation to vitamin-*A*; in order to avoid error, however, it is better in all such experiments to ensure sufficient supply of vitamin-*D* by irradiation. C. R. HARINGTON.

Antirachitic value of irradiated cholesterol and phytosterol. VII. Effect of irradiated cholesterol on phosphorus and calcium balance. A. F. HESS and E. SHERMAN (J. Biol. Chem., 1927, **73**, 145—151).—Administration of irradiated cholesterol causes no increase of blood-calcium in the normal animal, nor does it prevent the fall in blood-calcium following parathyroidectomy; when administered to rachitic rats, however, it causes an increase in the retention of both calcium and phosphorus. C. R. HARINGTON.

Influence of irradiation on oxidation products of cholesterol. F. W. SCHULTZ, M. R. ZIEGLER, and M. MORSE (J. Biol. Chem., 1927, **73**, 209—213).—α- and β-Cholesteryl oxides, hydroxycholesterol, and α-cholestantriol showed no antirachitic activity either before or after irradiation with ultra-violet light. C. R. HARINGTON.

Synthesis of vitamin-*E* by plants grown in culture solutions. H. M. EVANS and D. R. HOAGLAND (Amer. J. Physiol., 1927, **80**, 702—704).—The Canadian field-pea grown in culture solutions of inorganic salts synthesised vitamin-*E*. The solutions were not sterile. R. K. CANNAN.

Acid production by *Aspergillus niger*. H. AMELUNG (Z. physiol. Chem., 1927, **166**, 161—209).—Of the two strains of *Aspergillus* used, one gave rise to citric and gluconic acids, and the other to oxalic acid as well, when grown in solutions of various carbohydrates. Citric acid was produced from compounds with 3, 5, or 6 carbon atoms in the chain, *i.e.*, from glycerol, glycerose, xylose, arabinose, dextrose, lævulose, mannose, galactose, mannitol. Gluconic acid was formed from dextrose, sucrose, and maltose only. No acid was obtainable from substances with 4 and 7 carbon atoms, *i.e.*, erythritol, glucoheptose. It is doubtful whether gluconic acid is an intermediate stage in the fermentation of dextrose by these moulds. Addition of calcium carbonate to the medium has no appreciable effect on the yield of citric acid. Acid production is most rapid between 34° and 36°; below 5° and above 50° the mould does not grow, nor is acid formed. H. D. KAY.

Nitrate assimilation in moulds. S. KOSTYTSCHEV (Z. physiol. Chem., 1927, **166**, 135—141; cf. Kostytschev and Tscvetkova, A., 1921, i, 83).—A reply to Klein, Eigner, and Muller (A., 1926, 1280). C. HOLLINS.

Carotinoid pigments of algæ. H. KYLIN (Z. physiol. Chem., 1927, **166**, 39—77).—The extraction identification by means of absorption bands (capulary method) of ten carotinoid pigments, carotin (1), calorhodin (2), phyllorhodin (3), xanthophyll (4), xorhodin α (5), myxorhodin β (6), phylloxanthin (7), fucoxanthin α (8), peridinin (9), and fucoxanthin β (10), in various types of algæ is described. 1, 3, 4, and 7 are present in higher plants and in green algæ. In the nine species of *Rhodophyceæ* examined, 1, 3, and 4 were present, but 7 was absent. *Calothrix scopulorum* (*Cyanophyceæ*) contains 1, 2, 5, and 6, and two new pigments—*fuscorhodin* and *fuscochlorin*, the colour reactions of which are described. In three varieties of *Phæophyceæ* examined, 1, 4, 7, 8, and 10 are present, and the same five pigments are found in diatoms. *Peridineæ* contain only 1, 7, and 9.

Hæmatochrome, which is found with carotin, xanthophyll, and the alkali compound of chlorophyll in *Euglena sanguinea*, is shown to exist in three modifications, α, β, and γ, differing in solubility. The sodium salt described by Krukenberg ("Vergleichend physiologische Vorträge," Heidelberg, 1886, p. 122) and Zopf (Biol. Zentr., 1895, **15**, 417) is a derivative of a different substance into which hæmatochrome is converted by alkali. C. HOLLINS.

Protein analogies of the mycelium of *Fusarium lycopersici*. I. T. SCOTT (Missouri Agric. Exp. Sta. Res. Bull., 1926, **92**, 1—44).—The living mycelium of *F. lycopersici*, when placed in dilute buffered and unbuffered single-salt solutions at different reactions, causes the attainment of an equilibrium value near p_H 5·4. The equilibrium value for dead mycelium appears to be different. The toxicity of mercuric and cupric ions and of methylene-blue is greater on the alkaline side of p_H 5·4, and that of cyanide ions and eosin on the acid side. The living tissue of *F. lycopersici* appears to behave analogously to an amphoteric protein colloid with an isoelectric point near p_H 5·4. CHEMICAL ABSTRACTS.

Influence of proteolytic enzymes of mushrooms on the decomposition of nitrogenous substances. I. *Cantharellus cibarius*. J. BARES (Chem. Listy, 1927, **21**, 202—209).—The proteolytic action of extracts of *Cantharellus cibarius* is of the trypsin type. The amino-index of such extracts, for the digestion of Witte's peptone, collagen, blood fibrin, caseinogen, egg-albumin, and oat protein, although slightly higher than that of pancreatic trypsin, indicates considerable digestive ability. R. TRUSZKOWSKI.

Formation of oxygen from carbon dioxide by protein-chlorophyll solutions. H. E. DOLK and A. G. VAN VEEN (Biochem. Z., 1927, **185**, 165—168).—The reduction of carbon dioxide by chlorophyll solutions containing protein reported by Eisler and Portheim (A., 1923, i, 424) could not be repeated. C. R. HARINGTON.

Effect of ionised air on rate of respiration of barley seedlings. N. I. MIDDLETON (Ann. Bot., 1927, **41**, 345—356).—Barley seedlings showed increased rates of respiration when the air passing over them was ionised by means of polonium, deposited on copper foil. The maximum increase observed was 29·11% ± 5·62. The acceleration varied according to the degree of ionisation, but an exact relationship has not yet been worked out. With the highest degree of ionisation tried, there was a scarcely significant increase in rate of respiration. The effect

disappeared if the polonium was placed some little distance from the seedlings; it therefore appeared to be due to the ions themselves, and not to ozone or other gaseous product associated with ionisation.

C. T. GIMINGHAM.

Effect of ionised air on assimilation and respiration of green leaves. K. WHIMSTER (Ann. Bot., 1927, **41**, 357—374).—With air ionised by means of polonium, an increase in the respiration rate at 25° of leaves of *Pelargonium zonale*, amounting to 85·7% ±7·1, was observed. No definitely significant effect on the rate of assimilation was demonstrated. The carbon dioxide production and absorption were followed in a closed system, by the indicator method of Bolas (New Phytologist, 1926, **25**, 127), using bromocresol-purple. C. T. GIMINGHAM.

Relation of temperature to the physiological values of salt solutions as indicated by the growth of wheat roots. S. F. TRELEASE and H. M. TRELEASE (Bull. Torrey Bot. Club, 1926, **53**, 605—610).—When Marquis wheat is grown in culture solutions (total concentration of potassium dihydrogen phosphate, calcium nitrate, and magnesium sulphate, 0·06*M*) in darkness, and the rate of root elongation compared with that in a control solution containing the three salts in equal amounts, greater growth at 30° than at 14° or 19° is observed with solutions having high ratios of potassium phosphate to calcium nitrate, and in solutions containing high concentrations of magnesium sulphate or calcium nitrate.

CHEMICAL ABSTRACTS.

Starch production in the leaves of the potato. E. J. MASKELL (Ann. Bot., 1927, **41**, 327—344).—The rate of starch production in the leaflets of potato plants, grown without potassium manures and with three different types of potassium manures, has been followed in the field by means of a quantitative application of Sachs' iodine test (cf. Ursprung, A., 1917, i, 504). Observations were confined to the later period of growth of the plants. Statistical analysis of the experimental data showed that potassium manures containing chlorides did not appreciably improve the rate of starch production, but that potassium sulphate did so. The rate of translocation of starch from the leaflets on the potassium sulphate plots was also increased, but the improved rate of starch production did not appear to be wholly due to that factor. It also varied significantly with certain periodic factors, of which intensity of solar radiation and age were important. The use of a standard scale of colour tones for grading the colour intensities developed in the leaf by the iodine test is discussed. The tone scale found to be satisfactory is tone scale 59″″″ of Ridgway's "Colour Standards and Nomenclature." C. T. GIMINGHAM.

Development of a pink colour in lignified tissues by the chloroamine reaction. F. M. WOOD (Ann. Bot., 1927, **41**, 281—285; cf. A., 1926, 1065).—The chloroamine reaction, used primarily to detect protein in the cell-wall, produces either a pink, yellow, or brown colour in lignified tissues. The pink colour was developed in xylem and sclerenchyma, but not in any other tissue; it appeared chiefly in the secondary xylem of aerial stems of more than 1 year's growth. In tissues in which the cellulose base showed the presence of oxycellulose by Knaggs' test, the pink colour did not appear either in xylem or sclerenchyma. The compound responsible appeared to be a constituent of tissues, the function of which is largely mechanical support. C. T. GIMINGHAM.

***P.D.* in the apple.** L. MICHAELIS (Biochem. Z., 1927, **185**, 11—13).—A reply to Jost (this vol., 388).

C. R. HARINGTON.

Behaviour of pectic materials in apples and other plant tissues. M. H. CARRÉ and A. S. HORNE (Ann. Bot., 1927, **41**, 193—237; cf. A., 1922, i, 1222; ii, 401; A., 1925, i, 758; Ann. Bot., 1925, **39**, 811).—Microscopical and microchemical study of the distribution and developmental changes undergone by the various pectic structures in the tissues of the apple fruit, from the flowering period to the final stages of senescence, has given results in agreement with those obtained by a purely chemical investigation. When the fruit "sets," the pectic substances are uniformly distributed in the middle lamella and cell-walls; from this period to the maturity of the apple, a specialised pectic framework is developed which comprises structures of definite shape—crescents, discs, globules. During senescence, the framework becomes less stable and quantities of semi-soluble pectic matter appear in the cell-walls. The changes which occur during senescence have been imitated by microchemical treatment with hydrolytic reagents, and are interpreted as brought about by enzymic activity. The authors find no ground for supposing that dissolution of the pectic substances is a primary cause of the death of the tissues. Changes of the pectic complex in apples affected by physiological or fungal diseases, or subjected to the action of anæsthetics, were also studied. Some of the structures observed in the pectic framework of the apple were not found in the tissues of most of the other plants examined. Ruthenium-red proved entirely satisfactory as a stain for pectic substances.

C. T. GIMINGHAM.

Pectic constituents of peaches and their relation to softening of the fruit. C. O. APPLEMAN and C. M. CONRAD (Maryland Agric. Exp. Sta. Bull., 1926, **283**, 1—8).—The transformation of protopectin into pectin (the sum being constant during ripening) is the only pectic change during ripening or softening of peaches, and is chiefly responsible for the softening. Pectic acid and calcium pectate were absent. The transformation is retarded by low temperatures and accelerated by high temperatures. The pectic change in peaches left on the tree is much slower than in picked fruit.

CHEMICAL ABSTRACTS.

Presence of sodium in plants. G. BERTRAND and J. PERIETZEANU (Bull. Soc. chim., 1927, [iv], **41**, 709—713).—See this vol., 488.

BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

AUGUST, 1927.

General, Physical, and Inorganic Chemistry.

Calculation of the spectroscopic terms derived from equivalent electrons. H. N. RUSSELL (Physical Rev., 1927, [ii], **29**, 782—789).—An extension of Breit's notation affords a simple method for the calculation of the spectroscopic terms which result from an atomic configuration containing several equivalent electrons, in which Pauli's restriction is operative. A. A. ELDRIDGE.

Terms arising from similar and dissimilar electrons. R. C. GIBBS, D. T. WILBER, and H. E. WHITE (Physical Rev., 1927, [ii], **29**, 790—793).—Following Hund's scheme, the terms arising from similar f electrons from 1 to 14 have been worked out and tabulated. Tables are also given for one, two dissimilar, and three (two similar) electron systems. A. A. ELDRIDGE.

Intensity of spectral lines. A. E. BRODSKY (Z. Physik, 1927, **42**, 899—904).—By the application of classical thermodynamic principles to an orbital electron transition considered as a "reaction," an expression $I=\alpha x e^{-x}$ has been derived for the intensity, I, of lines of frequency ν radiated by a gas or vapour, where $x=h\nu/kT$ and α is a function of $Te^{1/T}$. This expression is similar in form to Bleeker's (A., 1926, 657). It has been examined by applying it to the data of Bleeker and Bongers for I and ν (A., 1925, ii, 77) relating to the sharp and diffuse subordinate series of rubidium and cæsium. For these, when a temperature of 1700° is assigned to the radiating vapour, it is shown that $\log\alpha$ is constant within 1·4—3·5%. This agreement with theory is considered to be satisfactory. R. W. LUNT.

Intensity distribution in spectrum lines, and its application to photometric measurements. L. S. ORNSTEIN and M. MINNAERT (Z. Physik, 1927, **43**, 404—412).—The intensity distribution in a spectral line has been calculated on the assumption that the true line-width is very small and that the observed width is due to the width of the slit and to refraction, and is of the form $I_x=\int x^{-2}\sin^2 x.dx$, where I_x is the intensity at a distance x from the centre of the line, and $\sigma=-Bs\lambda^{-1}f$, where B is the width of the refracting aperature, s the slit width, λ the wave-length, and f the focal length of the collimator. The intensity distribution computed thus from the optical constants of the apparatus for the mercury lines 5461 4078, 3342, 3126, 3024, 2537, and 2482 Å. agrees exceedingly well with the intensity distribution measured photometrically, for which a special eveloper is necessary to reduce the Eberhard effect to a minimum. A number of important applications are described. R. W. LUNT.

Structure of the second order spectrum of carbon. C. MIHUL (Compt. rend., 1927, **184**, 1648—1649).—Three new multiplets resulting from combinations between terms of multiplicity $r-4$ are described for the C II spectrum. They consist of the triplet $^4P^4S$, and the two multiplets $^4P^4P'$ and $^4P^4D$. The corresponding electronic configurations based on Hund's theory are evaluated. J. GRANT.

Spectrum of ionised neon (Ne II). T. L. DE BRUIN (Nature, 1927, **119**, 925—926).—A number of the Ne II lines have been classified in a term scheme analogous to that of F I. A. A. ELDRIDGE.

Reversal of neon lines. H. NAGAOKA and T. MISHIMA (Proc. Imp. Acad. Tokyo, 1927, **3**, 136—139).—The reversal of 18 lines of the neon spectrum in the range 7032—5852 Å. has been examined by an echelon spectroscope (resolving power 435,000 at 5000 Å.) and by a Lummer-Gehrcke plate (resolving power 400,000 at 5000 Å.). The reversals are found to be slightly asymmetric, and no definite relation with absorption can be traced. The lines of the type $1s_2-2p_m$ show diffuse reversals, $1s_3-2p_m$ are generally narrow, $1s_4-2p_m$ are sharp when m is even. Within the limits of these experiments no conclusion can be reached concerning the observed reversals with the mode of excitation, the magnetic separation, and absorption. R. W. LUNT.

Electrically excited resonance spectrum of argon. K. W. MEISSNER (Z. Physik, 1927, **43**, 449—453).—A glass cylinder, 120×20 mm. in diameter, containing argon is provided at each end with a side-tube containing an electrode. Surrounding this tube are a number of small tubes, parallel to the axis, connected in series and ending in two electrodes. This external tube system also contains argon. An examination has been made of the spectrum of the light emitted axially from the inner cylinder, both when it is energised with 9—10 milliamp. direct current and when the external tube is energised with direct current. It is found in the latter case that the following resonance lines corresponding with the $2s_i-2p_k$ transitions are intensified: 8668, 8521, 8408, 8265, 8104, 8006, 7948, 7724, 7635, 7515, 7504, 7383, 7273, 7147, 7067, 6965, and 6677. R. W. LUNT.

Detailed explanation of spectra of metals of the second group. M. SAHA (Phil. Mag., 1927, [vii], **3**, 1265—1274).—The principles of non-mechanical vector addition of quantum numbers

previously applied by Landé, Russell, and others to the fundamental levels of the atom have been extended to the examination of all the higher terms, and for metals of the second group all details of the spectra are satisfactorily explained. The resulting scheme of electron arrangement is in effect a modification of the scheme of Main Smith and Stoner.

A. E. MITCHELL.

Relative intensities of some lines in the mercury spectrum. J. VALASEK (Physical Rev., 1927, [ii], 29, 817—821).—The intensities of the most intense lines associated with transitions to and from the $2p_2$ state in mercury were measured photographically. When only transitions giving rise to radiation are considered, there appear to be more transitions to $2p_2$ than down from $2p_n$. A. A. ELDRIDGE.

Production of the continuous spectrum of mercury by rolling it in a vacuum. M. DUFFIEUX (Compt. rend., 1927, 184, 1434—1436; cf. A., 1925, ii, 340).—A detailed description is given of the phenomena observed at increasing temperatures when a large drop of mercury is contained in a spherical glass vessel rotating round a horizontal diameter. At 10—40°, unstable luminous phenomena were produced depending probably on the electrical state of the glass. At about 50°, a mauve luminous discharge was produced between the tail of the drop (the positive extremity) and the glass. The green and violet mercury rays, and sometimes yellow rays, were distinguishable. At 100°, the positive extremity of the arc was separated from the glass by a dark space, and before 120° was reached, the top of the vessel lit up with a brilliant green glow of increasing intensity, which emitted only the continuous spectrum of mercury. No modification occurred at the highest temperature reached (200°). J. GRANT.

Reversal of series lines of thallium. H. NAGAOKA and T. FUTAGAMI (Proc. Imp. Acad. Tokyo, 1927, 3, 140—142).—Reversal in the sharp and diffuse series of thallium has been examined in the ranges 5350·5—2315·9 Å. and 3529·4—2379·6 Å., respectively. The spectra were excited by discharging a condenser of 1·7 microfarads capacity charged to 20 kilovolts across a gap of 0·2—0·3 mm. between thallium electrodes. The amount of reversal decreases as the frequency increases; the reversal of the sharp series is asymmetric, whilst that of the diffuse series is symmetric. R. W. LUNT.

Fine structure and term constants of the bismuth spectrum. S. GOUDSMIT and E. BACK (Z. Physik, 1927, 43, 321—334).—The fine structure of the following bismuth lines has been determined by a grating method: 4722·5, 4308·3, 4121·8, 3888·2, 3596·1, 3510·9, 3397·2, 3076·6, 3067·7, 3024·6, 2993·3, 2989·0, 2938·3, 2898·0, 2696·7 Å. From the $\Delta\nu$ values thus obtained term constants have been assigned to the above lines. R. W. LUNT.

Direct measurement of X-ray energy. W. RUMP (Z. Physik, 1927, 43, 254—295).—An elaborate technique has been devised whereby the energy of a beam of *X*-rays can be measured directly by allowing the incident beam to fall into a cavity surrounded by lead or mercury, which functions as a perfect absorber. The absorber is immersed in a thermostat, and the energy received is measured by the expansion of a gas in contact with the outer surface of the absorber; the sensitivity obtained was 1×10^{-6} g.-cal. sec./cm.^{2} of cavity aperture (12·6 cm.^{2}). The apparatus was calibrated with the known energy of the α-, β-, and γ-radiation from radium, and data were reproducible within 1%. Using a Coolidge type of *X*-ray tube with a constant current of 10 milliamp., the total *X*-ray energy was found to vary as the square of the applied stationary potential in the range 43—150 kilovolts. The efficiency of the tube as a generator of *X*-rays increased correspondingly from 0·46 to 1·64%. Elaborate determinations have been made on the ionisation produced in air by *X*-rays. Data are given for the number of ions produced as a function of the energy absorbed, and of the mean energy, V, of the ions computed from $h\nu=Ve$, where ν is the mean frequency of the *X*-radiation. R. W. LUNT.

Absolute measurement of light quanta in an X-ray beam. W. KOSSEL and M. STEENBECK (Z. Physik, 1927, 42, 832—835).—The technique of Eliger and Holthusen has been adapted to the measurement of the number of ions liberated in unit volume of a gas traversed by a beam of *X*-rays by using suitable precautions to ensure that the ions are liberated in a uniform field. From measurements of the number of ions liberated under these conditions, radiation at the rate of 100 *X*-ray quanta per minute can be observed. The method has thus a sensitivity a million times that of the thermal method. R. W. LUNT.

Intensity of X-ray spectra as a function of the exciting potential. D. NASLEDOV and P. SCHARAVSKI (Z. Physik, 1927, 43, 431—441).—The intensity of the following lines of the *K*-series has been determined by an ionisation method as a function of the exciting potential up to five times the minimum exciting potential: Ag$K\alpha$, Ag$K\beta$, Pd$K\alpha$, Pd$K\beta$, Mo$K\alpha$, and Cu$K\alpha$. The intensity varies *linearly* with the square of the applied potential, and vanishes at approximately $kV^2=500$, except for copper, when it vanishes if the curve is produced backwards from $kV^2=4225$, at $kV^2=-5000$. The intensity I can therefore be expressed in the form $I=c(V-V_0)^n$, where V_0 is a constant characteristic of the metal. R. W. LUNT.

Intensity of X-ray lines as a function of the number of electrons reaching the cathode. D. NASLEDOV and P. SCHARAVSKI (Z. Physik, 1927, 42, 870—882).—The authors' earlier work on copper has been extended to an examination of the lines Mo$K\alpha$, Mo$K\beta$, Pd$K\alpha$, Pd$K\alpha$, and Ag$K\alpha$. As in the case of copper, the intensities increase linearly with the current up to a certain critical value; they then increase linearly but at a diminished rate. This critical point is independent of the potential applied to the tube in the range examined, 50—83 kilovolts. For molybdenum and palladium, the critical current is 6 milliamp., and for silver between 6 and 7 milliamp. An approximately linear relationship is thus to be traced between the value of this critical current in copper (4 milliamp.), the above metals, and the corresponding atomic numbers. R. W. LUNT.

Selective displacement of 0·0153 Å in *X*-ray spectral lines. F. H. LORING (Chem. News, 1927, **134**, 385—388; **135**, 17—18, 65—67).—Theoretical. A continuation of previous work (this vol., 602).

W. E. DOWNEY.

Effect of chemical combination on *X*-ray absorption. W. B. MOREHOUSE (Physical Rev., 1927, [ii], **29**, 765—774).—The *X*-ray absorption by aqueous solutions of the reactants producing reactions expressed by the equations (*a*) $KI+I_2+2Na_2S_2O_3=KI+2NaI+Na_2S_4O_6$, (*b*) $K_2Cr_2O_7+12KI+14HCl=8KCl+2CrCl_3+3I_2+6KI+7H_2O$, (*c*) $NaOH+HCl=NaCl+H_2O$, (*d*) $KOH+HCl=KCl+H_2O$, (*e*) I_2 (aqueous alcoholic)$+2Na_2S_2O_3=2NaI+Na_2S_4O_6$, and of the solutions after reaction, has been measured. The results indicate that the mass absorption coefficient for an element depends on its valency. Absorption by iodine in the free state appears to be greater than that in combination.

A. A. ELDRIDGE.

Theory of the intensity of scattered *X*-rays. G. E. M. JAUNCEY (Physical Rev., 1927, [ii], **29**, 757—764).

Laboratory demonstration of the Zeeman effect. K. W. MEISSNER (Z. Physik, 1927, **43**, 454—455).—Plane polarised light from a neon–helium discharge tube is passed through a second discharge tube, whereby the light from the first tube is absorbed. If now a magnetic field be applied to the first tube, the frequency is slightly changed, and can therefore pass through the second tube and be focussed on a screen.

R. W. LUNT.

Zeeman effect and spherical harmonics. C. G. DARWIN (Proc. Roy. Soc., 1927, **A**, **115**, 1—19).—The problem of a charged spinning spherical body moving in a central orbit in a magnetic field is solved by the method of the wave mechanics in spherical harmonics. It leads to a system of equations which are competent to determine the frequencies and intensities of the lines in the standard Zeeman effect. The model yields strictly the odd multiplicities only, but the same set of equations is also applicable in every respect to the even. Formulæ are given from which the intensity of any component in any strength of field can be obtained. A few examples are worked out. The development in spherical harmonics elucidates clearly the physical meaning of the quantum numbers k, m, r, m_k, m_r, but much more obscurely j. To elucidate the force of j, a new method of attacking the problem is outlined.

L. L. BIRCUMSHAW.

Tentative explanation of the Zeeman effect of types D_1 and D_2. F. J. VON WISNIEWSKI (Z. Physik, 1927, **42**, 910—914).—A theory of the Zeeman effect for weak fields and of types D_1 and D_2 has been developed by considering the two possible solutions of the equation of motion of an electron about a solid nucleus, and in a magnetic field.

R. W. LUNT.

Duration of light-emission of atoms. H. KAERSCHBAUM (Ann. Physik, 1927, [iv], **83**, 287—295; c. A., 1926, 652).—The earlier work has been extended to the metals calcium, strontium, and barium. The following results were obtained for the damping constant ($\times 10^7$) and the mean duration of the light in seconds ($\times 10^{-8}$), respectively: Calcium: spark, 15·4, 0·65; arc, 2·8, 3·4. Barium: spark I, 8·3, 1·2; spark II, 3·7, 2·7. Strontium: spark I, 8·0, 1·25; spark II, 2·78, 3·6; arc, 5·05, 1·98. Differences are observed between different spark lines in barium and strontium. The electric deflection of spectral lines has been investigated for the three elements. All the available values for the mean direction of the light for different elements are tabulated.

R. A. MORTON.

Duration of the afterglow in mercury vapour. (FRL.) M. ASTERBLUM (Z. Physik, 1927, **43**, 427—430).—The continuous afterglow of mercury vapour has two maxima, at 3300 and 4850 Å. The duration of the afterglow at these maxima is the same, and decreases in intensity logarithmically with time.

R. W. LUNT.

Light-period of the ultra-violet hydrogen series. W. WIEN (Ann. Physik, 1927, [iv], **83**, 1—18).—A fine stream of hydrogen positive rays crosses the focal circle of the grating of a vacuum spectrograph so that the lines H_a 1215·68, H_b 1025·7, H_c 972·5, H_d 949·8, and H_e 937·8 Å. can be photographed on Schumann plates. The intensity of the radiation emitted by the canal-ray stream decreases along its length, so that the spectral lines exhibit a fading which is a measure of the period of line-excitation. The more usual methods for measuring the intensities of spectral lines are not applicable to vacuum spectroscopy in this region, since no material is available for the construction of wedges, and the mechanical methods for reducing the intensity are scarcely practicable. A screening arrangement was, however, devised for reducing the intensity of the positive-ray stream, which was calibrated by measurements on the heating effect of the charged particles. The decrease in intensity of H_a is given by $I=I_0e^{-\beta y}$, in which y is the distance traversed in the positive-ray stream and β is 4·3. The Doppler shift $\delta\lambda=0{\cdot}085$ mm. and $v(=\delta\lambda/\lambda c)$ is $3{\cdot}44\times10^7$ cm./sec., so that the duration constant $2\alpha(=\beta v)$ is $14{\cdot}8\times10^7$ for both H_a and H_b, a value some three times as great as that found with the Balmer series. Slack (A., 1926, 875) by excitation with electrons at 10·2 volts obtained for 2α the value $8{\cdot}3\times10^7$.

R. A. MORTON.

Behaviour of Schumann plates in the vacuum spectrograph in the observation of canal-rays. W. WIEN (Ann. Physik, 1927, [iv], **83**, 19—22).—The observations recorded (preceding abstract) were greatly hindered by fogging of the plates, and the effect has now been studied in detail. The fog is formed with hydrogen and oxygen positive rays, but only to a much smaller extent with nitrogen. This observation supports direct spectrographic tests, which make it improbable that the effect is due to short-wave radiation. A more likely explanation is a chemical interaction between atomic hydrogen or oxygen and the almost gelatin-free silver halide of the Schumann plate. The observations on the effect of pressure variations on the development of the fogging may be interpreted in terms of this mechanism.

R. A. MORTON.

Electron emission from thoriated tungsten. S. DUSHMAN and J. W. EWALD (Physical Rev., 1927,

[ii], 29, 857—870).—The emission for a monatomic film of thorium on tungsten is greater than that for metallic thorium. The electron emission ($I=3T^2\epsilon^{-30,500/T}$, in amp./cm.^{2}) was measured for different states of activation of the thoriated filament.

A. A. ELDRIDGE.

Chemical activity of slow electrons. E. RABINOWITSCH (Z. Elektrochem., 1927, **33**, 185—188).—Solid oxides such as lime, thoria, and cerie oxide have been submitted to bombardment by electrons under various conditions in an attempt to decompose them, and hence to determine their heats of formation from the critical electron velocity required for this purpose. With slow electrons of an energy comparable with the energy of decomposition of the oxides, traces of gas could be pumped out of the discharge tube, but oxygen could not be definitely detected in it. With electrons of about 1000 times this velocity, oxygen was obtained from rare-earth oxides, but even then the efficiency was very small, only about one impact in 400 producing decomposition. This result is not unexpected, considering that, when gas molecules are decomposed by slow electrons, the high efficiencies obtainable are due to secondary processes caused by impacts of molecules activated by the primary process, whilst in a solid these secondary effects are not possible. The small quantities of gas obtained were removed from the discharge tube by continuous pumping; otherwise most of the liberated oxygen recombines and no appreciable rise in pressure occurs. Ceric oxide blackens under the bombardment, but the amount of the decomposition product was not sufficient for analysis. Difficulties in determining the applied voltage occurred owing to the badly-conducting oxide layer becoming charged on the surface. The results of Cole (A., 1926, 1189) on the blackening of photographic emulsions by low-speed electrons are discussed in the light of similar experiments by the author. H. J. T. ELLINGHAM.

Smallest carriers of electricity in gases. H. SCHILLING (Ann. Physik, 1927, [iv], **83**, 23—80).—The most important experimental result is that all attempts to obtain with the purest gases values of w greater than those normally found for the ordinary carriers of electricity in air have been unsuccessful. The largest values found are: $w^-=2{\cdot}5$ and $w^+=2{\cdot}0$ cm./sec. volt/cm., corresponding with carrier-radii of $4{\cdot}7$ and $4{\cdot}1\times10^{-8}$ cm., respectively. The radius is thus about three times that of a single molecule in air. The multiple of the molecular radius required to correspond with the radius of the negative carrier varies from 3·0 with air to 5·0 with helium and 6·0 with ethyl alcohol. The literature of this subject is critically reviewed. R. A. MORTON.

Nature of phosphorus ionisation. II. W. BUSSE (Ann. Physik, 1927, [iv], **83**, 80—120; cf. this vol., 633).—The relations between temperature and ion-formation have been investigated, and the effect of increasing temperature has been shown to differ from that of decreasing temperature. The ionisation–temperature curves show maxima and minima and a noteworthy small peak at temperatures between 35° and 40°, *i.e.*, just below the flashing temperature. In dry air, ionisation occurs only at higher temperatures. The position and magnitude of the maximum are greatly influenced by the temperature of the air stream. The moisture present favours a rapid rise to maximum ionisation. The fact that moisture appears to be essential for ion-formation, in conjunction with the earlier conclusion that the negative ions take up multiple charges preferentially, leads to the view that the ionisation occurs as a result of the dissociation of an acid formed in the course of the oxidation of phosphorus. It is shown that the charge which occurs at the initial introduction of the air stream over the phosphorus is, apart from special exceptions, equal to the charge at the stage immediately preceding ignition. On the other hand, the maximum in a curve corresponds with a charge several times as great as the initial charge. The amount of dissociating acid present remains fairly constant, so that ionisation by stages must occur. This notion gives an explanation of the numerous maxima in the curves. The maximum charge appears to be eight times the initial charge, so that an acid of maximum basicity 8 may dissociate by steps. The evidence points to reaction between phosphorus pentoxide and water. The possible role of different oxy-acids of phosphorus is discussed; the conclusion is reached that pyrophosphoric acid must be the dissociating substance responsible for the ion-formation. R. A. MORTON.

Probability of ionisation of mercury vapour by electron impact. T. J. JONES (Physical Rev., 1927, [ii], **29**, 822—829).—The curve showing the number of positive charges produced in a 1 cm. path by an electron moving through mercury vapour at 1 mm. pressure as a function of the electron energy gives a maximum value of 20·5 at 90 volts. The number of positive charges formed at an impact is maximal (0·35) at 90 volts. When, however, experimental values for the electronic mean free path are employed, the latter curve gives no indication of reaching a maximum. It is considered unlikely that only singly-charged ions are produced, since above 400 volts the number of positive charges formed at an impact appears to be greater than unity.

A. A. ELDRIDGE.

Polarisation of the light from hydrogen canal rays. K. L. HERTEL (Physical Rev., 1927, [ii], **27**, 848—856).—Light from hydrogen canal rays, principally H_β, is partly (up to 10%) polarised. The half-value period of the polarisation is about one third of that of the intensity. The effect of a transverse electric field was examined. A. A. ELDRIDGE.

Ionisation of gases and stellar temperatures. G. TIERCY (Arch. Sci. phys. nat., 1927, [v], **9**, 87—107).—Saha (A., 1920, ii, 659; 1921, ii, 4, 162; 1923, ii, 5) regards the ionisation of a gas as akin to dissociation of one gas into two others. The expression $\log[x^2/(1-x^2)]P=-U_0/4{\cdot}571T+2{\cdot}5\log T+C$ (x is the fraction dissociated, P the pressure in atm., U_0 the ionisation potential in volts, T the absolute temperature, C the entropy constant) serves to connect the temperature of a star with the degree of ionisation of its constituents. Nernst's expression $-1{\cdot}62+1{\cdot}5\log m$ (m being the atomic mass) was used to fix the entropy constant as −6·5. On the basis of experiment, −5·5 seems to be a more trust-

worthy value. The entropy constant may be obtained from the equation — $\log c_\lambda$, R being the gas constant, n_λ the relative minimum numbers of gaseous particles, n_0 for the original gas, n_i and n_e for the constituents, and c_λ the concentration of each, c_0, c_i, and c_e. When a g.-mol. of gas dissociates completely into two gases, or when a gas ionises completely, n_i and n_e are both unity. If simple dissociation occurs, the constant obtained corresponds with a g.-mol. of the original gas and with a g.-atom of neutral gas in the gas of ionisation. On the other hand, when ionisation occurs, the constant must be expressed in terms of a g.-mol. of original neutral gas, so that the coefficients n_λ must be doubled, *i.e.*, $C=R\Sigma 2n_\lambda \log c_\lambda$. Since $n_i=n_e=1$, and $c_i=c_e=\frac{1}{2}$, $C=1{\cdot}99(4 \log \frac{1}{2})$, *i.e.*, $-5{\cdot}52$, in agreement with the experimental value.

Nernst's expression thus fails to account for the fundamental difference between simple dissociation and ionisation. The value $-5{\cdot}52$ in conjunction with the Saha expression leads to values for the temperatures of different classes of stars which agree well with those obtained by Russell (Nature, 1914, 93, 227) on other grounds. R. A. Morton.

Ionisation by collisions of the second kind in mixtures of hydrogen and nitrogen with the rare gases. G. P. Harnwell (Physical Rev., 1927, [ii], 29, 830—842; cf. this vol., 604).—A study of the effect of the presence of a rare gas in ionised hydrogen and nitrogen. The evidence supports the view that a type of collision of the second kind takes place at which an atom is ionised by colliding with an ion of an atom of higher ionising potential. The following reactions are predicted and supported by the experimental evidence: for hydrogen, $He^+ + H_2 = He + H_2^+$; $Ne^+ + H_2 - Ne + H_2^+$; $A + H_2^+ = A^+ + H_2$; for nitrogen, $He^+ + N_2 = He + N_2^+$; $Ne^+ + N_2 = Ne + {}^{17}N_2^+$; $Ne + {}^{24}N_2^+ = Ne^+ + N_2$; $A + N_2^+ = A^+ + N_2$, where ${}^{17}N_2^+$ and ${}^{24}N_2^+$ represent, respectively, the nitrogen ions produced at the expense of 17 and 24 volts. It appears that the probability of the occurrence of a transfer is an inverse function of the difference in ionising potentials. A. A. Eldridge.

Ionisation by collision. H. G. L. Huxley (Phil. Mag., 1927, [vii], 3, 1056—1061).—A discussion of the theory of sparking potentials advanced by Taylor (Proc. Roy. Soc., 1927, A, 114, 73).

A. E. Mitchell.

Potential gradient in the positive column. II. Oxygen, air, water vapour, helium, argon, krypton, xenon, and mercury. A. Günther-Schulze (Z. Physik, 1927, 42, 763—772).—The relationship observed previously for nitrogen and hydrogen (this vol., 392) relating the gradient in the positive column, G, with the mean free path, corrected for the temperature of the gas, l, and with the tube radius r, viz. $G=Cl^{-2/3}r^{-1/3}$, where C is a constant, has been found to hold for the polyatomic gases oxygen, , water vapour, for which gases the constant C has been evaluated. Owing to the instability of the discharge, the value for water vapour is somewhat uncertain. In the rare gases and mercury vapour, e relationship $G=Cl_0(r+\alpha i)^{-1}$ obtains, where l_0 ne mean free path at 1 mm., i the current, and α a constant. These relationships are valid, as in hydrogen, nitrogen, and neon, only when l is small compared with r, and provided that the pressure is so low that the positive column extends throughout the whole diameter of the discharge tube. R. W. Lunt.

Voltage necessary to maintain a luminous discharge in hydrogen. W. A. Noyes, jun. (Phil. Mag., 1927, [vii], 3, 1262—1265).—A discussion of some of the apparent differences between the results of Gibson and Noyes (A., 1922, ii, 812) and of McCurdy (A., 1924, ii, 808) on the voltage necessary to maintain a luminous discharge in hydrogen and mercury vapour. Some of the work of the former with hydrogen has been repeated, with results similar to those obtained previously. It is concluded that there are no real differences between the two sets of results, and that, under certain conditions, the discharge may disappear at a voltage which is approximately the ionisation potential or some multiple of it.

A. E. Mitchell.

Two magnetic moments of the atom. R. Ferrier (Compt. rend., 1927, 184, 1641—1643).—The analogy between an atom and a small magnet from the point of view of its magnetic moments is discussed with reference to the effect exercised on a particle by a magnetic field (Bohr moment), and also to the magnetic field (Weiss moment) produced by the particle itself. The apparent discordance is reconciled with the ordinary laws of electromagnetism, and an explanation of paramagnetism and diamagnetism is suggested. J. Grant.

Attempts to separate isotopes of mercury by chemical means. H. S. King (J. Amer. Chem. Soc., 1927, 49, 1500—1511).—Considerations of molecular structure lead to the conclusion that chemical reactions of the type $Hg_2X_2=Hg+HgX_2$ should effect a partial separation of the isotopes of mercury. Unsuccessful experiments are described in which X=I, CN, $\frac{1}{2}O_2$, Cl, and Ph; the reaction $Hg_2Cl_2+2PhMgBr=Hg+Ph_2Hg+2MgBrCl$ was also unsuccessful (cf. Richards, King, and Hall, A., 1926, 771).

S. K. Tweedy.

Nature and origin of the earth's surface structure. J. Joly and J. H. J. Poole (Phil. Mag., 1927, [vii], 3, 1233—1246).

Radioactivity of the earth's basaltic magma. J. H. J. Poole (Phil. Mag., 1927, [vii], 3, 1246—1252).—Determinations of the radioactivities of specimens of authentic Oregonian plateau basalts have shown these to have the same mean thorium contents as the Hebridean and Deccan plateau basalts previously examined by Joly and Poole (A., 1924, ii, 812). It is concluded that the apparently Oregonian basalts examined previously did not belong to that series, and that all the three main series of plateau basalts are derived from the same sub-crustal basaltic magma. Examination of various eclogites shows that the radium and thorium contents of these are even less than those of the plateau basalts; this points to the conclusion that these really represent the lower layers of the earth's primary basaltic magma. The bearing of this result on the general ideas of the earth's surface structure is discussed.

A. E. Mitchell.

Radioactivity of matter exposed for a long period to solar radiation. (MLLE.) S. MARACINEANU (Compt. rend., 1927, **184**, 1547—1549; cf. this vol., 605).—The radioactivity of the portion of lead roofing used in the earlier experiments could not have been due to its origin, since the unexposed parts possessed no such activity, and that of the exposed part decreased when it was removed from the roof. Nor was the radioactivity due to radioactive deposits from the atmosphere. Lead exposed to the south had a higher radioactivity than that exposed to the north. Zinc and copper roofs also possessed a radioactivity, highest on the exposed side, but less than that of the lead, whereas calcareous stone and iron had none. H. DESLANDRES (Compt. rend., 1927, **184**, 1549—1550) comments on the above phenomena and believes them to be of cosmic origin.

J. GRANT.

Charge of α-particles emitted per sec. by 1 g. of radium. H. JEDRZEJOWSKI (Compt. rend., 1927, **184**, 1551—1553).—By means of an elaborated form of Rutherford and Geiger's method, the mean value of the total charge of the α-particles emitted in 1 sec. from 1 g. of radium has been found to be 33·4 e.s.u., corresponding with $3{\cdot}50 \times 10^{10}$ α-particles.

J. GRANT.

Scattering of α-particles. J. R. OPPENHEIMER (Z. Physik, 1927, **43**, 413—415).—Rutherford's equation for the scattering of α-particles has been deduced from quantum mechanics, and its valitity has been examined. R. W. LUNT.

Atomic disintegration by α-particles from polonium. W. BOTHE and H. FRANZ (Z. Physik, 1927, **43**, 456—465).—Polonium has been chosen as the source of α-particles, since it produces these with practically uniform velocity and without appreciable β- and γ-radiation. The Geiger point-in-cylinder method has been used to detect the H-particles produced, and the electroscope deflexions have been photographically recorded on a moving film. All the elements from boron to calcium have been examined with the exception of neon and argon. Positive results were obtained in boron, nitrogen, magnesium, and aluminium only; for these elements, curves are given for the number of H-particles per minute as a function of their penetration in air.

R. W. LUNT.

Energy distribution in the γ-radiation of radium-C. D. SKOBELZYN (Z. Physik, 1927, **43**, 354—378).—The earlier technique for β-rays (*ibid.*, 1924, **28**, 278) has been developed so that observations can be made of the tracks of the electrons produced by γ-rays from radium-*C* in gas subjected to a magnetic field of the order of 1000 gauss. From the observed track curvatures the energy distribution has been computed. In the range $h\nu$=610—1778 kilovolts the intensity values obtained are considerably greater than those of Ellis; the value at $h\nu$=2210 is the same. R. W. LUNT.

Atomic nuclei and their transformations. (SIR) E. RUTHERFORD (Proc. Physical Soc., 1927, **39**, 359—372).—A lecture delivered on Feb. 25, 1927.

Theory of sub-electrons. T. PECZALSKI (Compt. rend., 1927, **185**, 49—51).

Calculation of the mean value in the electron theory of Lorentz. V. BURSIAN (Z. Physik, 1927, **43**, 416—426).

Number of radiating atoms in a hydrogen discharge tube. W. H. CREW and E. O. HULBURT (Physical Rev., 1927, [ii], **29**, 843—847).—About 90% of the energy radiated from a long hydrogen tube filled with moist hydrogen at 0·54 mm. pressure, and excited with 66 milliamp. at 7 kilovolts, is carried by the first three lines of the Balmer series. The number of quanta of these lines emitted per atom per sec. is calculated to be 2·84, 0·43, and 0·10, respectively. A. A. ELDRIDGE.

Limits of the periodic system of the elements. E. MEYER (Z. Elektrochem., 1927, **33**, 189—192).—A discussion of the probability of the existence of elements of atomic number greater than 92. It is suggested that, if the electrons are arranged around the nucleus of an atom in concentric spherical shells the radii of which are in the ratio $1^2 : 2^2 : 3^2$, etc., the number of electrons in the respective shells should be $(1+1)$, 2^2, 3^2, etc. This would give a secondary periodicity in which helium, carbon, phosphorus, gallium, barium, and uranium would be the last members of the successive periods. On this basis uranium is the element with six completed shells, and may thus be the true end member of the series of elements. Evidence supporting this arrangement is discussed. The hydrogen nucleus is regarded as an element of zero atomic number.

H. J. T. ELLINGHAM.

Process of quantisation. G. P. THOMSON and R. G. J. FRASER (Phil. Mag., 1927, [vii], **3**, 1294—1305).—Mathematical. Use is made of the probability that when the motion of an atom in a stationary state is interrupted by collision or otherwise, the subsequent adjustment of the system towards a system satisfying the quantum postulates takes a finite time, to establish a correspondence between the pressure broadening of a spectral line on both the classical and the quantum theories. Thus information is derived regarding the process of quantisation. The deductions are in agreement with the experimental results of Füchtbauer and Joos (A., 1922, ii, 242) on the pressure-broadening of spectral lines. A. E. MITCHELL.

Contribution to modern ideas on the quantum theory. H. T. FLINT and J. W. FISHER (Proc. Roy. Soc., 1927, **A**, **115**, 208—214).

"Axiality" of light emission and the structure of chemical atoms. J. STARK (Physikal. Z., 1927, **28**, 421—427).—Theoretical. It is concluded that the smallest atom-ion, the positive elementary quantum of smallest mass, the hydrogen atom-ion or "archion" from which all heavier atoms are built up, is a rotatory motion with a definite axis and frequency as characteristic as the elementary electric charge. The mass for this elementary rotatory motion of the "archion" is its impulse of rotation. This elementary impulse of rotation demands the quantisation of the impulses of rotation in the stable state of the chemical atom. W. E. DOWNEY.

Line intensities in the hydrogen chloride fundamental band. D. G. BOURGIN (Physical

Rev., 1927, [ii], 29, 794—816).—Values of the intensities of the absorption lines of the hydrogen chloride fundamental band for tube-lengths from 0·0998 to 2·97 cm. have been obtained; the results yield indirect evidence of the isotopic doubling, and confirm the predicted asymmetry in the intensities of corresponding lines in the P and R branches, the summation rule, and the new formulation of the quantum theory. The lines are narrower and "deeper" than was supposed, and the exponential law of transmission fails. Values of the Einstein probability of transition coefficients are computed to be $B_{0,1}=5{\cdot}12\times10^{15}$ for the first line of the positive branch and $A_{0,1}=58$ for the first line of the negative branch. The preferred value of the variation of the molecular moment with nuclear displacement as determined for the region of the equilibrium position is $0{\cdot}828\times10^{-10}$ e.s.u. A. A. ELDRIDGE.

Index of refraction of water for short continuous waves. L. E. MCCARTY and L. T. JONES (Physical Rev., 1927, [ii], 29, 880—886).—The index of refraction of water for short continuous waves (300—700 cm.) is about 9, in agreement with other results, and approximately constant over the range of frequencies used. A. A. ELDRIDGE.

Molecular spectrum of sodium. H. SCHÜLER (Z. Physik, 1927, 43, 474—479).—From a consideration of the yellowish-red band spectrum excited in sodium vapour by the passage of a continuous current, it is concluded that the spectrum consists of the resonance series of Na_2 which is excited by the sodium D-light and of a Na-series similar to the Lyman–Wittmer H_2-series. R. W. LUNT.

Absorption bands of liquid and vapour amines. E. O. SALANT (Nature, 1927, 119, 926).—The characteristic absorption band of the N–H linking around (A., 1926, 453) is a fundamental, the band at 6 μ being weak, both for secondary and for tertiary amines (cf. also Ellis, this vol., 291).
A. A. ELDRIDGE.

Absorption of light by certain aromatic amino-acids in the ultra-violet. H. HÜNECKE (Ber., 1927, 60, [B], 1451—1457).—According to spectrographic measurements of *o*-aminobenzoic acid, its sodium salt, methyl ester, and hydrochloride in water, the acid exists mainly in the true acidic form, $NH_2{\cdot}C_6H_4{\cdot}CO_2H$. *o*-Dimethylaminobenzoic acid, on the other hand, is chiefly present in water as the "zwitter ion," $\cdot NHMe_2{\cdot}C_6H_4{\cdot}CO_2^+$, probably containing appreciable amounts of the true acid. In trimethylaminobenzoic acid only the "zwitter ion" can be present. In the carboxylic acids of pyridine and quinoline, the acid form is favoured; the proportion of "zwitter ion" cannot at present be determined. H. WREN.

Influence of solvent on absorption spectrum, rate of reaction, and equilibrium. V. G. HEIBE [FELGER and G. ROSSLER] (Ber., 1927, 60, [B], 1406—1419).—The displacement of the centre of an absorption band and the change in height are two distinct processes, the first of which is immediately due to solvation. The second process can occur in different ways according to the structure of the molecule. Relationships are developed between the displacement of absorption bands and the rate and equilibrium of chemical reactions. The possibility of the experimental detection of the deformation of molecules during catalysis is thus given.
H. WREN.

Relation between the absorption spectra and molecular structure of the alkali halides in the vapour state. J. FRANCK, H. KUHN, and G. ROLLEFSON (Z. Physik, 1927, 43, 155—163).—An argument is developed to show that the photochemical decomposition of a polar molecule such as sodium iodide proceeds with the formation of two normal atoms, and also of one normal and one excited atom; that therefore the quantum associated with the low-frequency limit of the first absorption band should correspond with the heat of thermal dissociation measured by thermal methods, and that the difference between the quanta associated with the low-frequency limit of the first and second bands should be equal to the quantum corresponding with the transition $2P_2-2P_1$ in the halide atom. Data obtained on the absorption of sodium, potassium, and cæsium iodides, sodium and potassium bromides, and potassium chloride have shown that the above relationships do obtain approximately. R. W. LUNT.

Absorption and fluorescence spectra of silver iodide molecules, and the nature of their molecular structure. J. FRANCK and H. KUHN (Z. Physik, 1927, 43, 164—171).—The theory previously developed (preceding abstract) has been applied to the absorption of silver iodide vapour. The sum of the heat of dissociation measured thermally, 47,000 g.-cal., and the quantum associated with the transition $2P_2-2P_1$ in the iodine atom 22,000 g.-cal., is 69,000 g.-cal., which is held to be sensibly identical with the quantum corresponding with the low-frequency limit of the first absorption band of silver iodide, 76,000 g.-cal. Silver iodide therefore decomposes in the vapour state to silver and excited iodine atoms. Similarly, the sum of heat of dissociation of hydrogen iodide and the $2P_2-2P_1$ quantum is equal to 91,000 g.-cal., which is in good agreement with the quantum corresponding with the low-frequency absorption limit, 88,000 g.-cal., calculated from the spectroscopic data of Coehn and Stuckardt (A., 1917, ii, 5). It is therefore concluded that the linking of the silver iodide molecule is non-polar. R. W. LUNT.

Extinction of the fluorescence of dyes in solid and in liquid solutions. V. L. LEVSCHIN (Z. Physik, 1927, 43, 230—253).—The fluorescence of rhodulin-orange-*N* and of fluorescein in sugar solution has been examined for concentrations in the range 10^{-2} to 10^{-4} g. per g., and from 4900 to 5900 Å. The ratio of the fluorescence to the absorbed energy falls rapidly as the concentration increases; similar results are obtained with fluorescein in ethyl alcohol, in glycerol, and in water, and with rhodulin in water, in the range 10^{-2} to 10^{-4} g. per c.c. The results also show that for an aqueous solution of fluorescein this ratio is independent of the wave-length in the above range. The influence of temperature in the range 20—80° on this ratio has also been examined; for $c>4\times10^{-3}$ it increases, for $c=2{\cdot}5\times10^{-4}$ it decreases, as the temperature increases. R. W. LUNT.

Measurement of the duration of fluorescence. E. GAVIOLA (Z. Physik, 1927, 42, 853—861).—An optical system has been devised for the measurement of the duration of fluorescence of the order of 10^{-9} sec. with an accuracy of 10%. The ray incident on the fluorescent material passes through crossed Nicols between which is placed a Kerr cell containing nitrobenzene; the reflected ray passes through crossed Nicols between which are placed a second Kerr cell and a plate of Iceland spar. The Kerr effect is without inertia, and it is therefore possible to interrupt rapidly the incident and reflected rays by applying to the Kerr cells a potential of frequency approximately 2×10^7 cycles per sec. The phase difference in the reflected ray, due to the persistence of the fluorescence, is measured by the rotation of the fourth Nicol necessary to produce extinction.

In this way the duration of the fluorescence has been determined for uranium glass, ruby, and for the following substances in solution in water, glycerol, and methyl alcohol: uranin, fluorescein, rhodamine-B, rhodulin-orange, erythrosin, eosin, eosin-5B, uranyl sulphate, uranyl sulphate in sulphuric acid, and quinizarin in pentane. R. W. LUNT.

Influence of temperature and concentration on the rate of decay of the fluorescence of dyes. E. GAVIOLA (Z. Physik, 1927, 42, 862—869).—Using the technique described in the preceding abstract, the influence of temperature and concentration on the time for which fluorescence persists has been examined for the following substances: fluorescein, rhodamine-B, and rhodulin in solution in methyl alcohol and in glycerol. The time interval diminishes with increasing concentration and with increasing temperature; correspondingly, the intensity of the fluorescence and the degree of polarisation diminish. An approximately linear relationship is observed between this time interval and the intensity of the fluorescence. The order of magnitude of the persistence of fluorescence is 5×10^{-9} sec.

R. W. LUNT.

Yield of fluorescence at the *K* level for the *K*α lines. V. POSEJPAL (Compt. rend., 1927, 184, 1541—1543).—A general expression for the yield of fluorescence at the *K* level, based on the author's previous assumptions (this vol., 91), is deduced, and shown to give results in good agreement with experiment. J. GRANT.

Fluorescence of cadmium. W. KAPUŚCIŃSKI (Bull. Acad. Polonaise, 1927, A, 1—26).—The fluorescence of cadmium vapour at temperatures below 1000° has been examined. It is excited by the light from the condensed spark between electrodes of cadmium, zinc, mercury, copper, aluminium, carbon, and iron, and from mercury, cadmium, and iron arcs. The fluorescence consists of a large band between 5100 and 3800 Å., with secondary maxima in the range 4200—3950 Å. At temperatures below 500° the fluorescence is excited by radiation in the neighbourhood of 2300 Å.; at 850° the effective absorbing region extends from 3100 to 2100 Å.

R. W. LUNT.

Band-types and absorption-edge series in alkaline-earth phosphors. F. SCHMIDT (Ann. Physik, 1927, [iv], 83, 213—246).—The spectral distribution of phosphorescence light has been to a considerable extent reduced to order. The position of maximum intensity (λ) of the *d*-excitation is connected with the dielectric constant of the phosphor by means of the relation $\lambda_0=\lambda/\epsilon^{\frac{1}{2}}$, in which λ_0 is termed the absolute wave-length and is a constant for analogous bands of the same metal in different diluents. The sulphide phosphors are divided into five groups showing the same absolute *d*-positions and λ_0 values within a group. The first group includes only Biα; the band-type is due to tervalent sulphide (oxide) linkings with the metal, and the λ_0 values of 77, 113, and 147 μμ are well separated. The second group includes Cuα, Mnα, Znα, Pbβ, Agβ, Biβ, and the λ_0 values of 78, 98, 121, 146, and 174 μμ exhibit close spacing, whilst the band-type is ascribed to bivalent sulphide (oxide)–metal linking. The third group, Pbα and Agα, shows λ_0 values of 103, 121, and 147 μμ, whilst the fourth group consists of Cuβ only; the narrow spacing 78, 94, 113, 136, 160 μμ is shown, and the band-type is regarded as due to univalent sulphide–metal linking. The fifth group, Cuγ, Pbγ, Znδ, shows 86, 99, 118, 137, 154 μμ as the λ_0 values. In order to classify the bands the idea of absorption-edge series is used. The relations $\nu_n=K/n^2$ or $\nu_{obs.}=K/\epsilon^{\frac{1}{2}}\times n^2$ (K is a constant for a given band-type, ν_n and $\nu_{obs.}$ correspond with λ_0 and λ, and n has integral values) reproduce the observed series. The results for sulphide phosphors, oxide phosphors, and selenide phosphors are tabulated.

The SrS–Ag phosphors have been studied afresh and the *d*-positions of type III more accurately measured. Two new *d*-positions are recorded, so that there are now five of these. The distribution of excitation with time for the γ-band of silver has been measured. It is also shown that by raising the heating temperature and by increasing the duration of the heating process in the preparation of CaS–Cu and SrS–Cu phosphors, the respective dielectric constants are decreased. The occurrence of definite types of bands characteristic of a given metal does in these cases actually follow the expected lines when the dielectric constant of the same phosphor is varied in the process of preparation. The failure to obtain a constant for the type V of the sulphide bands is discussed and an explanation advanced.

R. A. MORTON.

Triboluminescence. G. RENZO (Gazzetta, 1927, 57, 278—290).—A number of organic and inorganic compounds have been examined in order to investigate Karl's theory that the origin of triboluminescence is in the impurities in the substances which exhibit this phenomena. Whilst the results are not completely conclusive, it is concluded that triboluminescence occurs in pure substances; in particular, potassium bromate repeatedly recrystallised is characterised by a strong luminescence, which is diminished by the addition of the impurities to be found in the mother-liquors. R. W. LUNT.

Ionisation potential of methane. E. PIETSCH and (FRL.) G. WILCKE (Z. Physik, 1927, 43, 342—353).—The ionisation potential of methane has been redetermined by investigating the current–voltage curve for platinum electrodes in methane at 10^{-2} mm.

The cathode was coated with barium oxide and calcium fluoride (10 : 1) to facilitate the electron emission, and the methane was specially purified. The following critical potentials were observed: 9·65±0·4, 11·14±0·1, 12·49±0·1, 13·59±0·1, 14·58±0·05, 15·40±0·05, 16·29±0·07, and 18·22±0·18 volts. They were identified respectively as: ionisation of mercury, first excitation of hydrogen molecule, critical potential of hydrogen molecule, ionisation of hydrogen atom, ionisation of methane, decomposition of methane, ionisation of hydrogen molecule, and the dissociation of the hydrogen molecule with the formation of one hydrogen ion. The value 15·40 volts assigned to the decomposition of methane agrees with the value of 15—16 volts obtained by the author previously for decomposition by electron collision (A., 1926, 1109), and with the value 15·7 volts obtained for the thermal decomposition. On the assumption that the critical potential observed at 18·22±0·18 volt corresponds with the dissociation of a hydrogen molecule, with the formation of one hydrogen ion (H^+), the heat of dissociation is equal to this value, less the ionisation potential of the hydrogen atom, 13·59±0·1 volt; the value thus obtained, 4·63±0·18 volt (=106·7±4×10³ g.-cal.), is in good agreement with the recent determination of the heat of dissociation, 106·7±3×10³ g.-cal., by Bodenstein and Jung (A., 1926, 680). R. W. Lunt.

Electron emission under the influence of chemical action at higher gas pressures, and some photo-electric experiments with liquid alloys. O. W. Richardson and M. Brotherton (Proc. Roy. Soc., 1927, A, 115, 20—41; cf. Brotherton, A., 1924, ii, 377).—The emission of electrons when alloys of sodium and potassium react with carbonyl chloride at pressures of not less than 0·001 mm. has been examined, using a modified form of the apparatus previously described (*loc. cit.*). With an alloy of fixed composition and constant gas pressure, the electron emission increases rapidly with increase in the number of drops per sec., and when the rate and size of the drops are kept constant, the emission is independent of the gas pressure over a range of pressure from 0·005 to 0·05 mm. In the case of a drop of alloy at the centre of a large spherical electrode, if the contact *P.D.* between the two surfaces is taken into consideration and a Maxwell distribution of energy for a temperature of about 3300° Abs. is assumed, then the energy of the emitted electrons can be calculated. The photo-electric determination of the contact potential gave figures much higher than the chemical determination, but for an alloy containing 77% of potassium (NaK_6) the two are identical. In previous experiments, the average energy of the electrons expressed as an equivalent temperature was found to be 3300° Abs., whilst the temperature now found, as a mean of 44 determinations, is 2368° Abs. The results strengthen the view that the phenomenon is a direct chemical emission, and not due to secondary thermionic effects. The difference between the values obtained in the photo-electric and chemical determinations of the contact potential can be explained by the assumption that the chemical reaction does not take place uniformly over the surface of the drops, but occurs in localised patches which gradually extend to the periphery. This is in agreement with threshold frequencies determined with and without carbonyl chloride, the difficulty of obtaining saturation in certain cases, and the breaking down of the agreement with the Maxwell formula in the region of zero emission velocity. Certain hysteresis effects are also discussed. L. L. Bircumshaw.

Dielectric constants of ethyl ether and ethyl alcohol vapours. R. Sänger (Physikal. Z., 1927, 28, 455—457; cf. A., 1926, 993).—The values of the dielectric constants of ether and alcohol vapours accord with the formula $\varepsilon-1=A+B/T$ (ε the dielectric constant, T temperature Abs., A and B constants). The electric moments of the molecules are calculated from the determined values of the constant B.
W. E. Downey.

Molecular scattering of light in aqueous solutions. I. S. Venkateswaran (Indian J. Phys., 1927, 1, 235—244).—The scattering of light by aqueous solutions of nitric, hydrochloric, and sulphuric acids has been studied experimentally. The optical anisotropy of the nitric acid molecule is found to be greater than that of the sulphuric acid molecule. These aqueous solutions behave more like single liquids than like binary mixtures.
W. E. Downey.

Law of periodicity. II. Optical properties of unsaturated compounds. P. Petrenko-Kritschenko (Ber., 1927, 60, [*B*], 1324—1326; cf. A., 1926, 1121).—Well-marked periodicity is observed in the optical properties of a series of compounds so arranged that the mutual influence of double linkings in their molecules continuously increases (groupings, –C:C·C·C:C–, C:C·C:C–, C:C:C, benzene, benzene derivatives containing a double linking in α-position to ring, furan, thiophen, and pyrrole, naphthalene).
H. Wren.

Colours of chromous, vanadous, and tervalent uranium ions. K. Someya (Sci. Rep. Tohoku Imp. Univ., 1927, 16, 411—416).—See this vol., 432.

Colour of silver chromate. (Miss) F. Bush (J. Physical Chem., 1927, 31, 931—932).—The difference in the appearance of silver chromate is caused by the rate of precipitation, and not by the action of sunlight (cf. Hunt, Mem. Chem. Soc., 1845, 2, 316). The slower the addition of potassium dichromate to the silver nitrate, the darker and more lustrous do the crystals of silver chromate become. The presence of free acid and an increase in temperature produce similar effects. L. S. Theobald.

Measurement of the ratio h/k from the anomalous dispersion of thallium vapour. E. Fernie and F. Rasetti (Z. Physik, 1927, 43, 379—383).—By applying the Boltzmann distribution law to the number of atoms of element in two different quantum states in thermal equilibrium, an expression $\log d_1/d_2 = \text{constant}+h\Delta\nu/kT$ is obtained, where d_1 and d_2 are the coefficients of anomalous dispersion, corresponding with the quantum states ν_1 and ν_2, h is Planck's and k Boltzmann's constant, and T the temperature Abs. This has been applied to the temperature variation, in the range 1280—1500° Abs., of the

coefficients of anomalous dispersion of thallium vapour for the lines 3776 and 5350 Å., corresponding with the quantum states 6^2P_1 and 6^2P_2. The value of h/k so obtained is $3{\cdot}9\times10^{-11}$, in satisfactory agreement with the true value, $4{\cdot}8\times10^{-11}$. Normal values have been obtained for the refractivity of thallium vapour, in contradistinction to the anomalous values reported by McLennan (Proc. Roy. Soc., 1922, **A**, 100, 191). R. W. LUNT.

Selective absorption, rotation, and magnetic rotation of camphorquinone in toluene. A. KRETHLOV (Z. Physik, 1927, **42**, 840—852).—Measurements of the extinction of camphorquinone in toluene (0·17—4·7 g. per 100 c.c.) using a Konig–Marten spectrophotometer have been made for 33 wave-lengths between 6320 and 4400 Å. In this region, the Beer–Lambert law is obeyed within about 8%. The extinction–wave-length curve obtained corresponds with four maxima at 4840, 4690, 4540, and 4370 Å. These maxima are discussed with reference to Pfleiderer's data (Z. Physik, 1926, **39**, 663) on the rotation and the magnetic rotation in the same region of wave-lengths. R. W. LUNT.

Magnetic double-refraction in paramagnetic gases. K. S. KRISHNAN (Indian J. Phys., 1927, **1**, 245—254).—The theory of spatial quantisation is applied to the molecular magnetic moments of nitric oxide, and it is deduced that nitric oxide should exhibit double refraction. Actually no double refraction could be detected. This result is discussed, and it is concluded that paramagnetic molecules do not orientate, at least as a whole, in a magnetic field. W. E. DOWNEY.

Chemical valency. C. D. NIVEN (Phil. Mag., 1927, [vii], **3**, 1314—1334).—In part speculative. The Heisenberg–Hund model of the extra-nuclear electronic configurations in the atom is used to explain the properties of chemical compounds. Many properties are satisfactorily accounted for, and the general conclusions are in accordance with Werner's co-ordination theory. A. E. MITCHELL.

The parachor and chemical constitution. V. Evidence for the existence of singlet linkages in the pentachlorides of phosphorus and antimony. S. SUGDEN [with A. FREIMAN] (J.C.S., 1927, 1173—1186).—The parachors of phosphorus and antimony pentachlorides are lower than the sum of the atomic constants by 26 units. Since the additive nature of the parachor has been verified for a large number of substances, this is taken to mean that the pentachlorides possess a type of linking which has not been met with in the compounds previously studied.

From a discussion of electron valency formulæ and the effect of the number of electrons in a linking on the structural constants for unsaturated linkings, it is concluded that these compounds contain two singlet linkings, each consisting of one electron held in common by two atoms. Each singlet should give a contribution of −12·4 to the parachor, so that the pentachlorides studied contain two such linkings, in agreement with the formula of Prideaux (Chem. and Ind., 1923, **42**, 672).

The electronic theory of valency is extended to include linkings composed of an odd number of shared electrons, and is applied to the formulation of higher halides, co-ordination compounds, and "molecular" compounds for which, hitherto, it has not been possible to write electronic formulæ without violating the octet rule. J. S. CARTER.

Constitution of boron compounds. A. STOCK (Ber., 1927, **60**, [*B*], 1039—1040).—Ullmann's formulation of the hydrides of boron and related compounds is considered unsatisfactory, since it offers no adequate explanation of the chemical properties of these compounds (cf. this vol., 399). H. WREN.

[Electronic interpretation of the constitution of the boron hydrides and of compounds of boron.] E. MÜLLER (Ber., 1927, **60**, [*B*], 1323—1324; cf. A., 1925, ii, 841).—An adverse criticism of the views of Ullmann (this vol., 399). H. WREN.

Relation between complex formation and the structure of the central atom. H. LESSHEIM, J. MEYER, and R. SAMUEL (Z. Physik, 1927, **43**, 199—221).—A general classification of complex formation is described based on considerations of the orbital structure characterising the central atom of the complex. R. W. LUNT.

Molecular constitution of liquids. W. KISTIAKOVSKI (J. Chim. phys., 1927, **24**, 309—324).—Liquids may be classified according to their molecular constitution into seven groups: (1) those negligibly (*e.g.*, the noble gases), (2) feebly (hydrocarbons), or (3) sensibly polymerised (liquid nitrogen and oxygen, esters and ethers); (4) strongly polymerised with unassociated vapours (water, alcohols, nitriles, amines, nitro- and sulphonic acid derivatives); (5) strongly polymerised with associated vapours (sulphur, phosphorus, etc.); (6) ionic liquids (fused salts), and (7) electronic liquids (fused metals). The Guldberg–Guye ratio T_C/T_B, where T_C is the critical temperature and T_B the normal b. p., both on the absolute scale, is of the order 1·5 for substances of the first three groups; the ratio V_C/V_B, where V_C is the critical volume and V_B the liquid volume at the b. p., is of the order 2·67, and the critical pressure 37·5 atm. ±25%; none of these quantities can be used for classification, for whereas the polymerised substances of the fourth and fifth groups usually deviate widely from the normal values, some conform to them. Similarly, the formula for the latent heat of vaporisation at the b. p. Q_B (g.-cal.)$=RT_B\log R'T_B$, where R is the gas constant in g.-cal. and R in c.c.-atm., which usually fits substances of groups 1 and 2, occasionally fits those of group 3. The relationship $\log V_1/V_2=T_2/T_1$, where V_1 and V_2 are the volumes of vapour at T_1 and T_2, respectively, holds only for the first three groups, and thus serves to distinguish these from groups 4 and 5. S. J. GREGG.

Florentium or illinium? W. A. NOYES (Nature, 1927, **120**, 14).—A question of priority. A. A. ELDRIDGE.

***X*-Ray investigations for the identification of the element of atomic number 61 (florentium).** R. BRUNETTI (Gazzetta, 1927, **57**, 335—346).—When a monochromatic pencil of *X*-rays traverses a material layer, it undergoes absorption, the atomic coefficient,

α, of which is a function of the frequency of the incident radiation ν and of the atomic number Z of the element, $\alpha=CZ^4/\nu^3$. The value of C remains constant until ν reaches a critical value ν_0, for which the quantum $h\nu_0$ of the incident radiation equals the energy necessary to detach an electron from one of the orbits of the absorbing atom; C then undergoes a sudden variation to another constant value. At this point, a photographic plate receiving the radiations of the continuous spectrum will exhibit a distinct discontinuity, shown by a blackening with the weaker part towards the lower wave-lengths. Investigation in this way of the discontinuity of the L-orbit shows that Brazilian monazite undoubtedly contains the element of atomic number 61. The wave-length corresponding with the limit of the absorption of the element 61 is found to be 0·2744 Å., the calculated value being 0·2746 Å. T. H. POPE.

Demonstration model for illustrating the Laue effect. G. B. HAGEN (Physikal. Z., 1927, **28**, 453—455).—Small mirrors are arranged to reflect a beam of light. By a suitable arrangement of the mirrors, an effect on the beam of light similar to that obtained by interposing a crystal in the path of an X-ray beam is obtained. W. E. DOWNEY.

Theoretical determinations of crystal parameters. J. E. LENNARD-JONES and (MISS) B. M. DENT (Phil. Mag., 1927, [vii], **3**, 1204—1227).—The mathematical treatment previously adopted for the calculation of the parameters of the carbonate crystals (this vol., 96) has been extended to crystals of the rutile group, to crystals of potassium chlorostannate and of potassium chloroplatinate, and to the crystal of solid carbon dioxide. In the rutile group, it is shown that the parameters vary from crystal to crystal, the variation being in good agreement with experimental values, whereas the theoretical work of Born and Bollnov (Z. Physik, 1925, **33**, 741) leads to identical values for the parameters of all crystals of the group. For potassium chloroplatinate and potassium chlorostannate the theory indicates that the parameters are the same. The ratio of the distance between the metal and chlorine ions in these groups to the side of the unit cell is 0·17, which is identical with Scherrer and Stoll's experimental value for potassium chloroplatinate (A., 1922, ii, 514). The corresponding experimental value for potassium chlorostannate as determined by Dickinson (A., 1922, ii, 287) is 0·245. For the carbon dioxide crystal, the calculated distance between carbon and oxygen ions is in the region of 0·90 Å. This value is in fair agreement with the result of de Smedt and Keesom (A., 1925, ii, 484; Z. Krist., 1925, **62**, 312), but disagrees with that of Mark and Pohland (Z. Krist., 1925, **61**, 293). A confirmatory value of this parameter has been calculated from the heat of sublimation of carbon dioxide. A. E. MITCHELL.

Space-group of aluminium metaphosphate. S. B. HENDRICKS and R. W. G. WYCKOFF (Amer. J. Sci., 1927, [v], **13**, 491—496).—Laue, spectrum, and powder photographs were made from aluminium metaphosphate. Data from them fit a body-centred unit containing 16 molecules and having $a_0=13·63$ Å. The corresponding space-group is apparently Te_6. Since the structure is defined by at least 11 parameters, no determinations of atomic positions are possible. C. J. SMITHELLS.

X-Ray diffraction measurements on some of the pure compounds concerned in the study of Portland cement. E. A. HARRINGTON (Amer. J. Sci., 1927, [v], **13**, 467—479).—The crystal symmetry, axial angles, and lattice constants for a number of compounds have been determined in connexion with the constitution of Portland cement. The following values were obtained: Al_2O_3, rhombohedral, $\alpha=\beta=\gamma=55°\,17'$, 5·130 Å.; Fe_2O_3, rhombohedral, $\alpha=\beta=\gamma=55°\,17'$, 5·406 Å.; $Ca(OH)_2$, hexagonal, $\alpha=\beta=90°$, $\gamma=120°$, 3·580 Å.; $3CaO,Al_2O_3$, cubic, $\alpha=\beta=\gamma=90°$, 7·623 Å.; $5CaO,3Al_2O_3$, cubic, 10 084 Å.; CaO, cubic, 4·797 Å. C. J. SMITHELLS.

X-Ray investigations on the structure of the artificial ultramarines and the problem concerning their relations to the minerals hauyne, nosean, sodalite, lazurite, and nephelite. F. M. JAEGER, H. G. K. WESTENBRINK, and F. A. VAN MELLE (Proc. K. Akad. Wetensch. Amsterdam, 1927, **30**, 249—267).—Powder spectrograms of ultramarines of various colours and of nosean and hauyne are found to be identical. It is found impossible to attribute any definite place in the structure to a number of components of the total mass included within each elementary cell. The colour of the solid mass seems to be connected with the presence of sulphur. W. E. DOWNEY.

X-Ray examination of the lower ω-phenyl normal saturated fatty acids. A. L. PATTERSON (Phil. Mag., 1927, [vii], **3**, 1252—1262).—X-Ray examination of series of ω-phenyl derivatives of lower normal saturated fatty acids from phenylacetic acid to δ-phenylvaleric acid has given the following results. Phenylacetic acid occurs in rhombic crystals belonging to the space-group C_{2v}^5 (*b*) with *a*, *b*, and *c* 4·2, 4·90, and 10·1 Å., respectively. β-Phenylpropionic acid occurs in monoclinic prismatic crystals of the space-group C_{2h} (*a*) with *a*, *b*, and *c* 31·6, 9·83, and 5·54 Å., respectively. γ-Phenylbutyric acid occurs in rhombic crystals of the space-group C_{2h}^5 (*b*) with *a*, *b*, and *c* 17·8, 4·9, and 10·3 Å., respectively. A preliminary survey of δ-phenylvaleric acid has given $b=7·13$, $c=11·32$, and $d_{100}=8·73$ Å. The numbers of molecules per unit cell are respectively 4, 8, 4, and possibly 4. Bragg's measurements of benzoic acid (A., 1922, ii, 128) put this in the space-group C^5_s (*a*) with *a*, *b*, and *c* 21·6, 5·18, and 5·44 Å., respectively, with 4 molecules per unit cell. The effect of the addition of each CH_2-group is discussed. A. E. MITCHELL.

X-Ray spectrographic observations on cellulose acetate. W. JANCKE (Kolloid-Z., 1927, **42**, 186—187).—X-Ray spectrographic investigations, using monochromatic radiation from a copper anticathode, reveal a difference between the fibres of artificial cellulose acetate and acetylated cotton wool. The data are not sufficient to decide whether this is due to a different grouping of the micro-crystals, or to a difference in modification. E. S. HEDGES.

Variability of long diffraction spacings in paraffin waxes. G. L. CLARK (Nature, 1927, **120**,

12).—Values for long spacing and side spacings are tabulated for samples of commercial paraffin waxes having m. p. 57·2°, 54·4°, 51·7°, and 48·9°. The spacings are affected by the rate of cooling of the wax and by the presence of small quantities of other substances. In particular, lead oleate impresses its own spacing on the layers. A. A. Eldridge.

Rate of growth of crystals in different directions. (Miss) M. Bentivoglio (Proc. Roy. Soc., 1927, **A**, **115**, 59—87).—A modification of Wulff's method (Z. Krist., 1901, **34**, 449) for measuring the relative rates of growth of the faces of a crystal is described. The crystal, mounted on a long fine pin, is placed at the centre of a spherical flask filled with 500 c.c. of solution, the zone of faces to be measured being horizontal, and the flask is rotated on a horizontal axis, parallel to that of the zone, at a rate of 4 or 5 revolutions per hr. The crystals investigated were the isomorphous double sulphates of magnesium–ammonium, iron–ammonium, and magnesium–potassium, of the general formula $R''R'_2(SO_4)_2,6H_2O$, belonging to the monoclinic system; and potassium tartrate, $K_2C_4H_4O_6,0{\cdot}5H_2O$, and ammonium tartrate, $(NH_4)_2C_4H_4O_6$, crystallising in the polar class of the monoclinic system. It is found that the various faces of a crystal grown under uniform conditions have characteristic relative rates of growth. The similar faces of a simple form grow at the same rate, even when of different sizes. Thus a misshapen crystal, if grown under uniform conditions, tends towards, but never attains, the ideal form with equal faces. On a combination, unlike faces grow at different rates, and like faces grow at the same rate, except when adjacent to an abnormally developed face of another, fast-growing, form which causes impoverishment of the solution in its neighbourhood and destroys the uniformity of the conditions. Except in this case there is a constant ratio, under the given conditions, between the rates of growth of any two different forms. With polar crystals, devoid of centrosymmetry, the rates of growth of parallel faces may be widely different. In the isomorphous series of double sulphates examined, the order of increasing rates of growth for different forms is widely different in the different salts. The main factors determining the form of a crystal are discussed, and for each of the sulphates investigated an "ideal form" is constructed, which is that which a crystal would possess if its faces had grown from the beginning at the observed rates. L. L. Bircumshaw.

Etch planes in metallic single crystals. H. H. Potter and W. Sucksmith (Nature, 1927, **119**, 924).—Iron crystals were etched with 10% alcoholic nitric acid solution, nickel crystals with concentrated ferric chloride solution, and aluminium crystals with sodium hydroxide followed by ferric chloride. For iron, the etch planes are (100); for aluminium the planes are (100), with faint reflexions in a few cases from (110) planes. In nickel, (111) and (100) facets are formed. A. A. Eldridge.

Effect of grain-size on the hardness of pure iron. T. Ishigaki (Sci. Rep. Tôhoku Imp. Univ., 1927, **16**, 285—293).—The effect of crystal size on the Brinell hardness of "Armco" iron has been measured, and also the effect on the "initial hardness," H_0, given by the relation $H_0-K/\pi D$, where K is the tangent at the origin to the load–depth curve and D the diameter of the steel ball. The Brinell hardness increases at first rapidly and then slowly, as the grain number, measured by the method of Jeffries, increases, whilst the initial hardness increases almost linearly, except with single crystals. The increase in Brinell hardness was 23%, and that of the initial hardness 51% per 1000 grain number, the amount of change being much greater than that found by other workers for copper and bronze. W. Hume-Rothery.

Determination of mol. wt. by centrifuging. II. T. Svedberg (Z. physikal. Chem., 1927, **127**, 51—70; cf. A., 1926, 340).—A new method for the determination of the mol. wt. of proteins by means of the ultra-centrifuge has been developed. This method, which is more rapid and more accurate than the previous one (*loc. cit.*), is based on the measurement of the velocity of sedimentation of the molecules. It has been applied, with the aid of a special ultra-centrifuge of the oil-turbine type capable of developing a centrifugal force approaching 90,000 times the gravitational force, to the determination of the mol. wt. of carbon monoxide–hæmoglobin. It was found that this protein is nearly homogeneous, comprising 80—90% of molecules of weight 66,800 with approximately equal amounts of molecules of weights 33,400 and 100,200. G. A. Elliott.

Possibility of an allotropic change at the point of transition to the superconducting state. W. H. Keesom and H. K. Onnes (Arch. Neerland., 1927, IIIA, **10**, 221—223).—Bridgman's hypothesis that metals which show superconductivity undergo a polymorphic change at the transition point has been tested for lead. The *X*-ray diffraction pattern obtained at the temperature of liquid helium was found to be the same as that obtained at the ordinary temperature, and it is concluded that no change in the crystalline state occurs. C. J. Smithells.

Disturbance of superconductivity by magnetic fields and by currents. The hypothesis of Silsbee. W. Tuyn and H. K. Onnes (Arch. Neerland., 1927, IIIA, **10**, 224—258).—Little data have been available with which to test Silsbee's hypothesis connecting the threshold values of the current and the magnetic field. Recent data obtained in other researches are reviewed in this connexion, and appear to support the hypothesis. C. J. Smithells.

Properties of superconducting metals in the form of thin films. G. J. Sizoo and H. K. Onnes (Arch. Neerland., 1927, IIIA, **10**, 259—265).—The temperature at which the resistance of sputtered films of tin about 0·5 μ thick disappeared was determined. It varied with different specimens, and changed slightly with time, but in general was 0·1—0·2° lower than for wires. This is attributed to the granular structure of the films. The effect of the current and of a magnetic field on the conductivity was found to be the same for films and wire. Sputtered films of bismuth did not exhibit superconductivity at 1·24° Abs. C. J. Smithells.

Influence of elastic deformation on the superconductivity of tin and indium. G. J. Sizoo and H. K. Onnes (Arch. Neerland., 1927, IIIA, **10**, 266—279).—The temperature at which the electrical resistance of wires of tin and indium disappears was found to be raised by tension and lowered by pressure. For indium, a pressure of 200 kg./cm.^{2} lowered the temperature 0·006°. C. J. Smithells.

Magnetic disturbance of the superconductivity of tin. G. J. Sizoo, W. J. de Haas, and H. K. Onnes (Arch. Neerland., 1927, IIIA, **10**, 280—304).—Superconductivity can be disturbed by an external magnetic field, and it is found that the curve connecting field strength and resistance is in the form of a hysteresis loop. Single crystal wires of tin do not show this effect, which is attributed to the discontinuity at the crystal boundaries.

C. J. Smithells.

Electrical conductivity of solid cuprous bromide. P. Fischer (Z. Elektrochem., 1927, **33**, 170—172).—The specific conductivity of solid cuprous bromide has been measured using direct current, and is shown to increase with temperature. Although this suggested that its conductivity was electrolytic, passage of a current through a cylinder of the salt between platinum electrodes did not produce any loss of weight, indicating electronic conductivity (cf. Friederich and Meyer, this vol., 114). When an anode of silver or copper was substituted for platinum, an extremely low value for the specific conductivity was obtained, and it decreased with increasing temperature. The anode remained unattacked. Mixtures of cuprous bromide and potassium bromide exhibit a maximum specific conductivity when the concentration of the latter is about 10%.

H. J. T. Ellingham.

Thermo-electric and electro-thermal properties of single crystals of bismuth. T. Terada and T. Tsutui (Proc. Imp. Acad. Tokyo, 1927, **3**, 132—135).—A preliminary account of the thermo-electric effect in single crystals 15—25 cm. long and 1 mm. diameter of bismuth and cadmium. The effect in cadmium, if any, is very much smaller than in bismuth. By establishing a temperature gradient of 2000° cm.$^{-1}$ across the wire for a few cm. of its length, an *E.M.F.* of 0·003 volt was generated between the ends of the wire. It was found that this *E.M.F.* was approximately proportional to the size of the azimuth of the plane of the thermal gradient to a certain plane containing the axis of the wire. It is shown that this result is to be anticipated if it be assumed that the *E.M.F.* observed is of the form $E=e_{11}\delta T/\delta x+e_{12}\delta T/\delta y+e_{13}\delta T/\delta z$, where x, y, z are the three crystallographic axes, and z is chosen to coincide with the axis of threefold symmetry.

An inverse effect has also been observed by attaching fine insulated thermo-junctions to the opposite sides of a wire through which a current is flowing.

R. W. Lunt.

Magnetic properties of vanadyl chloride and sulphate, and the atomic moment of vanadium. Serrakis (Compt. rend., 1927, **184**, 1430—1432).—Determinations of the variation of the coefficient of magnetisation and of the thermal behaviour of vanadyl chloride and sulphate show that in each case there is a displacement of the Curie point unaccompanied by a change of moment. Quadrivalent vanadium has therefore at least two atomic moments having the values 8 and 9 Weiss magnetons, and corresponding with the chloride and sulphate, respectively. J. Grant.

Thermal conductivity of gas carbon. R. Holm (Z. Physik, 1927, **43** 466—473).—An elaborate technique is described for the measurement of the thermal conductivity of gas carbon. The value of the thermal conductivity k is found to be (gas carbon, mark *A*, Siemens & Co.) 0·039 ±0·002 watt cm.$^{-1}$ per degree, *i.e.*, 0·0093±0·0005 g.-cal. cm.$^{-1}$ sec.$^{-1}$ per degree in the range 25—45°. R. W. Lunt.

Latent heat of vaporisation of benzene at temperatures above the b. p. J. A. Sutcliffe, F. C. Lay, and W. L. Prichard (Proc. Roy. Soc., 1927, **A**, **115**, 88—102).—A detailed description is given of an apparatus for the determinaton of the latent heat of vaporisation of liquids at temperatures above their b. p. The experimental method consists in supplying a measured quantity of electrical energy to a vacuum vessel (employed as calorimeter) containing mercury, in which the bulb of a steel bomb is immersed. The liquid under observation is allowed to evaporate slowly from the bomb, through a fine steel capillary tube, at a rate controlled by manipulation of a needle valve at the top of the capillary tube so that the mean temperature of the calorimeter during the experiment is practically identical with that of a surrounding thermostat. The weight of liquid evaporated is determined by weighing the bomb before and after each experiment, suitable corrections being applied to the loss of weight of the bomb. By the application of the method to the determination of the heat of vaporisation of benzene, consistent results in g.-cal. per g. were obtained at five different temperatures, as follows: L=92·72 at 86·86°, 89·20 at 105·42°, 85·53 at 125·25°, 81·74 at 143·49°, and 79·86 at 151·80°. Each value is the mean of several experiments. The results are in agreement with those obtained by Griffiths and Marshall at temperatures below the b. p. The values calculated from the empirical equation $L=106\cdot868-1\cdot47106+10^{-1}t-1\cdot46582\times10^{-4}t^2-3\cdot60266\times10^{-7}t^3$, in which L is the heat of vaporisation and t is the temperature, are in close agreement with the results obtained by direct experiment at all the temperatures at which experiments have been performed by Griffiths and Marshall and by the authors. The value at the b. p. calculated from the equation is 93·94 g.-cal. per g., in close agreement with that obtained by Nagornov and Rotinjanz (A., 1911, ii, 965), but lower than the value (94·37 g.-cal. per g) calculated on the assumption that the linear relation between the latent heat and the temperature continues to hold accurately from 50° to the b. p. L. L. Bircumshaw.

[M. p. of] monopotassium phosphate. A. R. Merz (J. Amer. Chem. Soc., 1927, **49**, 1511—1512).—Pure monopotassium orthophosphate fuses with loss of water at 252·6° to 254·3°, and not at 96° as reported in the literature. S. K. Tweedy.

M. p. and heats of crystallisation of homologous series. III. Myristic acid derivatives. W. E. GARNER and J. E. RUSHBROOKE (J.C.S., 1927, 1351—1358).—If it be assumed that the increment in the heat of crystallisation per methylene group is the same for all homologous series above C_{10}, then the empirical equation for the m. p. of the even members of the monobasic acids, previously derived (A., 1926, 1087), may be expressed in the general form $T=(x+1{\cdot}030n)/(y+0{\cdot}002652n)$, where n is the number of carbon atoms in the chain, and x and y are constants depending on the nature of the terminal group. To test this equation, the heat of crystallisation of one member of each of a number of homologous series has been determined, viz., myristamide, myristyl alcohol, and methyl and ethyl myristate. The values of x and y for each series may then be deduced (*loc. cit.*), and hence the m. p. for other members of these series. Calculated and experimental values are in fairly good agreement. The effect of the chemical constitution of the polar terminal group on the m. p. is discussed from the point of view of the theory of m. p. previously put forward (*loc. cit.*). The heat of crystallisation of the terminal group is shown to be the chief factor in determining the "equilibrium constant" of the group, and hence the m. p. of the compound.

M. S. BURR.

Course of the m.-p. line of helium at very low temperatures. J. J. VAN LAAR (Proc. K. Akad. Wetensch. Amsterdam, 1927, **30**, 244—248).—Polemical against Keesom (A., 1926, 893). It is shown that if dp/dt becomes 0 at $\pm1°$ Abs., it does not follow that dp/dt would also have to disappear at $T=0$.

W. E. DOWNEY.

Heat of combustion of calcium cyanamide. N. KAMEYAMA and S. OKA (Proc. Imp. Acad. Tokyo, 1927, **3**, 161—163).—The heat of combustion of calcium cyanamide ($CaCN_2$, 98·25; $CaCO_3$, 0·81; CaO, 0·94%) in oxygen has been determined in a bomb calorimeter of the Berthelot–Mahler type. Benzoic acid was mixed with the cyanamide to facilitate ignition, and the heat of combustion was obtained by allowing for the amount of benzoic acid present. The mean value of 2016±3 g.-cal. per g. of $CaCN_2$ was obtained corresponding with the equation $2CaCN_2+3O_2=2CaO+2CO_2+2N_2+322{,}340$ g.-cal.

R. W. LUNT.

Variation of the velocity of sound in gases with temperature. E. J. IRONS (Phil. Mag., 1927, [vii], **3**, 1274—1285).—From the experimental results of Dixon, Campbell, and Parker (A., 1921, ii, 621) and of Partington and Shilling (A., 1923, ii, 214), formulæ to represent experimental data for the variation of the velocity of sound in gases with the absolute temperature have been developed.

A. E. MITCHELL.

Chemical constant of benzene. N. DE KOLOSOVSKI (Bull. Soc. chim. Belg., 1927, **36**, 358—361).—The chemical constant of benzene calculated from available data by the general method is 2·619±0·325.

L. M. CLARK.

Chemical constants and absolute entropy. W. H. RODEBUSH (Proc. Nat. Acad. Sci., 1927, **13**, 185—188).—Disregarding the b.-p. region, the vapour-pressure data for potassium and sodium are represented satisfactorily by the equations $\log p=-4780/T-1{\cdot}40\log T+11{\cdot}670$, and $\log p=-5730/T-1{\cdot}25\log T+11{\cdot}580$, respectively. The entropies at 298° Abs. and 1 atm. of the vapours of potassium, sodium, mercury, and lead are 38·2 (36·9), 36·7 (35·4), 41·7 (41·8), and 42·9 (41·9), respectively. The numbers in parentheses are the values predicted by the Tetrode equation. Theoretical points are discussed.

J. S. CARTER.

Densities of magnesium at its m. p. H. ENDO (Bull. Chem. Soc. Japan, 1927, **2**, 131—134).—The mean coefficient of linear expansion of magnesium between 20° and the m. p., 650°, is 0·00003025. Taking $d_4^{20}=1{\cdot}7410$, the value of d_4^{650} calculated from the coefficient of expansion is 1·6468. Assuming the volume change on melting is 0·0255 c.c./g., the value of d_4^{650} for liquid magnesium is 1·5804.

J. S. CARTER.

Density of cementite. T. ISHIGAKI (Sci. Rep. Tohoku Imp. Univ., 1927, **16**, 295—302).—The densities of hot-forged, annealed steels of varying carbon content were measured, and the density of cementite was determined by extrapolation of the density–composition curve to the composition of cementite. Corrections were applied for the effects of impurities, and the value attained for pure cementite was 7·662, in good agreement with the value 7·680 found by Westgren and Phragmen from *X*-ray crystal analysis (B., 1924, 518).

W. HUME-ROTHERY.

Densities of saturated vapours at corresponding temperatures. W. HERZ (Arch. Pharm., 1927, **265**, 212—213).—The densities of saturated vapours of 41 compounds at two corresponding states have been calculated from published data. The densities at $9/10T_c$ and $2/3T_c$ ($s_{9/10}$ and $s_{2/3}$, respectively) have been compared with d_c and with each other. The ratio $d_c:s_{9/10}$ varies between 6·978 and 3·653, being large for alcohols and small for noble gases, whilst $d_c:s_{2/3}$ varies from 220·4 to 24·57, and $s_{9/10}:s_{2/3}$ from 34·53 to 6·30. There is no constant relationship between the densities of saturated vapours in the sense of the theory of corresponding states.

S. COFFEY.

Electron affinity of hydrogen and the density of the hydrides of the alkali metals. J. KASARNOVSKI and M. PROSKURNIN (Z. Physik, 1927, **43**, 512—515).—The values obtained for the densities of sodium and potassium hydrides using a pyknometer containing dry *cyclo*hexane, 1·40 and 1·47±0·03, respectively, have been used to calculate the grating energy of these substances from Born's equation. The values obtained are 211,000 and 181,000 g.-cal. respectively. The corresponding values of E_H D_H from the Born cycle are −51,000 and −50,000 g.-cal. These are thought to be in good agreement with the mean value of −62,000 g.-cal., calculated from the available data for the hydrides of lithium, calcium, and barium, since there is an error of the order of 10,000 g.-cal. in the heats of sublimation of these metals. The most recent spectroscopic data for the heat of dissociation of hydrogen, D_H is 50,000 g.-cal.; hence the most probable value for E_H is −1000 g.-cal. This value agrees satisfactorily with that com-

puted from Pauling's model of the hydrogen atom (this vol., 287), $E_H = -1850$ g.-cal. The low values obtained for the densities of sodium and potassium hydrides by Moissan, and by Hüttig and Brodkorb, are therefore held to be inaccurate.

R. W. LUNT.

Isometrics of gaseous methane. F. G. KEYES and H. G. BURKS (J. Amer. Chem. Soc., 1927, **49**, 1403—1410).—A previous investigation is repeated with improvements in experimental technique (Keyes, Smith, and Joubert, J. Math. Phys. Mass. Inst. Techn., 1922, **1**, 191). The temperature range was 0—200°. The isometrics of methane show curvature, which increases as smaller volumes are approached, but decreases as the temperaure rises. The Keyes equation of state for methane is $p(\text{atm.})=5{\cdot}1173T/(v-3{\cdot}64e^{-2{\cdot}25/v})-9370/(v+0{\cdot}42)^2$. An equation for the degree of aggregation is deduced, it being assumed that the curvature of the isometrics is caused by aggregation.

S. K. TWEEDY.

Equation of state for easily liquefied hydrocarbons. I. Weight of a litre of *n*-butane. L. VAN BOGAERT (Bull. Soc. chim. Belg., 1927, **36**, 384—394).—The normal density of *n*-butane (prepared by a Wurtz reaction with valeronitrile) is found by the compensating-globe method to be 2·51837 g. (corr.) at 0° and 710 mm. The slight discrepancy between this value and that of Ouedinoff is attributed to a systematic error in the earlier work, either in the pressure measurements or because of an impurity in the gas. An improved manometer is described. Valeronitrile prepared by the method of Adams and Marvel (A., 1920, i, 283) may be separated into two fractions, one of which (b. p. 140·7±0·03°; d_4^0 0·81646; d_4^t 0·80361) has a disagreeable odour and contains only 0·06% of carbylamine.

S. K. TWEEDY.

Viscosities of methyl alcohol, acetone, and ethyl ether at low temperatures. S. MITSUKURI and T. TONOMURA (Proc. Imp. Acad. Tokyo, 1927, **3**, 155—158).—The viscosities of methyl alcohol, acetone, and ethyl ether have been determined in the range 0—120° by a modified form of Ostwald viscosimeter. An interesting device has been employed to obviate the necessity of visual observation of the motion of the liquid between two points in the apparatus. At these points, two pairs of platinum wires are sealed, which constitute two small condensers. Using a heterodyne method at a frequency of 4×10^6 per sec., the instants at which the liquid comes in contact with each pair of wires can be accurately observed by the abrupt change which takes place in the heterodyne note.

R. W. LUNT.

Surface tension of liquid metals. II. Surface tension of bismuth, cadmium, zinc, and anti-

L. L. BIRCUMSHAW (Phil. Mag., 1927, [vii], 3, 1286—1294).—Previous work (A., 1926, 895) has been extended to molten bismuth, cadmium, zinc, and antimony. Determined values are given of the surface tensions in the ranges 300—962° for bismuth, for zinc, 330—600° for cadmium, and 640—974 for antimony. It is shown that the surface ms cadmium passes through a maximum at 495°. Calculations of the total surface energy of e molten metals indicate that bismuth, cadmium, and antimony are all highly associated in the liquid state.

A. E. MITCHELL.

Densities of hydrocyanic acid–water mixtures. M. SHIRADO (Bull. Chem. Soc. Japan, 1927, **2**, 122—124).—Values of d_{18}^{18}, d_4^{18}, and $(d_4^{18})_{\text{vac.}}$ for the complete range of hydrocyanic acid–water mixtures are tabulated. The value of $(d_4^{18})_{\text{vac.}}$ of the pure acid is 0·6913. The following values of d_1^{18} at the concentrations of hydrocyanic acid indicated are illustrative of the variation of density with composition: 0·9927, 5·05%; 0·9838, 10·04%; 0·9578, 20·29%; 0·9376, 26·90%; 0·8290, 60·23%; 0·6919, 100%. Over the concentration range 27—100% of acid, d^{18} varies almost linearly with the concentration of acid. The present values of d_1^{18} for mixtures rich in acid are in complete agreement with those of Walker and Marvin (B., 1926, 271).

J. S. CARTER.

Densities of nicotine–water mixtures. N. SATA (Bull. Chem. Soc. Japan, 1927, **2**, 139—143).—The density–composition curves for nicotine–water mixtures at 30°, 40°, 50°, and 60° have been investigated. Both components have approximately the same density, the values of d_4^{30}, d_4^{40}, d_4^{50}, and d_4^{60} of nicotine being 1·00124, 0·99383, 0·98630, and 0·97890, respectively. The curves at the lower temperatures show a maximum value which tends to disappear as the lower temperature limit for partial miscibility (about 60°) is approached. The densities of the conjugate solutions have been determined at various temperatures between 65° and 120°. At lower temperatures, the nicotine phase is the heavier, but reversal occurs at 96°, and an S-shaped curve is obtained on plotting densities of the conjugates against temperature.

J. S. CARTER.

Critical solution temperatures of mixtures of alcohol and some hydrocarbons. A. BOUTARIC and G. CORBET (Compt. rend., 1927, **184**, 1446—1447).—The determination of the critical solution temperatures of two liquids is often facilitated by the addition of a third substance (*e.g.*, colza oil) which renders the separation of the two layers more easily visible, and raises the temperature at which it occurs. The critical temperatures are plotted as a function of the concentration of the third substance, and the latter is extrapolated to zero to obtain the true result. The critical solution temperature of benzene and methyl alcohol is 29°. Benzene and pure ethyl alcohol are miscible in all proportions, but light petroleum and absolute alcohol are not.

J. GRANT.

General property-function of mixtures [of metals] free from mixed crystals. J. DEJMEK (Physikal. Z., 1927, **28**, 409—417).—Theoretical. An extension of Lichtenecker's work (this vol., 189) on the logarithmic rule for the properties of mixtures. It is shown that the rule correctly describes the properties of mixtures in absence of secondary phenomena.

W. E. DOWNEY.

Magnetic, electric, and thermal properties of nickel-cobalt alloys. H. MASUMOTO (Sci. Rep. Tohoku Imp. Univ., 1927, **16**, 321—341).—The intensity of magnetisation of nickel-cobalt alloys has been measured for different field strengths at

the ordinary temperature. The magnetisation–composition curves have a maximum at 15% and a minimum at 6% of nickel in all fields between 50 and 600 gauss. In weak fields, two minima are shown at 30% and 70% of nickel, the former corresponding with the change from the hexagonal close-packed to the face-centred cubic structure; these minima vanish with increasing field strength. The magneto-striction effect has also been measured. Alloys with 50% to 87·5% of cobalt give complex effects showing a contraction in small and an expansion in large fields. The remaining alloys show contraction only. The 30% nickel alloy has the minimum contraction and maximum expansion. The thermal and electrical conductivities of these alloys have also been measured and vary similarly with the composition, showing maxima at about 25%, and two minima at 10% and 70% of nickel.

W. HUME-ROTHERY.

Coefficient of thermal expansion in nickel–cobalt and iron–cobalt alloys, and magneto-striction of iron–nickel alloys. H. MASUMOTO and S. NARA (Sci. Rep. Tôhoku Imp. Univ., 1927, **16**, 333—343).—The coefficient of expansion of nickel–cobalt and iron–cobalt alloys has been measured. As nickel is added to cobalt, the coefficient of expansion decreases at first very slowly up to 30% of nickel, and then increases comparatively rapidly, reaching a maximum at 40% of nickel. The coefficient then decreases gradually to a minimum at 65% of nickel, and then increases uniformly up to the value of pure nickel. The comparatively rapid increase occurring at 35% of nickel nearly corresponds with the concentration at which the lattice change takes place. As iron is added to cobalt, the coefficient of expansion decreases gradually to a minimum at 47% of iron, rises to a maximum at 65%, then falls to a minimum at 73% of iron, and finally increases to the value for pure iron. There is possibly a break in the curve at 4% of iron, corresponding with the change in lattice. In the magneto-striction of iron–nickel alloys, alloys containing between 5% and 80% of nickel show expansion in all fields. The 81% nickel alloy shows no effect, whilst the alloys rich in nickel show contraction. The elongation–composition curves at all fields show maxima at 20% and 60% of nickel, and a minimum at 25%.

W. HUME-ROTHERY.

Magnetic determination of the solidus and solubility lines in the iron–carbon system. K. HONDA and H. ENDO (Sci. Rep. Tôhoku Imp. Univ., 1927, **16**, 235—244).—The solidus line in the iron–carbon system has been determined by measurements of the magnetic susceptibility of slowly heated specimens of Swedish steels of varying carbon content. The susceptibility of steels diminishes linearly with rise of temperature up to the solidus point or to the solubility point of cementite, when it decreases more rapidly, the curves showing distinct breaks at these points. The solidus line thus determined lies between the lines of Carpenter and Keeling (B., 1904, 608) and of Gustowsky (Métallurgie, 1909, 731), and nearly coincides with those obtained by Asahara (A., 1924, ii, 188) and by Kaya (B., 1926, 325). The limits of solubility of cementite in austenite were similarly obtained by cooling experiments, in which the formation of graphite is avoided; the results agree with those of previous investigators. The materials used contained both silicon and manganese.

W. HUME-ROTHERY.

Magnetic susceptibility of some binary alloys at high temperatures, and their equilibrium diagrams. H. ENDO (Sci. Rep. Tohoku Imp. Univ., 1927, **16**, 201—234).—The diamagnetic susceptibilities of bismuth, cadmium, copper, lead, antimony, tin, tellurium, thallium, and zinc have been determined at temperatures from 20° to 1100°. The results agree with those obtained by Honda (A., 1910, ii, 686). The susceptibilities of different alloys have been measured in both solid and liquid states, to find which of the solid phases correspond with compounds which retain their individuality in the liquid state. Breaks or minima in the susceptibility–composition curves show that the following compounds exist as such in the liquid state in their respective binary systems, with partial decomposition in some cases: Bi_2Te_3, PbTe, $PbTl_2$, Sb_2Te_3, ZnSb, Zn_3Sb_2, SnTe, CdSb, Cu_3Sn, Cu_2Zn_3. On the other hand, several of the solid phases in the complex copper–zinc and copper–tin systems do not correspond with any irregularity in the liquid. Thermal, magnetic, and microscopical analyses of the system antimony–tellurium have been carried out, and show that the limit of solubility of tellurium in antimony is 3% at the ordinary temperature. Alloys containing 3—55% of tellurium represent mixtures of the antimony solid solution (α) and the β solid solution, consisting of antimony dissolved in the compound Sb_2Te_3. When no intermetallic compound is present, the susceptibility–composition curve for the liquid alloys is straight or slightly curved; the systems investigated were bismuth–antimony, lead–bismuth, bismuth–tin, lead–tin, and lead–antimony. In the system antimony–tin, the β (SbSn) solid phase does not seem to correspond with any molecular compound in the liquid.

W. HUME-ROTHERY.

Solvent properties of liquid sulphur dioxide and liquid ammonia towards certain organic substances. F. DE CARLI (Gazzetta, 1927, 57, 347—355).—Liquid sulphur dioxide dissolves many aromatic hydrocarbons. When the latter are liquid at the ordinary temperature the miscibility is complete, whereas solid hydrocarbons usually form 15—30% solutions. Naphthalene is completely miscible, but anthracene and stilbene are only very slightly soluble at the ordinary temperature, whilst additive compounds such as decaline are practically insoluble. The carboxylic acids of aromatic hydrocarbons are almost insoluble in liquid sulphur dioxide, whereas the alcohols, aldehydes, ketones, phenols, ethers, amines, amides, nitriles, and nitro-derivatives dissolve readily. Instead of treating crude 30—32% anthracene oil with liquid sulphur dioxide under pressure to obtain a solid 70—80% anthracene, it seems more advantageous to use the sulphur dioxide to remove the impurities from 85—90% anthracene obtained by other means. Liquid ammonia scarcely dissolves hydrocarbons, whether of open- or closed-chain type. The most readily soluble derivatives

are those of acid character, phenols and carboxylic and sulphonic acids being completely miscible to form dense solutions which yield the solvent very slowly at the ordinary temperature. Amines, amides, nitriles, nitro-derivatives, benzaldehyde, and anisaldehyde dissolve readily, but cuminaldehyde, cinnamaldehyde, and salicylaldehyde are only slightly soluble. Ketones, alcohols, and certain esters are readily soluble, but terpenes, heterocyclic compounds, and open-chain compounds, even if unsaturated, do not dissolve in liquid ammonia. T. H. POPE.

New kinds of mixed crystals. D. BALAREV and G. KANDILAROV (Z. anorg. Chem., 1927, **162**, 344—348).—Barium sulphate, precipitated in different ways, contains up to 3·6% of water, *i.e.*, 1 mol. of water to each mol. of barium sulphate. Part at least of the water is held mechanically, as on crushing the crystals the water content diminishes. Barium sulphate crystals, stained purple by contact with potassium permanganate solution, show no change of structure under the microscope after many days, indicating that the staining is due solely to capillary effects, and not to chemical reaction. Even large crystals of barium sulphate appear to have large internal free surfaces. The velocity of staining shows that the effect is concerned, not merely with the internal surfaces, but also with the number and size of the capillaries. The fineness of the capillaries is indicated by the fact that a porous pot in the walls of which barium sulphate has been deposited acts as a semi-permeable membrane to barium chloride solution. H. F. GILLBE.

Solvent properties of furfuraldehyde and its derivatives. J. P. TRICKEY (Ind. Eng. Chem., 1927, **19**, 643—644).—Furfuraldehyde and its derivatives are good solvents for cellulose nitrate, whilst their low rate of evaporation renders them particularly suitable as solvents in the lacquer industry. Measurement of the relative viscosities (expressed as times of flow from a pipette) at 25° of 8% solutions of cellulose nitrate gave the following results: in amyl acetate, 14·4; ethyl lactate, 35·4; furfuraldehyde, 25·9; methyl pyromucate, 53·6; propyl pyromucate, 64·2; *n*-butyl pyromucate, 80·8; *iso*amyl pyromucate, 79·7; furfuryl alcohol, 91·6; furfuryl acetate, 37·6; tetrahydrofurfuryl alcohol, 69·7. Qualitative data concerning the solubility of various gums and resins in the above solvents are given. W. J. POWELL.

Selective solvent action. IV. Effect of temperature on the solubilities of semi-solutes in aqueous alcohol. R. WRIGHT (J.C.S., 1927, 1334—1337).—If the formation of complexes occurs between the constituents of a mixed solvent, rise of temperature should cause the dissociation of these complexes, and hence affect the solvent power for solutes soluble in one or both of the constituents, due to the fact that more solvent becomes available at the higher temperature. The solubility of five non-hydrated inorganic salts has been determined in 50% by weight aqueous alcohol at 100° and 20°, and the ratio compared with the ratio of the solubilities in water at the same temperatures. The former ratio was considerably larger than the latter, indicating the breaking up of the alcohol–water complexes with rise of temperature. The data of other investigators, for the solubility of potassium nitrate in aqueous alcohol, of concentrations ranging from 5·5% to 90%, at 20° and 60°, when treated in the same way, give the largest deviations from the ratio for pure water in a solvent containing about 20% of alcohol. For alcohol-soluble solutes, similar results are obtained when the solubility of the substance in water, which is never negligible, is taken into consideration. The method employed for the determination of the solubilities is described. M. S. BURR.

Adsorption of vapours by ferric hydroxide gel. J. H. PERRY (Ind. Eng. Chem., 1927, **19**, 746—748).—The adsorption of vapour from vapour–air mixtures by active ferric hydroxide gel containing 6·36% of water is represented by graphs which may be divided into three classes (cf. Munro and Johnson, A., 1925, ii, 191): (i) the adsorption efficiency is never 100%, and decreases continuously until the saturation value is reached (chloroform, acetone, etc.); (ii) the adsorption is 100% efficient for some time, and then proceeds to the saturation point, which is reached only after a long time (carbon tetrachloride, ethyl alcohol, benzene); (iii) the curves are almost linear up to saturation, probably indicating chemical reaction (methyl alcohol). The addition of air to sulphur dioxide or ammonia causes a marked lowering of the saturation capacity of the gel. The gel absorbs about 15% of its weight of water with 100% efficiency, after which the efficiency falls off up to saturation (18% of its weight of water). Pure commercial chloroform contains ethyl alcohol.

S. K. TWEEDY.

Adsorption by metallic hydroxides. IV. Precipitated chromium hydroxide. K. C. SEN (J. Physical Chem., 1927, **31**, 922—930; cf. this vol., 617).—Adsorption by chromium hydroxide differs from that by ferric and aluminium hydroxides in that no true equilibrium can be obtained and the equilibrium is not reversible. Reproducible results are obtained, however, when the time of contact is constant, the adsorption increasing with time. Arsenious acid is adsorbed to a greater extent than sodium arsenite, whereas no difference is found in the case of aluminium hydroxide. Citric, malic, racemic, sulphuric, oxalic, succinic, benzoic, and hippuric acids are considerably adsorbed. Sodium hydroxide is adsorbed to a lesser extent, whilst the adsorption of salts is small. L. S. THEOBALD.

Adsorption from mixed solvents. N. A. SCHILOV and (MLLE.) S. M. PEVSNER (J. Russ. Phys. Chem. Soc., 1927, **59**, 158—170).—See A., 1926, 238.

Electrical adsorption theory. S. G. MOKRUSCHIN and O. A. ESSIN (J. Russ. Phys. Chem. Soc., 1926, **58**, 737—744).—The phenomena of electrostatic adsorption are investigated from the point of view of the law of chance, the molecules being regarded as dipoles (Langmuir). Adsorption is regarded as the neutralisation of opposite electrostatic charges, on the adsorbent and adsorbed particle, without their chemical interaction. The thickness of the resulting "double layer" is of the order of 3×10^{-6} cm., *i.e.*, 300 times as great as the average molecular diameter. The surface of the adsorbent is assumed to consist

of units capable of adsorbing one molecule or ion of opposite charge. An expression is developed for the number of particles adsorbed: $m=K(1-1/2n)$, where m is the number of particles adsorbed by a unit surface, n the total number of particles colliding with it, and K is a probability constant. Expressing m and n in terms of molar concentration, it is calculated that for $n = 8$ the probability is nearly equal to one, and within the limits of analysis, a formula capable of experimental verification is developed, viz., $a=S'(1-1/2\beta)$, where S' = the ratio of total surface to Avogadro's number, and β the ratio of eight times the molar concentration of the adsorbed substance to its concentration at maximum adsorption. The expression is tested by the results of Ghosh and Dhar (A., 1924, ii, 733) for the adsorption of various ions by freshly-precipitated barium sulphate, and found to give satisfactory agreement. M. ZVEGINTZOV.

Thickness of adsorbed vapour films. J. C. W. FRAZER, W. A. PATRICK, and H. E. SMITH (J. Physical Chem., 1927, **31**, 897—905).—The adsorption of toluene and water on plane surfaces of virgin glass has been studied by the method of McHaffie and Lenher (A., 1925, ii, 854). In the case of toluene, the thickness of the adsorbed film is never greater than unimolecular. Washing the glass surface with acids and water renders it no longer plane, and the silica left on the surface is sufficient to account for the multimolecular adsorption observed by previous workers (cf. McHaffie and Lenher, *loc. cit.*). Water vapour reacts with fresh glass surfaces in a similar manner. The significance of these results in relation to existing theories of adsorption is discussed.
L. S. THEOBALD.

Expansion of charcoal on sorption of carbon dioxide. F. T. MEEHAN (Proc. Roy. Soc., 1927, **A, 115**, 199—207).—The expansion of yellow pine charcoal on sorption of carbon dioxide up to a pressure of 1 atm. has been measured by means of an extensometer over the range of temperature 10—36°. The process is reversible, and the expansion is of the same order of magnitude as the moisture expansion in building materials. It is suggested that this type of expansion may be characteristic of rigid gels. Measurements of the expansion in the three grain directions show that it is independent of the direction of the grain. The uniformity of expansion in different directions indicates that the æolotropy of wood is destroyed on carbonisation and that wood charcoal is isotropic. At constant temperature, the relation of expansion to pressure is represented better by the equation $\log E/p-G+HE$ (where G and H are constants) than by the usual expression $E=kp^{1/n}$. The relation of expansion to temperature at constant pressure is given by the equation $1/E-AT+B$. No discontinuity is met with at the critical temperature of carbon dioxide. L. L. BIRCUMSHAW.

Swelling of active carbon. P. N. PAVLOV (Kolloid-Z., 1927, **42**, 112—119).—The swelling of various forms of carbon in different liquids was examined and compared with the adsorption of acetic acid from these liquids. The degree of swelling depends on the liquid in question, increasing in the following series: acetic acid < water < ethyl acetate < benzene = toluene = xylene < carbon tetrachloride. The swelling in water and the adsorption of acetic acid from water by different forms of carbon increase in the following order: graphite, sugar charcoal, animal charcoal, and this is regarded as a measure of the activity of the carbon. The swelling isotherms for carbon have a maximum and a minimum value. The existence of a minimum value enables the isoelectric point to be determined. Animal charcoal and sugar charcoal were found to have two isoelectric points, one in acid solution and the other in alkaline solution. E. S. HEDGES.

Experimental test of the dipole theory of adsorption. W. G. PALMER (Proc. Roy. Soc., 1927, **A, 115**, 227—236; cf. A., 1924, ii, 665; 1926, 239).—The method previously employed for the determination of the critical or cohering voltage, E, of films of gas at a metal surface has now been adapted for the study of adsorption from liquids in which the cohering junction is totally immersed. From values of E, the molecular heat of desorption can be calculated. E increases regularly in the homologous series of primary alcohols, fatty acids, and their ethyl esters according to the relation E^2/l=constant, where l is the length of the chain. The results are interpreted on the basis of views developed by Lorenz and Landé (A., 1923, ii, 13). For the substances examined, the principal doublets are $CH_2{\cdot}OH$, CO_2H, and CO_2Et, and it is shown that the molecular heat of adsorption will be proportional to the moment of the adsorbed molecules, and that this is proportional to $(K-1)$ for a fixed temperature, where K is the specific inductive capacity of the film. The heat of desorption of all the primary alcohols from a platinum surface is 7000 g.-cal. approx., but for the acids and esters the value is a little less. For pentane, E is practically the same for the vapour and the liquid. The mechanism of adsorption of non-polar molecules, such as hydrocarbons, is discussed. L. L. BIRCUMSHAW.

Thermodynamics of the adsorption isotherm. P. BERNAYS (Z. Elektrochem., 1927, **33**, 170).—It is shown that Reichinstein's relation between the partial pressures of the components of a gas mixture and their concentrations in an adsorption layer (A., 1924, ii, 22; 1926, 130) satisfies the thermodynamic condition given by Cassel (A., 1926, 127).
H. J. T. ELLINGHAM.

Interaction between iodine and starch. S. V. GORBATSCHEV and E. N. VINOGRADOVA (Z. physikal. Chem., 1927, **127**, 93—107).—The amounts of iodine taken up by starch granules in equilibrium with iodine solutions of varying concentration increase with temperature or on the addition of electrolytes. The evidence indicates that hydrogen ions are initially adsorbed and that by the removal of these by a rise of temperature or by the neutralising action of the anions of the electrolyte added the starch may adsorb further quantities of iodine. Acetates produce the greatest and sulphates the least adsorption; the position of iodides in the series is not abnormal. When the concentration of effective electrolyte is high, all the hydrogen ions become neutralised and the iodine–starch reaction reduces to

a simple adsorption with a negative temperature coefficient. G. A. ELLIOTT.

Surface tension of aqueous solutions of mono-, di-, and tri-ethylamine. A. SCHNELL (Z. physikal. Chem., 1927, **127**, 121—126).—Measurements were made at 5° for solutions of varying concentration by the Cantor "breaking method." The results may be expressed in terms of Szyszkowski's equation, and according to Langmuir's interpretation of this equation show that the cross-sectional areas of the molecules of the three amines are proportional to the reciprocals of the molecular volumes of the pure amines. Similarly, it is shown that the lengths of the molecules are equal. Traube's rule for homologous series is also valid for these compounds.
G. A. ELLIOTT.

Surface energy of the alkali halides and their solutions. F. DE BLOCK (Natuurwetens. Tijdsch., 1927, **9**, 65—71).—The results previously obtained for the free surface energy of salt solutions (*ibid.*, 1925, **7**, 73—77) are discussed in relation to those recently obtained by Rehbinder (A., 1926, 674). The relations between the surface energies of salts in the fused and crystalline conditions are also considered. S. I. LEVY.

Surface tension of molten metals and alloys. II. Surface tension of tin, lead, antimony, copper, tin–bismuth, lead–bismuth, copper–antimony, and copper–tin alloys, and cast iron. G. DRATH and F. SAUERWALD (Z. anorg. Chem., 1927, **162**, 301—320).—The surface tensions have been determined at temperatures up to 1200°. Copper differs from the other metals in that its surface tension increases with rise of temperature. The alloys fall into two main groups: alloys of bismuth and tin and of bismuth and lead show a very small negative divergence from the law of mixtures, whilst copper–antimony and copper–tin alloys exhibit a very much greater negative divergence. Certain of the copper–tin alloys resemble copper in having a positive temperature coefficient; the temperature coefficient of some of the alloys of the second group is zero. Considerable association and complex formation are suggested by the behaviour of copper and the alloys of the second group. H. F. GILLBE.

Densities of aqueous solutions of certain univalent perchlorates. II. A. MAZZUCCHELLI and A. ROSSI (Gazzetta, 1927, **57**, 383—390; cf. A., 1926, 675).—In agreement with results previously obtained, lithium, silver, and guanidine perchlorates exhibit molecular coincidence pressures which increase considerably with the concentration. Tammann's assumption of the approximately additive character of such pressures would suggest that this behaviour must be regarded as characteristic of the perchlorate anion, but the physical interpretation of the effects presents difficulties.

Guanidine perchlorate, $CH_6N_3ClO_4$, forms anhydrous, non-hygroscopic crystals, and in quantities of 2—3 mg. does not explode when struck on an anvil with a hammer. The values of d^{15} in terms of p, the percentage of salt in solution, are, for lithium perchlorate solutions, $0{\cdot}99913+5{\cdot}9396\times10^{-3}p+1{\cdot}1902\times10^{-5}p^2+5{\cdot}85\times10^{-7}p^3$, and for silver perchlorate solutions, $0{\cdot}99913+7{\cdot}9183\times10^{-3}p+8{\cdot}762\times10^{-5}p^2-5{\cdot}35\times10^{-7}p^3$. T. H. POPE.

Sodium perchlorate solutions. E. CORNEC and J. DICKELY (Compt. rend., 1927, **184**, 1555—1577).—Determinations of the solubility in water of sodium perchlorate at 0—100° are in agreement with those of Freeth (A., 1924, ii, 336). The transition temperature (anhydrous–monohydrate) is 52·75°. The density of a saturated solution of the anhydrous salt is independent of temperature, since the increase in density on cooling produced by contraction is exactly compensated by the decrease due to crystallisation. The influence of sodium chloride, sodium nitrate, and potassium perchlorate on the transition temperature was examined. J. GRANT.

Rotatory power of tartaric acid in solutions of calcium chloride. E. DARMOIS (Compt. rend., 1927, **184**, 1438—1440).—The dispersion of dilute solutions of tartaric acid in a solution of calcium chloride is feebler than that which would correspond with the two components hitherto assumed to be present. Parallel curves result when $[\alpha]$, and the ratio of the amounts of hydrochloric and tartaric acids required to produce the same concentration of hydrogen ions in solutions of these acids in calcium chloride solution, are plotted against the concentration of the tartaric acid. Thus variations of $[\alpha]$ and the p_H value are due to the same cause. The anomalies of tartaric acid may be due to the great variation of $[\alpha]$ from one solvent to another, and the smaller variation due to a change in concentration and the consequent production of simple and complex ions in water and other solvents, respectively. The α- and β-tartaric acids may be two isomeric weak or ψ-acids in equilibrium. J. GRANT.

Rotatory dispersion, in the ultra-violet region, of aqueous solutions of tartaric acid. R. DESCAMPS (Compt. rend., 1927, **184**, 1543—1546).—The dextrorotations of aqueous solutions of tartaric acid (approximately 1, 10, 20, and 50%) increase to a maximum and then fall to zero between λ 5780 and 3650 Å. At lower wave-lengths the rotation is lævo, and increases regularly up to the limiting wave-length employed (2536). The dextrorotations decrease and the lævorotations increase with the concentration. The observed constancy of the Darmois ratio, which is characteristic of a mixture of two substances, and the high lævorotations found even with dilute solutions confirm Longchambon's theory (A., 1926, 385).
J. GRANT.

Maximum absorption and the Kundt displacement. P. VAILLANT (Compt. rend., 1927, **184**, 1659—1660).—An attempt has been made to confirm the modified form of Kundt's rule suggested by the author (this vol., 508) according to which the displacement of the wave-length of maximum absorption λ_m towards the red is determined by the difference between two terms which are proportional respectively to the refractive index and the density of the solvent. The solutions used were obtained by diluting 5 c.c. of an alcoholic solution of eosin to 100 c.c. with each of three solutions made up from water and a glycerol–alcohol mixture having the same density as water,

and also five mixtures of alcohol and a benzene–mineral oil mixture having the same density as alcohol. The observed and calculated values of λ_m differ appreciably for three of the eight solutions.

J. GRANT.

Absorption of ultra-violet light by aqueous sugar solutions in relation to the constitution of the sugar molecules. P. NIEDERHOFF (Z. physiol. Chem., 1927, **167**, 310—311).—The amount of ultra-violet light absorbed by a dextrose solution (cf. this vol., 396) is very small compared with that absorbed by acetone. This is due to the fact that the majority of the sugar molecules in aqueous solution have the ring structure. Similar relations hold for lævulose and the other sugars examined.

A. WORMALL.

Diffusion of electrolytes. M. M. DUBININ (J. Russ. Phys. Chem. Soc., 1926, **58**, 623—629).—The solution to be investigated is allowed to diffuse through a tube fitted with pairs of electrodes at certain distances. The conductivity is measured from time to time, and results are expressed as concentrations. Applying Fick's law, and Planck's expressions for the conduction of heat and electricity in solutions of electrolytes, an expression capable of experimental verification is deduced. The results obtained with calcium chloride solutions show that Fick's law is a limiting case, applicable only to very dilute solutions, and the velocity of diffusion depends both on the concentration gradient and on the absolute value of the concentration. M. ZVEGINTZOV.

Condition of aqueous solutions of sodium urate. G. ETTISCH, L. F. LOEB, and B. LANGE (Biochem. Z., 1927, **184**, 257—272).—Observations on the dark-field illumination, ultrafiltration, and polarisation associated with the Tyndall effect suggest that solutions of sodium urate contain a sol in equilibrium with a true solution. An attempt is made to calculate the number and size of the sol particles and to derive the effect produced by temperature change and by the addition of alkali. Urate sol is considered as a "colloidal electrolyte."

R. K. CANNAN.

Preparation of colloidal lead. F. BISCHOFF and N. R. BLATHERWICK (J. Pharm. Exp. Ther., 1927, **31**, 27—34).—Using a high-frequency current of 10,000 volts, a colloidal solution of lead is prepared according to the Bredig method by arcing between lead electrodes in 400 c.c. of a solution containing 5 g. of dextrose and 4 g. of gelatin per litre, the reaction being adjusted to p_H 7·5 by the addition of potassium hydroxide. The larger particles are removed from the dark solution so obtained by centrifuging, and the resulting preparation is then stable for months if air is excluded. In particular, the toxicity does not increase with time. Besides dextrose, lævulose and glycerol also exert a marked action in preventing the rapid oxidation which occurs in the absence of any polyhydroxy-compound. The solutions of colloidal lead are precipitated with half-saturated sodium chloride solutions, and are very sensitive to acid. W. O. KERMACK.

Preparation of a stable colloidal solution of lead. M. TELKES (J. Amer. Chem. Soc., 1927, **49**, 1382—1386).—An apparatus is described by means of which a colloidal solution of lead in pure water is prepared in an atmosphere of hydrogen by passing an electric spark between lead electrodes immersed in the water. The resulting colloidal solution is black, and is stable when kept in an atmosphere of hydrogen, only the larger particles being deposited. The highest concentration of lead obtained in such a stable solution was 0·2%. When exposed to the air, the solution turns grey in a few hours, and all the lead is precipitated in a few days as a greyish-white powder, consisting chiefly of lead carbonate.

F. G. WILLSON.

Preparation and properties of colloidal molybdic acid. S. J. DIJATSCHKOVSKI and A. V. DUMANSKI (J. Russ. Phys. Chem. Soc., 1926, **58**, 630—638).—The behaviour of free molybdic acid, gradually liberated by the successive addition of small quantities of hydrochloric acid to a solution of sodium molybdate, was investigated by the electrolytic method described by Dumanski (this vol., 308). The free acid reacts in successive stages with the alkali molybdate to give complexes: $Na_2MoO_4 + H_2MoO_4 = Na_2O(MoO_3)_2 + H_2O$ etc. A theoretical method of calculating the amount of hydrochloric acid necessary for the formation of each complex is described, and the behaviour of sodium chromate, which under the same conditions gives similar results, compared. Cryoscopic experiments corroborate the electrolytic data. Two of the theoretically possible complexes, $Na_2O(MoO_3)_4$ and $Na_2O(MoO_3)_8$, were synthesised, and their conductivities and f.-p. depressions found to correspond with those obtained on adding the amount of acid required by the theory. Experiments with Zsigmondy's ultramicroscope showed that colloidal particles appear only when the octamolybdate $Na_2O(MoO_3)_8$ should be formed, the presence of which is confirmed by the characteristic brown precipitate obtained with potassium ferrocyanide.

The colloid was not coagulated either by cooling or heating or addition of electrolytes, and had an apparent mol. wt. of 1139; it thus could be classed with the semi-colloids. A second modification of the colloid—a suspension of the oxide MoO_3, which has much larger particles, exhibiting Brownian movement—also exists. M. ZVEGINTZOV.

Formation of cellulose hydrate. R. O. HERZOG (Z. physikal. Chem., 1927, **127**, 108—112; cf. this vol., 342).—Further examples are given which show that the *X*-ray changes associated with the formation of cellulose hydrate (mercerisation) may be reproduced by dispersion of cellulose to a sol without chemical change. Although the swelling of cellulose during mercerisation is reversible, this is not the case for the lattice changes which occur.

G. A. ELLIOTT.

Effect of gelatin on the size and distribution of macroscopic crystals grown from aqueous solutions. T. S. ECKERT and W. G. FRANCE (J. Physical Chem., 1927, **31**, 877—881; cf. France and McBurney, A., 1924, ii, 314).—The presence of gelatin (up to 1%) in aqueous solutions of copper sulphate and of lead nitrate decreases markedly the

average size of the crystals obtained by evaporation at 27°, but increases the uniformity of the size, the effect increasing with a rise in concentration of the gelatin. Two different grades of commercial material produced similar results. The influence of gelatin on microscopic crystals formed by electrical or chemical precipitation is thus similar to its influence on macroscopic crystals grown from aqueous solution by evaporation. L. S. THEOBALD.

Viscosity of some hydrophobic sols and the effect of addition of electrolytes. D. N. CHAKRAVARTI and N. R. DHAR (Kolloid-Z., 1927, 42, 124—134).—Viscosity measurements were carried out on sols of arsenious sulphide, ferric hydroxide, sulphur, silver, potassium stearate, dicyanine, Prussian-blue, copper ferrocyanide, crystal-violet, and molybdic acid. On addition of small amounts of electrolytes, the charge of the sols is raised and the viscosity lowered; with increasing concentration of the electrolyte, the viscosity passes through a minimum and then rises; at higher concentrations of electrolyte, before flocculation occurs, the charge is reduced and the viscosity rises rapidly. The variation of the viscosity of sols of Congo-red, aluminium hydroxide, Prussian-blue, copper ferrocyanide, and stannic acid with concentration and temperature was also studied. The temperature coefficients are almost identical with those of pure water, suggesting that the particles are enveloped in a sheath of water molecules. Ferric hydroxide and aluminium hydroxide sols are more strongly hydrated than sols of arsenious sulphide of equal concentration. The viscosity of ferric hydroxide sol is lowered by potassium chloride more than by equivalent quantities of hydrochloric acid or ferric chloride. Potassium chloride has an even greater effect on the viscosity of arsenious sulphide sol, but the effect is not so great as that produced by sodium hydrogen sulphide. The viscosity of hydrolysable sols is not diminished by acids to the same extent as by other electrolytes, showing that the repression of hydrolysis raises the stability of such sols.

E. S. HEDGES.

Ageing phenomena in viscosity and conductivity of some sols and electrolytes. N. R. DHAR and D. N. CHAKRAVARTI (Kolloid-Z., 1927, 42, 120—124).—The importance of defining the age of a sol in considering its properties is emphasised. The hydrophobic sols, ferric hydroxide, Prussian-blue, copper ferrocyanide, stannic acid, arsenious sulphide, and crystal-violet, undergo a fall in viscosity and an increase in conductivity with age. On the other hand, the hydrophilic sols potassium palmitate and potassium stearate increase in viscosity with age, whilst the conductivity decreases. Sols of Congo-red and molybdic acid occupy an intermediate position, in that there is a very slight fall in viscosity and an increase in conductivity with age. Sols of ferric hydroxide and stannic acid prepared in the cold vary with their age to a much greater extent than do sols of the same substances prepared under boiling conditions; heating hastens the ageing phenomena. Solutions of cerium nitrate and of nickel sulphate show a very slight increase in conductivity with time.

E. S. HEDGES.

Dispersion of high-molecular compounds by very soluble, strongly hydrated substances. P. P. VON WEIMARN (Kolloid-Z., 1927, 42, 134—140).—The classification of disperse systems into thermodynamically stable "solutoids" and thermodynamically unstable "dispersoids" is discussed and some difficulties are pointed out (*e.g.*, a lowering of temperature may cause a change from the solutoid to the dispersoid state). Casein, fibroin, and cellulose can be dispersed by heating with concentrated solutions of polyphenols in place of the inorganic salts which have been used formerly. By adding casein in small quantities with constant stirring to an aqueous solution of pyrogallol at its b. p. (105—108°), a sol containing 10% of casein can be obtained in a few minutes. With resorcinol as the dispersing agent, the action takes place with greater difficulty. The sols are very viscous even at the b. p. Elastic coagula are obtained by addition of water or alcohol. Natural silk disperses readily in boiling aqueous solutions of pyrogallol or resorcinol (115—125°), the sols (containing about 15% of silk) being very viscous. Addition of water causes a turbidity, but a gelatinous coagulum is produced by addition of alcohol. Cellulose in the form of filter-paper disperses with great difficulty in aqueous pyrogallol solutions of b. p. 145—155°. E. S. HEDGES.

Protective action of Rochelle salt on cupric oxide sol. I. S. K. BASU and M. LAKSHMANAN (J. Indian Chem. Soc., 1927, 4, 29—36).—At low concentrations, *e.g.*, 0·003 millimol. per litre, sodium potassium tartrate coagulates cupric oxide sol; at higher concentrations, the salt causes a reversal of charge in the sol and exerts a protective action, increasing with the concentration of the salt added until at a concentration of 800 millimol. per litre the sol begins to dissolve to a bluish-green solution. The adsorption of tartrate ions by the sol, when plotted against the sodium potassium tartrate concentration, gives a curve which is convex to the concentration axis. The mechanism of protection and coagulation is discussed. B. W. ANDERSON.

Colloid chemistry of "viscose" solutions. IV. Gel-coagulation. T. MUKOYAMA (Kolloid-Z., 1927, 42, 180—183).—In the ageing of viscose solutions, two processes may occur, according to the following scheme: (1) sol ⟶ gel ⟶ synæresis, (2) sol ⟶ coagulation. When processes (1) and (2) take place simultaneously, a coagel is produced. This process of gel-coagulation has been studied, and it appears to occur most readily when the viscose has an alkali content of about 5% and when the content of cellulose is low. The change is hastened by the addition of glycerol, but is prevented by adding an aged viscose sol to the fresh sol. E. S. HEDGES.

Alleged second isoelectric point of gelatin. B. N. GHOSH (J.C.S., 1927, 1250—1252).—The electric charge of gelatin, in contact with solutions of p_H ranging from 3·6 to 8·8, has been determined by an electro-endosmotic method. At p_H 4·8, the charge of the gelatin is zero, becoming negative above this value and positive below. There is no evidence of the second isoelectric point at p_H 7·7 mentioned by other investigators. The electro-endosmotic flow of

water through the set gel indicates that the latter has a porous, network-like structure. M. S. BURR.

Effect of colloidal and semi-colloidal ferric oxide sols on aqueous gelatin solutions. R. WINTGEN and M. VOHL (Kolloid-Z., 1927, 42, 140—149).—Experiments were carried out in the same manner as in previous work (cf. A., 1925, ii, 524; 1926, 1204). The mutual precipitation of chromic oxide sol and gelatin sol was formerly found to differ from that of ferric oxide sol and gelatin sol. It is now found that when most of the chloride ion is removed by thorough dialysis, the behaviour of a ferric oxide sol towards gelatin is similar to that of a chromic oxide sol. From the results, the "equivalent aggregate weight" of gelatin is deduced, giving a mean value of 32,600. This result is discussed in connexion with the values obtained by other workers by different methods. E. S. HEDGES.

Distribution of hydrogen ions between water and gelatin. J. J. JOUKOV, S. A. TSCHUKAREV, and J. N. BUSHMAKIN (J. Russ. Phys. Chem. Soc., 1926, 58, 639—658).—The action of acids and alkalis on gelatin was investigated by the electrometric titration of various acids by alkalis in solutions containing gelatin. The change in p_H of the acid solutions on addition of alkali was determined by a hydrogen electrode. With hydrochloric acid and sodium hydroxide, the presence of gelatin increased the value of the p_H in the acid region, but lowered it in the alkaline. For all concentrations, the isoelectric point was found to be p_H 5·6, which was higher than that usually accepted for gelatin (4·7), but depended on the nature of the gelatin. The amounts of free acid or alkali are proportional to the amount of gelatin at any fixed p_H, within the limits p_H 3 to p_H 10·5, so that a method is devised for calculating the amounts of acid or alkali necessary to obtain any value of in a gelatin solution of given concentration. The amount of hydrogen ion or hydroxyl ion "bound" by 1 g. of gelatin is constant for a given p_H and independent of the concentration of the gelatin, indicating that, probably, the hypothetical, easily hydrolysed compounds between it and the electrolytes do not exist, but the phenomena are due to the adsorption of ions by the gelatin micelle. Further, although the gelatin has acid properties, it "binds" acids more readily than alkalis.

Experiments with sulphuric and acetic acids gave identical results. The isoelectric point is independent of the nature of the acid. Earlier hypotheses are discussed in the light of the above results.

M. ZVEGINTZOV.

Hydration of gelatin in solution. M. KUNITZ (J. Gen. Physiol., 1927, 10, 811—836).—The volume of gelatin present in solution is calculated from the viscosity by means of the formula $\eta/\eta_0-(1+0{\cdot}5\varphi)/(1-\varphi)^4$ (where η is the viscosity of the solution, η_0 the viscosity of the solvent, and φ the volume occupied by the solute per unit volume of the solution). When the concentration of gelatin is corrected for the volume of water of hydration so determined, the relation between the osmotic pressure and the corrected concentration becomes linear. Calculation on this basis gives the mol. wt. of gelatin as 61,500 at 35°. Data are presented which support the view that the hydration of isoelectric gelatin is due to the osmotic pressure of quantities of a soluble substance present in the interior of the micelles (cf. Northrop and Kunitz, A., 1926, 1098). In gelatin at p_H other than that of the isoelectric point, the degree of hydration is increased by osmotic forces which appear as the result of the Donnan membrane equilibrium.

W. O. KERMACK.

Thermal disaggregation of gelatin. Organic natural substances of colloidal nature. M. FRANKEL (Z. physiol. Chem., 1927, 167, 17—36).—Experiments have been carried out to determine the effect of incubation at 36·5° on some of the properties of gelatin solution, when compared with control solutions at the ordinary temperature. Incubation increases the dialysability of the gelatin, and the amount of non-dialysable gelatin may fall to 50% or even less of the non-dialysable gelatin of the control. There is a marked fall in the power of gel-formation and in the optical rotation of the solution; after 650 hrs., the rotation was only 63% of that of the control solution. The importance of these observations lies in the fact that the phenomena occur under variations in the conditions which are biologically possible and that disaggregation takes place without the intervention of any enzyme. A. WORMALL.

Determination of velocity of cataphoresis of colloidal particles. A. F. GERASIMOV (J. Russ. Phys. Chem. Soc., 1926, 58, 601—609).—The velocity of cataphoresis of colloidal solutions was investigated by two varieties of the moving boundary method, to determine the effect of the nature of the electrolyte above the colloid and the influence of outside factors. The practical and theoretical limitations of the moving boundary method and the means of overcoming them are discussed. Experiments made with "collargol" in presence of sodium carbonate, sodium sulphate, and sodium hydroxide show that the velocity of cataphoresis increases at first, soon reaching a constant value. The rate of increase is proportional to the concentration, and differs for different electrolytes. It is probably due to the diffusion of ions into the colloid. The effects of the "separation potential," due to the lagging of the colloid behind the electrolyte, the diffusion of the colloid into the electrolyte, convection currents, and hydrostatic pressure are discussed and attempts at correction made, but without success. M. ZVEGINTZOV.

Role of some physical factors in the electro-capillary penetration of coloured colloids. W. KOPACZEWSKI and W. SZUKIEWICZ (Compt. rend., 1927, 184, 1443—1445; cf. B., 1926, 353).—The effect of substances having special physical properties on the electro-capillary penetration through filter-paper of 2% aqueous colloidal solutions of direct-black *W* (negative), congorubin *FF* (amphoteric), and direct-grey *4B* (positive) has been studied. In such experiments, account must be taken of the viscosity of the medium, which tends to reduce the capillary effect. A reduction in surface tension produces an increase in the electro-capillary penetration (A., 1926, 679). The electro-capillary properties of a hydrosol of sodium oleate (1%) show periodic variations. J. GRANT.

Solubility and diffusion of hydrogen in metals. G. BORELIUS (Ann. Physik, 1927, [iv], **83**, 121—135).—The solubility c of hydrogen at pressure p in metals at high temperatures is given by the empirical equation $c=\alpha e^{-\beta/T}\sqrt{p}$, in which β is a constant characteristic of the metal under investigation and α a temperature function which is apparently the same for all metals at high temperatures. The above equation is given a theoretical interpretation. The fraction of the volume of metal which is occupied by hydrogen must be of the order 1, and experiment shows it actually to vary between 0·1 and 1·0. The speed with which hydrogen traverses a metal sheet when the pressures on the sides are p and zero, respectively, is given by $m=\text{const.}(p^{\frac{1}{2}}-p_i^{\frac{1}{2}})$ at constant temperature, when $p_i^{\frac{1}{2}}$ is dependent on temperature. On the assumption that the diffusion is analogous to the passage of hydrogen through porous materials, the form of the equation, the order of magnitude of $p_i^{\frac{1}{2}}$, and also certain experimental results all receive rational explanation. The assumption also leads to the equation $m=kcT$ (where k is a constant), a relation which is confirmed by the data on iron, platinum, and palladium–platinum at high temperatures. Deviations with nickel and palladium–platinum at lower temperatures are explained by the restricted freedom of part of the dissolved gas. R. A. MORTON.

Permeability of iron and platinum to hydrogen. V. LOMBARD (Compt. rend., 1927, **184**, 1557—1559; cf. A., 1926, 349).—The permeability of iron to hydrogen at 517° at pressures below 760 mm. of mercury is proportional to the square root of the pressure. At 760 mm. of mercury, the permeability (d) of iron or of platinum follows the rule $d=a^t$, where a is a constant and t the temperature. The permeability of iron is the greater, and its value is similar to that of nickel. J. GRANT.

Permeability of membranes. II. Determination of ionic transfer numbers in membranes from concentration chains. L. MICHAELIS, R. McL. ELLSWORTH, and A. A. WEECH (J. Gen. Physiol., 1927, **10**, 671—683).—The transport number of an electrolyte in the pores of a narrow-pored collodion membrane (cf. Michaelis and Hayashi, A., 1926, 901) has been calculated from measurements of the *P.D.* between differently concentrated solutions of the same electrolyte on opposite sides of the membrane. The concentrations were always taken in the ratio of 2 : 1. The transport number of the chlorine ion increases rapidly as the concentration of the solution becomes greater. When associated with various cations, the transport number of the chlorine ion changes in the same way as it does in the absence of a membrane. W. O. KERMACK.

Permeability of membranes. III. Electric transfer experiments with dried collodion membranes. L. MICHAELIS, A. A. WEECH, and A. YAMATORI (J. Gen. Physiol., 1927, **10**, 685—701).—Direct determination of the transport numbers of various salts across a collodion membrane leads to results which, in spite of minor discrepancies, are in substantial agreement with those of the preceding paper (cf. preceding abstract). The mobility of the anions is less than that of the cations, and the transport number itself depends on the concentration of the salt. W. O. KERMACK.

Collodion membranes. I. Preparation and characterisation of uniform membranes. N. BJERRUM and E. MANEGOLD (Kolloid-Z., 1927, **42**, 97—112).—Collodion membranes prepared by the usual method are not uniform as regards permeability. As criteria of uniformity, the following characteristics of the membrane may be used: (1) thickness, (2) water content per c.c. of membrane, (3) permeability to water. The permeability depends on the thickness and on the time allowed for evaporation of the solvent from the membrane before immersing in water. Uniform flat membranes may be prepared by pouring a measured quantity of collodion solution from a burette on to a surface of mercury enclosed by an iron ring floating on the surface of the mercury. The rate of evaporation of the solvent is controlled by a fan revolving at a definite rate. The membrane is removed from the iron ring by immersing in water for some hours. Uniform cylindrical membranes may be prepared by placing a known quantity of collodion solution inside a horizontal glass cylinder, which is rotated, and through which is passed a current of dry air at a definite rate. The product of permeability to water and thickness is constant for membranes of equal water content. When the film is formed in an atmosphere containing water vapour or, better, acetone vapour, the permeability to water is increased, although no alteration takes place in the thickness or the water content. E. S. HEDGES.

Equation of state of a gaseous mixture. J. E. LENNARD-JONES and W. R. COOK (Proc. Roy. Soc., 1927, **A**, **115**, 334—348).—It is shown that the virial coefficient B in the equation $pv-RNT(1+B/v)$ is a quadratic function of the relative concentrations. This relation reproduces satisfactorily the results obtained by Holborn and Otto (A., 1924, ii, 385) for the isotherms of a helium–neon mixture, and by Verschoyle (A., 1926, 894) for the isotherms of a hydrogen–nitrogen mixture. A method for determining the forces between the unlike molecules of a mixture is deduced. It is shown that the pressure of a gaseous mixture may be greater than that of an equal concentration of either of the constituents. This is a natural consequence of the fact that the virial coefficient passes through a maximum value. L. L. BIRCUMSHAW.

Chemical equilibria in non-ideal gases the isometrics of which are linear. F. G. KEYES (J. Amer. Chem. Soc., 1927, **49**, 1393—1403).—The Keyes equation of state, $p=RT/(v-\beta e^{-\alpha/v})-A/(v+l)^2$, holds for a mixture of n_A mols. of A and n_B mols. of B, providing the isometrics of the mixture are linear, where $A=(n_A\sqrt{A_A}+n_B\sqrt{A_B})^2$; $\beta=n_A\beta_A+n_B\beta_B$; $\alpha=n_A\alpha_A+n_B\alpha_B$; and $l=n_Al_A+n_Bl_B$, RT being multiplied by n_A+n_B. An equation is deduced thermodynamically from this for the equilibrium constant of the reaction between two gases in a mixture, and is applied with moderate success up to 600 atm. to the ammonia equilibrium. S. K. TWEEDY.

Equilibrium in a gaseous phase between acid and base: volatility product. A. TIAN (Compt.

rend., 1927, **185**, 67—69).—The law of mass action suggests that the precipitation of solid salt from a mixture of the corresponding volatile acid and basic constituents will occur only when the product of the concentration of the acid and base reaches a certain value. The law has been tested experimentally for acetic acid and pyridine, and, allowing for the great experimental errors, appears to be verified.

J. GRANT.

Influence of intensive drying on the physical and chemical properties of matter. A. SMITS (Natuurwetens. Tijdsch., 1927, **9**, 55—65).—A *resumé* of facts and theories relating to the properties of substances intensively dried, and the supposed changes in the internal equilibria (cf. A., 1926, 1206).

S. I. LEVY.

Causes of the colour changes of cobalt chloride solutions. II. J. GRÓH and R. SCHMID (Z. anorg. Chem., 1927, **162**, 321—332).—The molecular extinction coefficients of cobaltous chloride solutions in acetone and in propyl alcohol have been determined in presence of lithium and calcium chlorides of varying concentrations. Assumptions such that a series of complexes are formed lead to anomalies, and it is postulated therefore that the observed variations in the extinction coefficient are due to variations in the concentration of only one complex. Determination of the solubility of lithium chloride in acetone solutions of cobaltous chloride indicate that the complex formed has the formula $CoCl_4''$, a view which is confirmed by conductivity measurements of solutions of cobaltous chloride in acetone in presence of various proportions of lithium chloride. Further, *E.M.F.* measurements show that an excess of chloride ion is present in mixed acetone solutions of lithium and cobaltous chlorides when the former is present in greater quantity than is required for the formation of $CoCl_4''$. Silver chloride is soluble in acetone when lithium chloride is present, whereas cobaltous chloride does not increase its solubility. Measurements of the solubility of silver chloride in acetone solutions of cobaltous chloride of constant concentration, but of increasing lithium chloride concentration, show that a sharp increase in the solubility occurs when lithium chloride is present in excess above that required for $CoCl_4''$ formation. This view of the nature of the complex is further supported by measurements of ionic mobility.

H. F. GILLBE.

Iodine–iodine equilibrium in solvents forming brown solutions. J. GRÓH [with (FRAU) M. RADVÁNYI, L. URBANEK, and K. LANYI] (Z. anorg. Chem., 1927, **162**, 287—300).—By spectrophotographic measurements and by determination of the increase of solubility of iodine in carbon disulphide and carbon tetrachloride when an active solvent (*i.e.*, one which gives a brown solution) is added, it has been established that 1 mol. of iodine combines with 1 mol. of the latter to form an additive compound. The equilibrium constant of this additive reaction has been determined in carbon disulphide solution in presence of methyl, ethyl, and propyl alcohols and ethyl ether, and in carbon tetrachloride solutions containing methyl, ethyl, and propyl alcohols, ethyl ether, and acetic acid. The heat of the reaction, calculated from the equilibrium constant at various temperatures, lies between 3000 and 4000 g.-cal./mol.

H. F. GILLBE.

Existence of hexatomic iodine molecules in solutions of iodine in carbon disulphide and carbon tetrachloride. J. GRÓH and J. SZELESTEY (Z. anorg. Chem., 1927, **162**, 333—343).—The velocity of the addition of iodine to erucic acid in carbon tetrachloride solution is proportional to the concentration of the acid, but not to that of the iodine. This is ascribed to association of the iodine molecules; only the associated molecules are capable of reacting, since the velocity of the reaction decreases with increasing dilution, *i.e.*, as the association diminishes. Further, investigation of the reaction velocity shows it to be proportional to the cube of the iodine concentration, *i.e.*, that the active molecule is I_6. The same is true of solutions in carbon disulphide. In neither solvent is the reaction complete, the equilibrium constant for the carbon disulphide solutions being 7·78, and for the carbon tetrachloride solutions 19·80.

Measurements of the reaction velocity at 35°, 15°, and 13·8° show that it diminishes rapidly with rise of temperature. It is assumed that the velocity coefficient measured is the product of the true velocity constant of the reaction and the association constant of iodine. By taking an average value for the former, viz., 2·5 for 10° rise of temperature, the heat of the reaction $3I_2 \longrightarrow I_6$ in carbon tetrachloride solution is 19,270 g.-cal./mol. of I_6 formed, and in carbon disulphide solution 17,070 g.-cal./mol.

H. F. GILLBE.

Spectrographic method for the determination of dissociation constants. R. A. MORTON and A. H. TIPPING (J.C.S., 1927, 1398—1399).—The dissociation constant of a weak acid obeying the dilution law is determined by measuring the maximum extinction coefficient for a mixture of the acid with violuric acid of known concentration (cf. A., 1926, ii, 9). The values are only approximate. The method can also be used for measuring the distribution of a base between violuric and another weak acid.

S. K. TWEEDY.

Dissociation constants of hypophosphorous, phosphorous, and phosphoric acids. I. M. KOLTHOFF (Rec. trav. chim., 1927, **46**, 350—358).—The ionisation constant of hypophosphorous acid, as determined by the classical method, increases from $1·0\times10^{-2}$, in a solution of concentration $0·001M$, to $6·2\times10^{-2}$ in $0·05M$ at 18°. Similarly, the first ionic dissociation constant of phosphorous acid increases from $1·6\times10^{-2}$ in $0·001M$ to $6·2\times10^{-2}$ in $0·1M$ solution. K_2 for phosphorous acid, determined by measurements of the p_H value of mixtures of the secondary phosphite with hydrochloric acid, by the quinhydrone electrode, is 2×10^{-7} at 18°. By measurements of the p_H values of mixtures of secondary sodium phosphate and sodium hydroxide solutions, and correction for the concentration of hydroxyl ions, K_3 for phosphoric acid is found to have a mean value of 5×10^{-13}, which is in good agreement with the value found by Abbott and Bray (A., 1909, ii, 660). Taking into consideration the activity of the ions, the conductivity data of

Abbott and Bray (*loc. cit.*) at 18° give values of K_1 for phosphoric acid varying from $8{\cdot}5\times10^{-3}$ to $9{\cdot}5\times10^{-3}$ for concentrations between $0{\cdot}01M$ and $0{\cdot}1M$. The same considerations, however, applied to the calculation of K for hypophosphorous acid, give an increase from $2{\cdot}0\times10^{-2}$ to $5{\cdot}3\times10^{-2}$ for solutions from $0{\cdot}001M$ to $0{\cdot}1M$. According to Kossel's theory, there should be a marked increase in ionisation constants in the order H_3PO_2, H_3PO_3, H_3PO_4, and no explanation of the anomalous behaviour of these acids is yet forthcoming. Hypophosphorous acid, which behaves as a strong monobasic acid, may be titrated, using methyl-orange as indicator. The first stage of phosphorous acid may also be similarly titrated, provided a comparison solution of 3·85 is used. A sharp end-point may be obtained for the second stage in the titration of phosphorous acid by using thymolphthalein as indicator. In the determination of phosphorous acid by oxidation with bromine to phosphoric acid, it was found that, although this reaction goes only slowly in strongly acid solution, it goes very rapidly when the solution is buffered to p_H 4—5. M. S. BURR.

System carbonic acid–carbon dioxide–water. I. Determination of the true dissociation constant of carbonic acid. F. J. J. BUYTENDYK, R. BRINKMAN, and H. W. MOOK (Biochem. J., 1927, **21**, 576—584).—The change in hydrogen-ion concentration in a hydrogen carbonate solution to which strong acid was added was studied by continuous observations of the p_H of the system, with an accuracy of 0·005 p_H and a time lag not exceeding 0·12 sec. The true dissociation constant of carbonic acid is 4×10^{-4}. The hydration constant of carbon dioxide at p_H 7·35 is $5{\cdot}85\times10^{-5}$, and the dehydration constant of carbonic acid at p_H 6 is 1·73. The velocity of dehydration is proportional to the hydrogen-ion concentration. At 7 the hydrogen carbonate system has practically no immediate buffering capacity. S. S. ZILVA.

Mechanism of titration with adsorbed indicators. J. HODAKOW.—See this vol., 743.

Ebullioscopic study of the complexes produced by mercuric chloride and the alkali chlorides. F. BOURION and E. ROUYER (Compt. rend., 1927, **184**, 1449—1452; cf. A., 1926, 796).—The ebullioscopic study of solutions containing mercuric chloride and the alkali chlorides affords evidence of the presence of the two complexes $M[HgCl_3]$ and $M_2[HgCl_4]$. The affinity constants for complexes of the latter type are $5{\cdot}45\times10^{-2}$ and $1{\cdot}31\times10^{-1}$ when M is K and Na, respectively. J. GRANT.

Activity coefficients of sulphuric acid in aqueous solutions with sodium sulphate at 25°. M. RANDALL and C. T. LANGFORD (J. Amer. Chem. c., 1927, **49**, 1445—1450).—The activity coefficients, γ, of sulphuric acid in sodium sulphate solutions are calculated from the *E.M.F.* of suitable mercurous sulphate–hydrogen cells. The relation of $\log\gamma$ to the fractional mean molality of the acid (cf. following abstract) is linear in the more dilute solutions and when ne fractional average molality of the acid is large. er these conditions, the principle of ionic strength agrees best with the facts. S. K. TWEEDY.

Activity coefficient of hydrogen chloride in aqueous solutions with barium and lanthanum chlorides at 25°. M. RANDALL and G. F. BRECKENRIDGE (J. Amer. Chem. Soc., 1927, **49**, 1435—1445).—From the *E.M.F.* of suitable calomel–hydrogen cells the activity coefficients, γ, of hydrogen chloride in pure aqueous solutions and in solutions of barium and lanthanum chlorides are calculated. For interpolation purposes the relation (M=molality or ionic strength) $M^{-\frac{1}{2}}\log\gamma=A+BM^{\frac{1}{2}}$ is more suitable than the functions usually employed. In mixtures of constant ionic strength, $\log\gamma$ is a nearly linear function of the ratio of the geometric mean of the molalities of the ionic constituents of the acid to the molality of pure acid at the same ionic strength. S. K. TWEEDY.

Vapour pressures and activities of aqueous solutions of sodium silicates. A. N. C. BENNETT (J. Physical Chem., 1927, **31**, 890—896).—The depressions of the dew-point of aqueous solutions of commercial sodium silicates and sodium hydroxide have been measured for solutions with the ratio $Na_2O:SiO_2$ varying from 1 : 0 to 1 : 3·95. The activity coefficients of the solutes calculated by the method of Lewis and Randall from these results are compared graphically with those obtained by Harned (A., 1925, ii, 397) and by Harman (this vol., 415). The introduction of an electromagnetic stirrer, which is described, increased the concordancy of the results. L. S. THEOBALD.

Activity of phenol in aqueous salt solutions. K. ENDO (Bull. Chem. Soc. Japan, 1927, **2**, 124—131).—An investigation of the influence of neutral salts on the partition of phenol between benzene and water shows that when the concentration of phenol in the benzene phase is maintained constant, the concentration C of phenol in the aqueous salt solution varies with the salt concentration S according to the equation $\log C_0/C=\beta S$, where C_0 is the corresponding concentration of phenol in the absence of salt and β a constant characteristic of the salt. The quantity β appears to be additive, *e.g.*, the differences between the β-values of corresponding sodium and potassium salts are constant within the limits of experimental error. The complete equation for the distribution of phenol between benzene and an aqueous salt solution at 25° is $B=2{\cdot}272\times10^{\beta S}C+37{\cdot}71\times10^{3\beta S}C^3$, where B and C are the molar concentrations of phenol in the benzene and aqueous layers, respectively. Measurements of the f. p. of aqueous solutions of sodium nitrate, with and without added phenol, furnish qualitative evidence in support of the theoretical deduction that the chemical potential X of phenol at a concentration C, in a salt solution of concentration S, is represented by the formula $X=Z_0+\alpha S+RT\log_e C$, where Z_0 is the potential for unit concentration in the absence of salt and $\alpha=2{\cdot}303\beta RT$. The activity coefficient of phenol is $e^{\alpha S/RT}$. J. S. CARTER.

Relation between the activity of hydrogen and metallic cations in solutions of salts of the heavy metals. (MLLE.) M. QUINTIN (Compt. rend., 1927, **184**, 1657—1659).—Electrometric and colorimetric determinations of hydrogen-ion activities have shown

that, in solutions of the sulphates and nitrates of zinc, cadmium, and copper, the activity of the metallic ion at all concentrations between $M/2$ and $M/2048$ is proportional to that of the hydrogen ion. By the choice of suitable conditions, the constant of proportionality can be made equal to unity. J. GRANT.

Vapour-composition relationships in the system bromine–water. F. H. RHODES and C. H. BASCOM (Ind. Eng. Chem., 1927, **19**, 480—481).—By the distillation method, it has been found that the percentage of bromine in the vapour given off by bromine water increases from 39·48 for a 0·2% solution to 97·7 for a 3·14% solution. The system with two liquid phases boils at 53·6° when the pressure is 748·8 mm. Under these conditions, the aqueous layer contains 3·50% of bromine and the vapour 98·85%. C. IRWIN.

Binary mixtures of volatile liquids in which the molecules of one component are partly associated. F. MICHAUD (Compt. rend., 1927, **184**, 1643—1645).—The partial vapour pressures of a normal component and of the free and associated molecules of a partly associated component can be calculated thermodynamically when the total vapour pressure as a function of the composition of the liquid phase and the compositions of the distillates are known. The dissociation of a volatile substance may then be studied by mixing it with a normal liquid, constructing the vapour-pressure isotherms, and determining the compositions of the distillates. In the case of mixtures of acetic acid and toluene the results are in substantial agreement with those obtained by experiment. J. GRANT.

System thallium–antimony. T. BARTH (Z. physikal. Chem., 1927, **127**, 113—120).—*X*-Ray examination of alloys of these metals reveals the presence of mixed crystals of the compound TlSb with thallium, although the compound is not known in the pure state. The crystal lattice is of the space-centred cubic type (similar to that of cæsium chloride), the edge of the unit cube being approximately $3{\cdot}85\times10^{-8}$ cm. It is shown that for crystals of this type the ratio of the intensity of reflection at the surfaces for which the sum of the indices is even, to the intensity at the surfaces for which this sum is odd, may readily be calculated from the ratio of the electron numbers for the two kinds of ions constituting the crystal. G. A. ELLIOTT.

Oxides. III. Oxides of antimony. A. SIMON and E. THALER (Z. anorg. Chem., 1927, **162**, 253—278).—The chief reasons for the conflicting statements in the literature concerning the oxides of antimony are the extreme slowness with which the equilibrium between antimony pentoxide and its decomposition products is attained, and the fact that many of the reactions which occur are irreversible. An oxide not previously described corresponds with the formula Sb_6O_{13}, *i.e.*, $Sb_2O_3{,}2Sb_2O_5$ or $2Sb_2O_4{,}Sb_2O_5$, and is probably an antimonyl antimonate having the structure $O{:}[Sb{:}(SbO_3)_2]_2$. This new oxide is very stable, and may be heated for a long period at 800° without decomposition commencing; when once decomposition has been initiated, however, it proceeds rapidly at lower temperatures. The tetroxide Sb_2O_4 is stable between 780° and 920°, but at 930° it decomposes very slowly but completely into antimony trioxide and oxygen. The colour changes which take place progressively as the temperature is raised indicate that the decomposition of antimony pentoxide involves the breaking down of a series of complex antimonyl antimonates, together with a change of valency from 5 to 3. The kinetics of the reactions favour this view. Quantitative investigation of the oxidation of the trioxide to the tetroxide by oxygen shows that this process takes place isothermally at 370°, with no indication of the production of intermediate oxides.

The slowness with which antimony pentoxide decomposes is the cause of great difficulty in the determination of the vapour-pressure curves. At 400°, 2 months are required for a constant oxygen pressure to be attained. Nevertheless, by employing a manometer of small volume, the vapour-pressure curves of the oxides Sb_2O_5, Sb_2O_4, Sb_6O_{13}, and Sb_2O_3 have been determined, and from the data so obtained the heats of dissociation of the various oxides have been calculated as follows (kg.-cal.): $2Sb+5O$, 210·325; Sb_2O_3+2O, 42·925; Sb_2O_4+O, 15·035; $\frac{1}{3}(Sb_6O_{13}+O_2)$ 8·49; $Sb_2O_4+\frac{1}{3}O$, 6·545; $2Sb+4O$, 195·29; Sb_2O_3+O, 27·89; $2Sb+3O$, 167·4. H. F. GILLBE.

Solubility of potassium ferrocyanide in water at temperatures up to 25°. R. H. VALLANCE (J.C.S., 1927, 1328—1334).—A number of methods of determining alkali ferrocyanides are critically discussed, and a new one is described involving the conversion of the ferrocyanide into the ferric condition by concentrated sulphuric and nitric acids and subsequent determination of the iron as ferric hydroxide. This method is employed in the determination of the solubility of potassium ferrocyanide in water, at temperatures from 7·4° to 25°. A break in the curve at 18° indicates a change in the solid phase. The density–temperature curve of saturated solutions also shows a slight change in direction above 17°. By the dilatometric method, the transition point is found to be 17·7°. The transition is not between two different hydrates, since crystals above and below the transition point exhibit no apparent difference, either in degree of hydration or in crystalline form. The work of earlier investigators suggests the existence of two stereoisomeric forms of potassium ferrocyanide. M. S. BURR.

Solubility of uric acid in carbonates; effect of carbon dioxide. S. LANG and H. LANG (Biochem. Z., 1927, **185**, 88—112).—Under conditions in which the free escape of carbon dioxide is prevented (*e.g.*, on shaking in a closed flask), the solubility of uric acid bears an exponential relationship to the concentration of carbonate or hydrogen carbonate. The actual solubility observed is much less than would be expected, owing to the fact that small amounts of free carbon dioxide have a great depressing effect on the formation of the acid urate. The possible physiological significance of these results is discussed. C. R. HARINGTON.

Crystallisation of saturated solutions at the b. p. Method of physico-chemical analysis. E. Cornec and P. Klug (Compt. rend., 1927, **184**, 1448—1449).—The temperature at which a salt first starts to separate from a boiling solution containing two salts depends on the ratio of the amounts of the salts present in the initial solution. It may be determined by means of time–temperature curves. The method has been applied to mixtures of the chlorides and bromides of sodium and potassium. Mixtures of ammonium sulphate with copper and with zinc sulphates give curves with three branches, corresponding in each case with two simple salts, and a double salt formed from 1 mol. of each constituent salt. J. Grant.

Setting of plaster of Paris and existence of soluble anhydrite. P. P. Budnikov (Kolloid-Z., 1927, **42**, 149—154).—Calcium sulphate was prepared in absence of water by mixing solutions of calcium chloride and sulphuric acid in methyl alcohol. The product was obtained in a colloidal form: it was dried at 38°, and when heated at 600—700° lost 7—9% of its weight. The question of the existence of a soluble anhydrite thus remains open. The velocity of dissolution in water and the velocity of rehydration, as determined by the change in electrical conductivity, are greater for the synthetic material than for the natural material which has been heated at 140°. E. S. Hedges.

Equilibrium between crystalline zinc hydroxide and aqueous solutions of ammonium hydroxide and of sodium hydroxide. H. G. Dietrich and J. Johnston (J. Amer. Chem. Soc., 1927, **49**, 1419—1431).—Orthorhombic bipyramidal crystalline zinc hydroxide is prepared by the evaporation of ammonia from a solution of pure zinc hydroxide in ammonia. The crystals exhibit no cleavage planes and form a satisfactory zinc standard for volumetric work. The preparation and properties of the crystalline *compounds*, $4ZnO,ZnSO_4,9H_2O$ and $4ZnO,ZnCl_2,8H_2O$, are described. The solubility of the hydroxide crystals in ammonium and sodium hydroxide solutions at 0°, 25°, and 35° is recorded. From the *E.M.F.* of the cell $Zn,Zn(OH)_2(cryst.)|$ NaOH soln.$|HgO,Hg$, the thermodynamic solubility product of the hydroxide is calculated as $3{\cdot}33\times10^{-7}$ at 25° (cf. Wijs, A., 1925, ii, 889). The activity coefficients of zinc hydroxide are calculated; they are very small in alkali solutions, indicating that nearly all the zinc is present as a complex ion. The upper limit for the solubility of zinc hydroxide in water is calculated as 2×10^{-5} mol./1000 g. at 25°. The following free energy changes (25°) are also calculated: $Zn(OH)_2 \longrightarrow Zn^{\cdot\cdot}+2OH'$, $\Delta F=22{,}490$ g.-cal.; $ZnO+H_2O(liq.) \longrightarrow Zn(OH)_2$, $\Delta F=108$ g.-cal. The dissociation constant of the zincate ion is estimated to be $3{\cdot}6\times10^{-16}$. S. K. Tweedy.

Ternary system barium iodide–iodine–water and the formation of polyiodides. A. C. D. Rivett and J. Packer (J.C.S., 1927, 1342—1349).—The system has been investigated at temperatures between −15·8° and 90°, and the results have been plotted on triangular diagrams. In addition to the hydrate, $BaI_2,2H_2O$, which appears a little below 0° and disappears at 98·9°, and BaI_2,H_2O, the temperature range of which has not been accurately determined, a third hydrate, $2BaI_2,15H_2O$, has been found which exists over the range −15·8° to 25·7°. The hepta- and hexa-hydrates, commonly assumed to exist, were not observed. No solid polyiodide was obtained, but remarkably high values for the solubility of iodine were found, especially at the higher temperatures. The saturated solution at 90° corresponds approximately with $BaI_2,10I_2$. For a constant water content of the solution, the ratio of iodine to iodide increases with increase of iodide concentration, and for constant iodide concentration it increases with temperature. The results are explained by supposing that water in a hydrated iodide ion is replaced by iodine, the heat of reaction of the simple ion with water being greater than that with iodine, so that the substitution of the latter for the former is endothermic. M. S. Burr.

System lead chloride–lead iodide–water. A. L. McR. Sowerby (J.C.S., 1927, 1337—1342).—The solubility curve for lead chloride and iodide together in water at 30° consists of three sections. The solid phase in equilibrium with solutions represented by the middle portion of the curve has a composition corresponding with the formula PbICl. This confirms the conclusions of Thomas (A., 1898, ii, 585). No other compound appears to be formed at this temperature. Two methods are described for the determination of small quantities of iodide in presence of chloride. M. S. Burr.

Ternary system sodium chloride–platinum chloride–water at 25°. T. A. Henke (J. Russ. Phys. Chem. Soc., 1926, **58**, 596—600).—The solubility data for the system indicate that the chloroplatinate is hydrolysed in solution.

M. Zvegintzov.

Reciprocal pair $NaCl+KClO_3$ $NaClO_3+KCl$. C. Di Capua and U. Scaletti (Gazzetta, 1927, **57**, 391—399).—Measurements of solubility have been made at 20° of the isotherms derived for the systems $NaCl–NaClO_3–H_2O$, $NaCl–KCl–H_2O$, $KCl–KClO_3–H_2O$, and $NaClO_3–KClO_3–H_2O$. The ternary solid mixtures which exist in contact with the quaternary solutions are (1) $KClO_3$, NaCl, and $NaClO_3$, and (2) $KClO_3$, NaCl, and KCl. The percentage compositions of the corresponding saturated solutions are, respectively, (1) Cl 8·50; ClO_3 22·80; K 1; Na 11·20; H_2O 56·5, and (2) Cl 16·95; ClO_3 1·41; K 5·82; Na 7·98; H_2O 67·84. The Janecke quadratic diagram has been constructed.

T. H. Pope.

Quaternary system $K_2O–NH_3–P_2O_5–H_2O$ between 0° and 25°. Separation phenomena between 0° and 70°. E. Janecke (Z. physikal. Chem., 1927, **127**, 71—92).—Aqueous solutions containing tripotassium phosphate and ammonia may separate into two liquid phases. Crystallisation of the liquid containing the greater proportion of phosphate gives the hydrate, $K_3PO_4,8H_2O$

G. A. Elliott.

Equilibria in systems in which phases are separated by a semi-permeable membrane. XIX. F. A. H. Schreinemakers (Proc. K. Akad. Wetensch. Amsterdam, 1927, **30**, 282—292).—

Theoretical. The phase rule is applied to investigate the influence of pressure on osmotic systems. W. E. Downey.

Rate of dissolution. A. E. Makovecki (J. Russ. Phys. Chem. Soc., 1926, 58, 726—728).—The generally accepted formula which connects the rate of dissolution with the rate of diffusion is criticised. Any solution is regarded as a two-component system consisting of the saturated portion and excess of "free" solvent, and the rate of dissolution is considered to be proportional to the surface of the solid solute and the active mass of the "free" solvent. Equations are developed for the determination of the latter, and solubility experiments with sodium chloride and copper sulphate described, which are in agreement with the hypothesis. M. Zvegintzov.

Displacement of chemical equilibrium at bounding surfaces. D. Deutsch (Ber., 1927, 60, [*B*], 1036—1039).—If a 0·01% aqueous solution of thymolsulphonephthalein containing $1{\cdot}6 \times 10^{-3}N$-hydrochloric acid is vigorously shaken with benzene, the colour of the turbid system changes to reddish-violet, but when quiescence is again established, the aqueous layer resumes its yellow colour and the benzene layer becomes colourless. The process is reversible, and benzene may be replaced by liquid paraffin or by air. If methyl-violet at p_H about >1 is used, an apparent increase of alkalinity is observed at the bounding surface. The effect cannot be merely optical, since it is not observed when the hydrogen-ion concentration of the solution is considerably different from that producing change of colour in the indicator, and, further, all changes in colour are those produced by a change in hydrogen- or hydroxyl-ion concentration on the indicator. Probably the effect is due to an alteration of the dissociation constants of the indicator at the surface. H. Wren.

Reaction provinces. W. P. Jorissen (Chem. Weekblad, 1927, 24, 294—296; cf. A., 1926, 1100).—The compositions of mixtures of three substances which will react under given conditions may be expressed by means of triangular diagrams, which mark out the limits of composition for the "reaction provinces." The slowing down and final arrest of the decomposition of ammonium dichromate by addition of potassium chloride and potassium sulphate are illustrated in this manner. The extent to which carbon dioxide and carbon tetrachloride vapour, separately and together, may be added to an explosive mixture of methane and air (9% methane) in order to render the whole non-explosive is shown both by a simple curve and by a triangular diagram. The conclusions of Tanaka and Nagai (A., 1926, 1106) on the limits of composition for explosibility in mixtures of hydrogen with air and ethyl bromide are discussed and criticised. S. I. Levy.

Reaction regions. XIV. Closed reaction region. W. P. Jorissen and C. Groeneveld (Rec. trav. chim., 1927, 46, 369—372; cf. A., 1926, 246; this vol., 314).—If a mixture of aluminium turnings or powder, sulphur, and silica be packed in a tube closed at one end and above it a layer of mixed sulphur and iron powder, ignition of the latter will bring about a reaction in the first mixture if the latter is of suitable composition. By taking definite proportions of two of the three constituents, determining the upper and lower limits of the amount of the third substance necessary to produce a reaction, and plotting on a ternary diagram, a closed curve is obtained. Mixtures of a composition represented by points within this curve will react; those outside will not. M. S. Burr.

Radiochemistry and photo-electricity. R. Audubert (J. Chim. phys., 1927, 24, 357—369).—The uncertainty involved in the application of the formula $Q=H(\nu'-\nu)$, where Q is the energy change, ν and ν' the frequencies for the direct and reverse reactions, and H the product of Planck's constant and Avogadro's number, may be avoided by taking as ν and ν' the threshold frequencies. This formula has been examined by means of *E.M.F.* measurements with a cell consisting of a solution of an electrolyte into which dip two electrodes, one kept dark and the other illuminated (cf. A., 1923, ii, 827). The threshold frequencies are obtained by assuming a linear form for the *E.M.F.*–frequency curve, and extrapolating to zero *E.M.F.* With ferric salts, the *E.M.F.* due to the light is positive, *i.e.*, the illuminated electrode behaves as anode. For ferrous sulphate, the observed *E.M.F.* is positive for p_H below 1·8, and negative for higher p_H. This effect is apparently due to the action of the light on the hydrogen ions bound electrostatically on the surface of the electrode, the true *E.M.F.* for ferrous salts always being negative. In this way, the value −30,000 g.-cal. is obtained for the energy of the reaction $2Fe^{\cdot\cdot}+2H^{\cdot}=2Fe^{\cdot\cdot\cdot}+H_2$, in good agreement with the value obtained from *E.M.F.* determinations with the cell Pt|acid solution|$KCl_{sat.}$|ferrous salt|Pt. Similar experiments with sodium iodide solutions give −26,000 g.-cal. for the heat of the reaction $3I'=I_3'+2\ominus$, whilst *E.M.F.* determinations with the cell Pt|NaI|$KCl_{sat.}$|NaI_3|Pt give −27,800 g.-cal. R. Cuthill.

Sorption and chemical phenomena. III. New class of heterogeneous chemical reaction. S. Liepatov (J. Russ. Phys. Chem. Soc., 1927, 59, 112—120).—The course of the reaction between nitroalizarin and barium and copper acetates suggests that the active mass of the solid phase is proportional to the total quantity present. The author considers that this type of heterogeneous reaction should be distinguished from the type exemplified by the reaction between barium carbonate and potassium sulphate where the solid phase does not react directly. It would seem that the latter does not represent a true type of heterogeneous reaction. E. Rothstein.

Experimental basis of the third law of thermodynamics. N. de Kolosovski (Z. Physik, 1927, 43, 509—511).—The Clausius-Clapeyron equation $d \log p/dT=\lambda/ART^2$ is considered as representing experimental observation for all substances. Since λ is always positive, it follows that $\lim._{T=0}dp/dT-\lim._{T=0}d \log p/dT=0$, and that $\lim._{T=0}\lambda/ART^2$, therefore $\lim._{T=0}\lambda=\lim._{T=0}\lambda/T=\lim._{T=0}\lambda/T^2-$ Since $\lambda/T=S_g-S_l$, where S is the entropy and g and l refer to the gaseous and liquid phases, it immediately follows that $\lim._{T=0}S_g-S_l=0$. A number of other

deductions from Nernst's heat theorem are derived similarly. R. W. LUNT.

Thermodynamic theory of capillarity. J. W. DEKKER (Ann. Physik, 1927, [iv], **82**, 1077—1155).—Mathematical. The influence of density on available volume, entropy, and kinetic pressure is discussed. Relative values for surface tension at different temperatures are calculated. R. A. MORTON.

Calorimetry at high temperatures and methods for determination of mean specific heat between high and ordinary temperatures. W. A. ROTH (Z. angew. Chem., 1927, **40**, 732—734).—A review of current methods and apparatus. J. S. CARTER.

Heat of dilution of salts at very small concentrations. II. W. NERNST and W. ORTHMANN (Sitzungsber. Preuss. Akad. Wiss. Berlin, 1927, 136—141).—Determinations of the heats of dilution of various salts at concentrations lower than those previously examined (A., 1926, 579) have given results which, in general, do not agree with Debye's theory, the values frequently being negative. R. CUTHILL.

Heats of ionisation in methyl alcohol. J. H. WOLFENDEN, W. JACKSON, and H. B. HARTLEY (J. Physical Chem., 1927, **31**, 850—861).—The heats of neutralisation of hydrogen chloride, hydrogen bromide, acetic and salicylic acids by sodium methoxide, and of aniline and ammonia by hydrogen chloride have been measured in methyl alcohol as solvent in an adiabatic calorimeter at 17°. The heat of formation of methyl alcohol from its ions is 11,200 g.-cal./g.-mol., a value similar to that for ethyl alcohol. The calculated heats of ionisation of acetic and salicylic acids in methyl alcohol are −4450 and −5180 g.-cal., respectively. The heats of formation of the ammonium and anilinium ions, respectively, in methyl alcohol are 17,630 and 9900 g.-cal. The heats of neutralisation of hydrogen chloride and bromide by sodium methoxide decrease with increasing dilution, as was also observed in aqueous solution by Richards and Rowe (A., 1922, ii, 425).

The specific heat of methyl alcohol calculated from the present data is 0·632. L. S. THEOBALD.

Latent heat of vaporisation of pure liquids and of solutions. M. S. VREVSKI (J. Russ. Phys. Chem. Soc., 1927, **59**, 69—76).—A current of air is passed through a solution immersed in a thermostat at a temperature near that required for the determination. As the liquid cools, it is heated by an electric spiral. Since the amount of current passed through the solution is known and the weight of vaporised water is measured, the latent heat can be calculated. The determinations are made either with a constant rate of increase in the temperature (the rate of increase for a solution through which air is not drawn having previously been determined), or the current is so adjusted as to keep the temperature constant. By this means, it was found that the latent heat of water at " is 552·4 g.-cal., and that of sulphuric acid (53·07%) at 96·5° is 595·1 g.-cal. E. ROTHSTEIN.

Latent heat of vaporisation of water and of aqueous solutions of sulphuric acid at 79·3°, and comparison of the thermal effect with the energy of diluting the solution with water. M. S. VREVSKI and B. P. NIKOLSKI (J. Russ. Phys. Chem. Soc., 1927, **59**, 77—88; cf. preceding abstract). The latent heats of solutions of sulphuric acid varying in concentration between 17% and 57% have been determined at 79·5°. When the concentration is above 60%, the latent heat rises too rapidly to be measured accurately. The difference between the latent heat of water and 17% sulphuric acid is 1·2 g.-cal. That between water and 57% sulphuric acid is 62·6 g.-cal. From the experimental results, the following empirical relation was deduced: if N is the number of mols. of water to 1 g. of acid, l is the latent heat of the acid, and l_0 that of water, then if $N>7·3$, $l=l_0+1268/N_2$. If $N<7·3$, $l=l_0+62/N+793/N^2$.

The experimental results are compared with the formulæ arrived at by various authors for the heat effect obtained by diluting solutions. The author reaches the conclusion that $(\partial Q/\partial N)_{N=N_2}-(\partial Q/\partial N)_{N=N_1} - RT \log_e p_1/p_2$. E. ROTHSTEIN.

Heat expenditure at the absolute zero. J. E. VERSCHAFFELT (Z. Physik, 1927, **43**, 152—154).—Criticism of Jazyna (*ibid.*, 1927, **41**, 211). Isothermal heat exchange is possible at the absolute zero, and matter can still possess energy at this temperature. R. A. MORTON.

Reaction regions. XV. Influence of mixtures of carbon dioxide and carbon tetrachloride vapour on the inflammability of a methane–air mixture. W. P. JORISSEN and G. M. A. KAYSER (Rec. trav. chim., 1927, **46**, 373—377).—The combined effect of two inhibitors, carbon dioxide and carbon tetrachloride, on the explosion of mixtures of air and methane has been studied. Under the conditions of the experiment, the explosive region for methane and air alone lay between 6·3% and 12·2% of methane. In order to make a 9% methane–air mixture non-explosive, 9% of carbon dioxide alone, or 6·4% of carbon tetrachloride, was necessary, but with the two together a smaller proportion was needed, *e.g.*, 4·5% of a mixture of the two containing 40% of carbon tetrachloride was sufficient. M. S. BURR.

Transference numbers of sodium and potassium in mixed chloride solution. S. A. BRALEY and C. W. RIPPIE (J. Amer. Chem. Soc., 1927, **49**, 1493—1494).—Repetition of the experiments previously described (A., 1923, ii, 456) at a total concentration of 0·2N shows that complex ions do not exist in mixed sodium and potassium chloride solution at this concentration (cf. MacInnes, A., 1925, ii, 872). The MacInnes equation for transport numbers in mixed solutions is confirmed. The erroneous nature of the results previously reported is attributed to the unsuitability of the chloroplatinate method of determining the alkali metals. S. K. TWEEDY.

Conductivity of hydrofluoric acid. M. AUMERAS (Compt. rend., 1927, **184**, 1650—1652).—The dissociation constant derived from conductivity data affords no evidence of the existence of a complex acid. J. GRANT.

Conductivity of dilute aqueous solutions of the alkali hydroxides at 25°. M. RANDALL and C. C. SCALIONE (J. Amer. Chem. Soc., 1927, **49**,

1486—1492).—The equivalent conductivities of dilute solutions (up to 0·06*M*) of the alkali hydroxides are recorded for 25°. Special precautions were taken in preparing the solutions; a special cell requiring only a small quantity of solution was used. Values of Λ_∞ are calculated by Randall's method (A., 1916, ii, 285). The conductivity ratios (Λ/Λ_∞) are practically the same as those for hydrochloric acid.

S. K. TWEEDY.

Lactic acid. III. R. DIETZEL and E. ROSENBAUM (Z. Elektrochem., 1927, **33**, 196—200; cf. A., 1925, i, 1036; 1926, 336).—The electrical conductivity of solutions of lactic acid and of potassium lactate has been measured at concentrations from *N*/8 to *N*/1024 at 18°. Lactic acid free from anhydride was prepared from barium lactate. The equivalent conductivity at infinite dilution of potassium lactate is found to be 115·5, whence that for lactic acid is 365·9. Values of the conductivity ratio, α, for lactic acid may be expressed by the relation: $2{\cdot}1418 \log 100\alpha = 0{\cdot}198 - \log c$, where c is the concentration in g.-mol./litre. This applies accurately over the whole concentration range investigated. The constant in the Ostwald dilution law for lactic acid exhibits a drift from $1{\cdot}35\times10^{-4}$ at *N*/8 towards a limiting value of about $1{\cdot}26\times10^{-4}$ in the more dilute solutions. This variation is much greater than that to be expected from experimental errors, and it is concluded that lactic acid cannot be regarded as a weak electrolyte. This view is supported by a calculation of conductivities on the basis of Ghosh's theory: excellent agreement is obtained over the whole concentration range, and the Ghosh equilibrium constant varies only between 1·257 and $1{\cdot}260\times10^{-4}$ over this range (cf. Auerbach and Zeglin's results for formic acid, A., 1923, ii, 55).

H. J. T. ELLINGHAM.

Absolute hydratation of the ions H·, Li·, Na·, K·, Cl′, and Br′ in their normal solutions. J. BABOROVSKÝ and J. VELISEK (Chem. Listy, 1927, **6**, 227—231).—Conduction of the electric current in *N*-solutions of alkali chlorides and bromides is due almost exclusively to electrolysis, the effect of electro-osmosis being negligible. On the basis of measurements of the electrolytic transport, the number of molecules of water attached to various ions in *N*-solutions is calculated to be 5 for potassium, 9 for sodium, 14 for lithium, 4 for chlorine, 3 for bromine, and 1·06 for hydrogen ions. Discrepancies observed between those values for hydratation of ions derived from measurements of the electrolytic transport of water and from considerations of the activity of the ions in question are explained by the assumption of two types of hydratation—dynamic and static. In the latter type, the ions are surrounded by molecules of comparatively loosely-bound water, which are to a large extent removed by the motion of the ions under the influence of an electric current.

R. TRUSZKOWSKI.

Transition compounds between salts and metallic alloys. II. M. PADOA (Gazzetta, 1927, **57**, 399—406).—The maximum electrical conductivities exhibited by the tin arsenides at certain temperatures (A., 1926, 226) are said to be analogous to the increments produced in the conductivities of compounds of similar type when subjected to the action of light. Pronounced maxima are shown by antimony arsenide, Sb_2As, at −10° and by antimony telluride, Sb_2Te_3, at 100°. Similar behaviour is observed with antimony selenide, Sb_2Se_3, but in this case, as in that of crystalline selenium, the effects appear to be complicated by phenomena of hysteresis.

T. H. POPE.

Electrical conductivity of the system: arsenic tribromide–ether. M. USSANOVITCH (J. Russ. Phys. Chem. Soc., 1927, **59**, 14–26).—See this vol., 315.

Electrochemical resonance. V. A. PLOTNIKOV (J. Russ. Phys. Chem. Soc., 1927, **59**, 5—13).—See this vol., 20.

Improved hydrogen electrode vessel and the *E.M.F.* of the mercury, mercurous bromide, bromide ion electrode. R. H. GERKE and J. R. GEDDES (J. Physical Chem., 1927, **31**, 886—889).—The *E.M.F.* of the cell H_2(1 atm.)|HBr,Hg_2Br_2|Hg is 0·2685 volt at 25°, and the potential of the electrode Hg|Hg_2Br_2|Br′ −0·1396 volt. An improved hydrogen electrode vessel is described.

L. S. THEOBALD.

Potential measurements in dilute solutions of electrolytes. A. BRESTER (Rec. trav. chim., 1927, **46**, 328—341).—In order to study the applicability of the theory of Debye and Hückel, the following potential measurements have been made in very dilute solutions of the electrolytes considered: Ag–$AgNO_3$, Ag–$AgClO_4$, Ag–Ag_2SO_4; Cd–$CdSO_4$, Cd—$CdCl_2$, Cd–$CdBr_2$, Cd–CdI_2. Employing the Debye formula corrected for ionic dimensions, good agreement up to a concentration of 0·1*N* is obtained between experimental and calculated values for the activity coefficients of silver salts in solution, assuming a silver ion diameter of 3×10^{-8} cm. in silver nitrate, 4×10^{-8} cm. in silver chlorate, and 1×10^{-8} cm. in silver sulphate solution. In stronger solutions, deviations increase, but this is also the region in which the influence of the dielectric constant is considered to make itself felt. In the case of cadmium sulphate, the agreement is not so good, and the ionic diameter is probably about $1{\cdot}2\times10^{-8}$ cm. The cadmium halides give abnormal values, which are probably due to incomplete ionisation. Values for the degree of ionisation have been deduced, and the ionisation constants calculated, using the modified mass action law for electrolytes. The results give somewhat greater constancy than the values obtained by neglecting the activity coefficients. The results show that the degree of ionisation diminishes from chloride to iodide, which is also shown by the inclination of the curves when potentials as ordinates are plotted against the square root of the corresponding concentrations as abscissæ.

M. S. BURR.

Electromotive behaviour of arsenious–arsenic acid solutions. F. FOERSTER and H. PRESSPRICH (Z. Elektrochem., 1927, **33**, 176—181).—In determining the oxidation–reduction potential of arsenious–arsenic acid solutions containing a small amount of iodide as catalyst, as recommended by Loimaranta, true equilibrium values, varying normally with the concentration ratio, are obtained only if the solutions are acidified to an extent corresponding at least with

N-hydrochloric acid. For the cell Pt|0·01M-H_3AsO_4, 0·01M-H_3AsO_3, 0·001M-KI, M-HCl|NH_4NO_3 satd. soln.|M-H_2SO_4, Hg_2SO_4|Hg, E=0·579 at 18°, whence, using Lewis and Randall's value for the activity of hydrochloric acid, and assuming that the activity coefficient of arsenic acid is equal to that of arsenious acid and that liquid junction potentials are negligible, substitution in the formula $\varepsilon_h={}_0\varepsilon_h+0·029$ log $([H_3AsO_4][H^·]^2/[H_3AsO_3])$ gives ${}_0\varepsilon_h=+0·574$ volt, in good agreement with the value calculated by Luther from the equilibrium constant at 25°. At higher acidities, especially above 4N, ε_h increases more rapidly than is to be expected from the activity data for hydrochloric acid, whilst any error due to neglect of liquid junction potentials would be in the opposite direction. Acidification with perchloric acid gives potentials identical with those obtained in solutions containing hydrochloric acid at the same molar concentration. It is concluded that in strongly acid solutions the activity coefficient of arsenic acid must be greater than that of arsenious acid at the same molar concentration. H. J. T. Ellingham.

Applicability of Nernst's theory to non-aqueous solutions. A. E. Brodsky (J. Russ. Phys. Chem. Soc., 1926, 58, 587—595).—The $E.M.F.$ of concentration cells in various solvents were investigated, with the view of testing Nernst's formula. The systems used were Hg|Hg_2Cl_2,KCl(C_1)|KBr(C_2),Hg_2Br_2|Hg, Hg|Hg_2Cl_2,KCl(C_2)|KCl(C_2),Hg_2Cl_2|Hg, and Hg|Hg_2Br_2,KBr(C_2)|KBr(C_2),Hg_2Br_2|Hg, in water at 14·5—15°, 50% ethyl alcohol (17°), and anhydrous methyl alcohol (13—13·5°). The method has been described in an earlier paper (A., 1926, 247, 688). The results are found to show considerable discrepancies with theory unless corrected for the degree of dissociation and for the diffusion potential, according to Henderson's formula, which is found to apply well for non-aqueous solvents. The results obtained are discussed from the point of view of the theory of Debye and Hückel. M. Zvegintzov.

Electrochemistry of fused salts. H. J. Bliks-lager (Rec. trav. chim., 1927, 46, 305—327).—The $E.M.F.$ of concentration cells, consisting of nickel electrodes in fused alkali chloride solutions of nickel chloride at 470° and 720°, respectively, have been determined, but the values found are considerably higher than those calculated from the simple formula of Nernst, assuming complete ionisation. This may be explained by supposing that complex ions, $NiCl_3^-$, with a few $NiCl_4^-$ ions, are formed, leaving very few nickel ions. The increase of $E.M.F.$ with temperature is proportional to the absolute temperature. Similar concentration chains of silver in silver chloride solution and lead in lead chloride solution give values in fairly close agreement with those calculated. Cobalt in cobalt chloride solution gives values which are not reproducible and are even higher than those for nickel, probably due to the greater complexity of the ions in cobalt chloride. The concentration polarisation observed when fused nickel chloride is electrolysed has been measured, and is also discussed from the theoretical point of view. The electrolytic separation of nickel–cobalt and iron–cobalt alloys from the fused salts has been studied. In the first alloy, no concentration of cobalt higher than 15·4% was obtainable from solutions containing a very high proportion of cobalt salt. The proportion of cobalt in the alloy increases with temperature. The experimental results have been compared with a formula deduced theoretically to show the relationship between the proportions of nickel and cobalt in the fused salt and in the alloy, as well as the influence of temperature. The iron–cobalt alloys prepared electrolytically always contain a large excess of cobalt. The results show that nickel is more positive than cobalt, and the latter than iron, cobalt lying nearer to iron than to nickel. It was not possible to prepare iron–manganese alloys from solution in fused chlorides, since only iron separated. Mixtures of nickel and alkali chlorides when heated are first yellow, then dark red, and finally blue. Measurements of the change of resistance with temperature indicate that the appearance of the blue colour coincides with the beginning of melting. M. S. Burr.

Current-potential curves of passive metals, with special reference to iron. W. J. Muller (Monatsh., 1927, 48, 61—70; cf. A., 1924, ii, 743).—The different methods of expressing current–potential relations of metal anodes showing passivity are discussed. The usual methods do not show the effect of time which the author's previous work (*loc. cit.*) has shown to be important. A new method is described in which the current–potential relations are shown by two curves, one expressing the behaviour of the passive and the other of the active form of the metal, tie-lines being added to join points corresponding with the same times. The previous results for iron are expressed in this way, and show that up to quite high current densities iron at first goes into solution in the active (bivalent) form, passivation occurring after a definite time, which depends on the conditions. W. Hume-Rothery.

Heyrovsky's theory of hydrogen over-potential and alternative suggestions. H. J. S. Sand (Rec. trav. chim., 1927, 46, 342—349).—Heyrovsky's theory of hydrogen over-voltage (A., 1925, ii, 675), according to which the latter is connected with the formation of molecular hydrogen by combination of negative and positive hydrogen ions, is criticised as leading to conclusions not in agreement with Herasymenko's experimental results (*loc. cit.*). The conditions required by these are discussed, and are shown to be fulfilled by the assumption of the formation of intermediate complex ions of the composition $H_3^{··}$, as indicated by the following equations: $H+2H^·=H_3^{··}$ and $2H_3^{··}=4H^·+H_2$, the current density being proportional to the rate of formation of these ions. This is valid only for small current densities. Alternative suggestions are also made. The hypothetical ion, $H_3^{··}$, is analogous to the unstable ion $H(OH)_2''$, the formation of which has been previously postulated (Sand and Weeks, A., 1924, ii, 152) to explain results obtained in alkaline solutions. M. S. Burr.

Application of the radiochemical theory to solutions of sodium iodide. R. Audubert (Compt. rend., 1927, 184, 1440—1443).—The method previously described (this vol., 429) has been applied

to the determination of the heat of reaction (Q) by the measurement of the *E.M.F.* produced when two platinum electrodes, one of which is illuminated, are placed in a solution of sodium iodide or of sodium iodide and iodine (NaI_3). Since the *E.M.F.* is greater than that due to the normal photovoltaic effect, the following equilibrium, dependent on the photochemical action of light, is assumed between the ions I′ and I′$_3$: $3I' + 2h\nu \rightleftharpoons I_3' + 2\epsilon + 2h\nu'$. The value found for Q (−26,000 g.-cal.) is in close agreement with that obtained by using the data given by the cell Pt|NaI|saturated KCl|NaI+I|Pt with various concentrations of sodium iodide and iodine, in the Helmholtz equation. J. GRANT.

Electrochemical behaviour of silver and copper amalgams. K. ARNDT and G. PLOETZ (Chem.-Ztg., 1927, **51**, 461).—The *P.D.* between copper and silver dental amalgams, the latter containing a large amount of tin, and 1% solutions of sodium chloride, lactic acid, or mixtures of the two, *i.e.*, media approximating to the fluids of the mouth, are those of copper and tin, respectively. Experiments in which the cells amalgam|1% solution of sodium chloride+lactic acid|gold were shorted show that after a week the silver and copper amalgams lost 15 and 39 mg. in weight, respectively. Corresponding amounts of tin and copper were found in the solution. J. S. CARTER.

Cell with diffusion anode. Relative velocities of reaction of liquid depolarisers. C. BAILLOD (Helv. Chim. Acta, 1927, **10**, 487—517).—Cells were constructed which comprised a hollow carbon anode containing a liquid depolariser which was caused to flow under pressure through the pores of the electrode, so that the surface of the anode was continuously covered with a layer of fresh depolariser and a cathode of amalgamated aluminium or zinc. When the velocity of diffusion of the depolariser exceeded a certain value, the output from the cell did not vary with time, and the maximum power which it then delivered constituted a measure of the relative velocity of reaction of the depolariser. Under these conditions, the fraction of the depolariser chemically utilised was small (about 12%). The relative reaction velocity of the depolariser increased rapidly with increasing hydrogen-ion concentration, and was greatest for concentrated nitric acid. The power delivered by the cell depended also on the nature of the electrolyte, being greatest for 20% sodium hydroxide solution or for N-nitric acid. On the other hand, the efficiency with which the aluminium dissolved was greatest (almost 100%) for electrolytes consisting of a 10% solution of sodium carbonate saturated with sodium chloride or of N-sulphuric acid, and least for N-nitric acid. G. A. ELLIOTT.

Burning gases in nitrous oxide. H. B. DIXON and W. F. HIGGINS.—See B., 1927, 513.

Theory of explosive reaction. II. H. MURAOUR (Bull. Soc. chim., 1927, [iv], **41**, 620—630; cf. B., 1927, 126).—The theory of explosive reactions previously outlined is discussed in greater detail. S. K. TWEEDY.

Kinetics of the oxidation of hydriodic acid by free oxygen in darkness and under the action of light. A. BERTHOUD and G. NICOLET (Helv. Chim. Acta, 1927, **10**, 475—486).—In absence of light, the process comprises two simultaneous reactions, of which one is very slow and independent of the concentration of the iodine produced, whilst the other, more rapid reaction proceeds with a velocity proportional to the square roots of the iodine and of the hydrogen-ion concentrations. The velocity of this reaction increases at first rapidly, and then more slowly with increasing concentration of potassium iodide. Under the action of feebly-absorbed red light, the oxidation proceeds much more rapidly; nevertheless, the reaction is essentially similar to the thermal reaction catalysed by iodine. The velocity of the photochemical reaction is, however, proportional to the square root of the intensity of illumination, and it has a very small temperature coefficient. The results indicate that the action of the light consists in the dissociation of the iodine molecules to form atoms which assist the reaction, presumably by the formation of an intermediate complex with oxygen. The reaction velocity under the influence of blue light, which is strongly absorbed, is also proportional to the square root of the intensity of illumination, but it increases to a maximum and ultimately decreases as the iodine concentration is raised. G. A. ELLIOTT.

Mutarotation. II. Relative velocities of mutarotation of α- and β-glucose: effect of acid and salt. J. C. ANDREWS and F. P. WORLEY (J. Physical Chem., 1927, **31**, 882—885; cf. Hudson and Dale, A., 1917, i, 320).—The velocity coefficients determined in aqueous hydrochloric acid *solutions* at 25°, for both forms of the sugar, lie on the same straight line. The addition of specially purified sodium chloride up to a concentration of 8·63 g.-mols./1000 g.-mols. of water has no effect on the rate of mutarotation of α-glucose in water. Heating the salt to 120° accelerates the rate, and after fusion of the salt an even greater effect is observed. L. S. THEOBALD.

Oxidisability of organic substances. G. LEJEUNE (J. Chim. phys., 1927, **24**, 391—426).—The experimental data leading to the conclusions already published (A., 1926, 482) are now given. The unimolecular velocity coefficient for the oxidation of primary alcohols by alkaline permanganate tends to decrease with increase in the number of carbon atoms if the solution is buffered to p_H 11·8 with carbonate, whereas with a hydrogen carbonate buffer of p_H 8·3 the reverse is true. In acid solutions, the oxidation with permanganate is much more rapid than with chromic acid. The effect of the p_H on the reactivity of secondary alcohols is similar to that observed with primary alcohols. With ketones, the magnitude of the temperature coefficient of the velocity coefficient is independent of the nature of the ketone. The rate of oxidation of acetone in alkaline solutions increases in a linear manner with the p_H. R. CUTHILL.

Reactions in the solid state at high temperatures. I. Reaction velocities of endothermic decompositions. W. JANDER (Z. anorg. Chem., 1927, **163**, 1—30).—The relation between time and reaction velocity in the solid state is discussed, and it is shown mathematically that if two substances

capable of reacting isothermally are in contact, the square of the thickness of the layer of reaction product formed must be proportional to the time of contact; an expression is derived for testing the relationship experimentally. An equation is also obtained for the relation between reaction velocity and temperature. Measurement of the carbon dioxide pressure over a mixture of barium carbonate and silicon dioxide shows that reaction commences at about 700°, and that its velocity at constant temperatures between 800° and 890° is in agreement with the theory. The theoretical relationship between reaction velocity and temperature is also satisfied. Similar results are found for a mixture of barium carbonate and molybdenum trioxide. For the former reaction, the velocity is inversely proportional to the square of the mean particle radius, as required by the theory.

H. F. GILLBE.

Thermal decomposition of azomethane over a large pressure range. H. C. RAMSPERGER (J. Amer. Chem. Soc., 1927, 49, 1495—1499).—The thermal decomposition of azomethane at 290° and at 330° is homogeneous over the pressure range 0·0259—70·79 cm. It is strictly unimolecular only at the lower pressures at 290° (cf. this vol., 425). The decomposition products exert the same influence in maintaining the rate as their equivalent of azomethane.

S. K. TWEEDY.

Inversion of the role of catalysts. P. SABATIER (Compt. rend., 1927, 185, 17—19).—A catalyst may often act on a system in two opposite senses, according to the existing conditions. Numerous examples are quoted, and the results shown to be compatible with the simpler theories of catalysis. In particular, certain metallic oxides (*e.g.*, of zinc) behave as dehydrogenation catalysts, but usually have an activity less than that of finely-divided metals. The behaviour of these oxides also as hydrogenation catalysts having less activity than metals is the basis of the Patart process for the synthesis of methyl alcohol, the high temperature required being compensated for by an increase in pressure. In presence of a more powerful catalyst (*e.g.*, nickel), this reaction passes the methyl alcohol stage, and methane is produced. J. GRANT.

Acid and salt effects in catalysed reactions. IX. General kinetic method for the determination of the degree of dissociation of water. H. M. DAWSON (J.C.S., 1927, 1290—1297).—The calculation of the ionisation constant of water from the results of ester hydrolysis by means of the equation $K_w=v_i^2/4k_hk_{OH}$ is described (cf. this vol., 632). The minimum velocity of reaction, v_i, must be measured in buffer solutions, preferably, for mathematical simplicity, of constant acid or constant salt concentration. The acid and salt effects associated with the use of buffer solutions for the stabilisation of p_H in reaction velocity measurements are discussed. From the results of Karlsson's experiments (A., 1925, ii, the values $K_w=1·25\times10^{-14}$ at 25° and 34×10^{-14} at 35·5° are calculated. S. K. TWEEDY.

Influence of water on the combination of the halogens with hydrogen. M. BODENSTEIN and W. JOST (J. Amer. Chem. Soc., 1927, 49, 1416—1418). Experiments are described indicating that the investigations of Lewis and Rideal (A., 1926, 1111) do not prove that intensive drying retards the reaction between hydrogen and bromine or iodine. The presence of phosphorus pentoxide in the heated gases is shown to vitiate the results. S. K. TWEEDY.

Chain-reaction theory of negative catalysis. H. L. J. BACKSTROM (J. Amer. Chem. Soc., 1927, 49, 1460—1472).—The autoxidation of benzaldehyde, of heptaldehyde, and of sodium sulphite solution at 20°, both in the light and in the dark, exhibits marked negative catalysis. An inhibitor for the light reaction invariably inhibits the dark reaction, although in the case of benzaldehyde the dark reaction is the more sensitive to inhibitors. Some inhibitors suppress the light reaction in the case of sodium sulphite more strongly than the dark reaction; alcohols exert parallel effects on both reactions. Quantum efficiency measurements indicate that a large number of molecules react for every light-quantum absorbed, and, in general, it is concluded that the above photochemical reactions represent instances of thermal chain reactions (cf. Christiansen, A., 1924, ii, 242). S. K. TWEEDY.

Activity of various metals and metal oxide catalysts in promoting the oxidation of methane by air. W. P. YANT and C. O. HAWK (J. Amer. Chem. Soc., 1927, 49, 1454—1460).—The catalytic oxidation of 3·75—4·1% of methane in air by various metals, metal oxides, and mixtures of oxides was investigated between 150° and 350°. Cobaltic oxide was the most efficient catalyst; excluding mixtures, it was followed by manganese dioxide and nickelic oxide. 10% of platinum-black when added to metallic nickel appears to act as a promoter. Mixtures of the oxides gave results corresponding with the proportion of each active material present. S. K. TWEEDY.

Reduction of mixed oxides. Copper and zinc oxides. W. ROGERS, jun. (J. Amer. Chem. Soc., 1927, 49, 1432—1435).—Zinc oxide in a mixture with copper oxide (prepared in the fused state) is completely reduced by hydrogen at 300°. It is considered that the presence of one oxide prevents the crystal units of the other oxide from arranging themselves in the normal way. The forces between the units in the lattice structure are thus altered, and the properties of each component would be expected to be different from those for the pure state. S. K. TWEEDY.

Catalytic activity of lead. F. A. MADENWALD, C. O. HENKE, and O. W. BROWN (J. Physical Chem., 1927, 31, 862—866).—The activity of various lead catalysts in the reduction of nitrobenzene by hydrogen has been compared by the method previously used (Brown and Henke, A., 1922, i, 445). Light red lead, heavy red lead, and a light and a heavy litharge, prepared from recrystallised lead nitrate by varying heat treatments, on reduction by hydrogen at 308° gave the catalysts used. The activity of the catalysts increased with use, but more slowly than is the case with copper catalysts. It also increased more rapidly in an iron than in a glass tube. The initial activity of the different samples varies, but the final activity is the same. The optimum temperature for the reduction of nitrobenzene is 308°, and one catalyst prepared from heavy litharge maintained a 97% yield

of aniline for approximately 200 experiments. Grinding the catalyst had no permanent effect on its activity, but hydrogen alone destroyed the activity. The optimum rate of flow is 14 litres of hydrogen and 4 g. of nitrobenzene per hr. at 308°. Appreciable yields of azobenzene (up to 25%) were obtained only during the first few runs. L. S. THEOBALD.

Catalytic actions of silver chloride in oxidation-reduction processes. R. LANG (Ber., 1927, **60**, [*B*], 1389—1390).—A solution containing the higher chlorides of manganese in 2·5*N*-hydrochloric acid, which does not decompose appreciably at the atmospheric temperature, rapidly and quantitatively yields chlorine and manganous chloride after addition of silver nitrate. If the acid is more dilute, a higher temperature is required for the change. Ceric nitrate dissolved in hydrochloric acid becomes almost instantaneously decolorised after addition of silver nitrate. H. WREN.

New kinds of mixed crystals. III. D. BALAREV and G. KANDILAROV (Z. anorg. Chem., 1927, **163**, 141—144; cf. A., 1926, 1195).—The presence of finely-divided barium sulphate reduces the velocity of oxidation of hydrogen chloride by permanganates in dilute solution. That the barium sulphate does not behave as a chemically inert substance is demonstrated by the fact that no diminution of the reaction velocity is caused by the presence of sand. For different permanganates, the magnitude of the effect is different, being greatest for potassium permanganate. The phenomenon is ascribed to variations in the extent of the adsorption of different permanganates by barium sulphate. H. F. GILLBE.

Electrolytic oxidation of concentrated formic acid solutions. F. MÜLLER (Z. Elektrochem., 1927, **33**, 173—176).—A 95% formic acid solution (sometimes with addition of 5% of sodium formate) has been electrolysed between platinum electrodes at 0·065 amp./cm.^{2} The theoretical amount of hydrogen was obtained at the cathode, but it was accompanied by considerable amounts of carbon dioxide. At the anode, however, the carbon dioxide obtained was always less than that corresponding with the process $2HCO_2' + \oplus = H{\cdot}CO_2H + CO_2$. This deficiency is shown to be due to the considerable solubility of carbon dioxide in the electrolyte. Diffusion of carbon dioxide in solution to the cathode causes it to be carried off with the hydrogen evolved there. When the electrodes are separated by a diaphragm, no carbon dioxide is obtained at the cathode. H. J. T. ELLINGHAM.

Action of iron as an impurity in the lead accumulator. I and II. F. M. LEA and J. T. CRENNELL.—See B., 1927, 528.

Oxidation of sodium plumbite to plumbate by alternating current. II. F. JIRSA and F. KORNALIK (Z. Elektrochem., 1927, **33**, 192—196).—The current efficiency, η, for the production of sodium plumbate by the passage of sinusoidal alternating current through sodium hydroxide solutions saturated with lead monoxide has been investigated under various conditions (cf. A., 1920, ii, 620). With electrodes of gold or cadmium, η is extremely small, with palladium it is somewhat higher, but with nickel electrodes it is about ten times as great as with palladium. With nickel electrodes, η decreases with increasing alkali concentration up to 1·5*N*, then increases up to 4·5*N*, and finally diminishes at higher concentrations: with palladium electrodes, however, these variations are reversed, the maximum being at 1·5*N*. Using alternating current at 49 cycles, the highest value of η recorded is 11·33% (calculated on current shown by an alternating-current ammeter), using 0·412 amp./cm.^{2} at nickel electrodes in 4·66*N*-sodium hydroxide saturated with lead oxide at 18°. Increasing the frequency over the range from 18 to 60 cycles decreases η considerably. With platinum electrodes, no oxidation to plumbate occurs, but the platinum is attacked, giving a brown deposit containing lead and platinum, the latter being partly in the metallic state and partly in the form of platinic oxide. It is believed that platinum dissolves essentially in the bivalent form, which subsequently changes to satisfy the equilibrium $2Pt^{\cdot\cdot} \rightleftharpoons Pt^{\cdot\cdot\cdot\cdot} + Pt$. The dissolution of platinum in pure *N*-sodium hydroxide by alternating current is also examined. H. J. T. ELLINGHAM.

Production of ozone in air by ultra-violet rays. J. DADLEZ (Compt. rend., 1927, **185**, 89—91).—The diminution of the ozone content of the air at increasing distances from quartz lamps of various makes and candle-powers has been measured. The minimum ozone content of air producing the first symptoms of distress in adults is 1·0—1·5 mg./m.^{3}, the effects being felt after 30 min. Since only 0·05—0·3 mg./m.^{3} of ozone are produced normally, there is little chance of danger in a large, well-ventilated room. The symptoms produced in an adult after various periods in atmospheres containing various amounts of ozone are described. J. GRANT.

Glow in hydrogen at high pressure. J. KAPLAN (Nature, 1927, **120**, 48).—During attempts to obtain atomic hydrogen by means of an incandescent tungsten filament in wet hydrogen at 20—350 mm. pressure, a blue glow was observed. The glow may be caused by some material liberated from the filament; it is not due to excitation of the hydrogen by electrons from the filament. The spectrum of the glow extends from 5000 to 4400 Å., and is probably continuous. A. A. ELDRIDGE.

Photolysis of hydrogen cyanide by the total and filtered radiations of the mercury arc. A. ANDANT and E. ROUSSEAU (Compt. rend., 1927, **184**, 1553—1555).—The method previously described (this vol., 538) has been applied to the irradiation of cherry-laurel water covered with a layer of olive oil, and containing pure manganous chloride (0·126%). After 4 hrs., the phenomenon of photocatalysi follows that of photolysis. The mercury radiatio 3650 Å. produces, under the same conditions, a photolytic effect of the same order as that produced by the whole of the mercury radiations up to 3130 A Allowing for the selective absorption of the ray 3650 Å., it appears that photolysis by ultra-violet radiation is inhibited by the presence of radiations of greater wave-length. J. GRANT.

Effect of added gases on the decomposition o ammonia sensitised by optically excited mercur

vapour. A. C. G. MITCHELL and R. G. DICKINSON (J. Amer. Chem. Soc., 1927, **49**, 1478—1485).—Whereas argon and nitrogen at 0·3 mm. pressure have no influence on the rate of photochemical decomposition of ammonia sensitised to 2537 Å. by optically excited mercury vapour, hydrogen at the same and lower pressures has a large inhibiting effect (Stuart, A., 1925, ii, 629). This is partly due to the fact that hydrogen can be activated by collisions of the second kind with excited mercury atoms, this activated hydrogen having no effect on the ammonia decomposition. Hydrogen can also take activation from activated ammonia (cf. Kuhn, A., 1924, ii, 249). The rate of decomposition of the ammonia increases with increasing pressure. The specific rate of activation of ammonia is 4% of that of hydrogen by excited mercury atoms. S. K. TWEEDY.

Light oxidation of alcohols as contribution to the knowledge of photochemical phenomena. J. BOESEKEN and S. L. LANGEDIJK (Proc. K. Akad. Wetensch. Amsterdam, 1927, **30**, 189—196).—Certain aromatic mono- and aliphatic α-di-ketones can behave as photocatalysts in the oxidation of alcohols to the corresponding aldehyde. The photoactive region lies between 400 and 410 μμ. The theoretical bearing of these results is discussed. The reaction has been used to effect the decomposition of optical antipodes. *l*-Menthyl benzophenone-*p*-carboxylate was dissolved in methylethylcarbinol, and exposed to light in presence of oxygen. The racemic alcohol was used, and after the experiment the fractionated alcohol was found to be lævorotatory. W. E. DOWNEY.

Photochemical reaction of bromine with fumaric and maleic esters. J. EGGERT [with F. WACHHOLTZ and R. SCHMIDT] (Oesterr. Chem. Ztg., 1927, **30**, 110).—Measurements of the rate of photochemical conversion of ethyl maleate into fumarate in carbon tetrachloride solution, in presence of bromine, show that the quantum efficiency varies with temperature and the wave-length of the light used, but is independent of the concentrations of ester, bromine, and added ethyl fumarate. The photochemical effect is merely the initiator of the process, which is essentially chemical. The process is complicated by the fact that, under the experimental conditions, both esters take up bromine, the quantum efficiency of this reaction varying with the concentration of bromine. A reaction mechanism is suggested according to which bromine atoms are responsible for the observed effects. Bromine molecules are first dissociated into their atoms, which form an intermediate complex on collision with ester molecules. The complex is very unstable, and undergoes rearrangement and subsequent decomposition. Collisions between bromine molecules and the complex are responsible for the appearance of dibromosuccinic ester. Experiments with the methyl esters and with an aqueous solution containing maleic acid, bromic acid, and a ferrous salt furnish evidence in support of the suggested mechanism. J. S. CARTER.

Addition of bromine to α-phenylcinnamonitrile under the influence of light. A. BERTHOUD and C. NICOLET (Helv. Chim. Acta, 1927, **10**, 417—429; cf. Berthoud and Bellenot, A., 1924, ii, 327; Plotnikov, "Lehrbuch der Photochemie," p. 250).—The addition of bromine to α-phenylcinnamonitrile and the reverse reaction both take place much more slowly in the dark than Bauer and Moser allege (A., 1907, i, 307). The rate of addition, d[dibromide]/dt, for small absorption is $k_1 I_0^{0.5}$[bromine]$^{1.5}$; for total absorption, $k_1 I_0^{0.5}$[bromine]. The thermal coefficient is 1·4. The photochemical decomposition of the dibromide occurs only in presence of bromine, which acts as an optical sensitiser. The rate of this reaction, $-d$[dibromide]/dt, when the nitrile is in large excess, is for small absorption $k_2 I_0^{0.5}$[dibromide][bromine]$^{0.5}$/[nitrile], for total absorption $k_2 I_0^{0.5}$[dibromide]/[nitrile]; whilst in absence of large excess of nitrile the denominator must be [nitrile]+m[dibromide]. The thermal coefficient is 1·96. The photochemical equilibrium is independent of intensity of illumination, and is represented by the expression K'=([nitrile]+m[dibromide])[bromine]/[dibromide], m becoming zero when the nitrile is in large excess. A theory of these results, which are quite different from those of Plotnikov, is developed. C. HOLLINS.

Oxidising agents in the study of the sensitivity of photographic emulsions. W. CLARK.—See B., 1927, 507.

Precipitation of metals and their oxides from salt solutions by hydrogen at high temperatures and pressures, and synthesis of minerals. I. Influence of other metals in the precipitation of copper. W. IPATIEV and N. KLINKOIA. **II. Precipitation of oxides from salts of chromium, manganese, and iron.** W. IPATIEV and A. KISSELEV. **III. Precipitation of metals of the iron group from solutions of their cyanides and salts with organic acids.** W. IPATIEV and I. N. KONDYREV. **IV. Precipitation of phosphorus, arsenic, and antimony from their salts at high temperatures and pressures.** W. IPATIEV and W. NIKOLAIEV (J. Russ. Phys. Chem. Soc., 1926, **58**, 664—686, 686—692, 692—698, 698—704).—I. The effect of temperature, pressure, concentration, and duration of reaction, as well as the presence of the salts of iron, nickel, zinc, and of free acids on the precipitation of copper from solutions of its salts (mainly copper sulphate) was investigated. The experiments were performed in glass tubes, but above 200° quartz vessels were used. Increase of concentration gave a precipitate containing cuprous oxide and basic salts, owing to secondary hydrolysis reactions. The amount of copper precipitated was proportional to the time. Rise of temperature favours deposition up to 150°, but above that inhibits it. Increase of pressure always favours deposition. The significance of these results from the point of view of the dynamics of the reactions is discussed. Above 150°, the sulphuric acid liberated was reduced by the hydrogen, the deposited copper acting as a catalyst, and cuprous oxide or basic salts were formed. At higher temperatures and pressures, cupric sulphide was obtained in a crystalline form. Addition of free sulphuric acid in small quantities favoured the precipitation of metallic copper, since it inhibited the secondary hydrolytic reactions. The addition of salts of nickel, zinc, and iron had no effect on the

precipitation of copper, provided some free acid was present to prevent the formation of basic salts of the metals.

II. The experiments were performed at higher temperatures (300°) and pressures (>150 atm.) in silver, gold, and platinum balls, as quartz vessels gave with the salts crystals of metal silicates. Basic salts and oxides of the metals were obtained as well-developed crystals, often identical with the naturally-occurring minerals. Chromic acid gave at 300° and 150—180 atm. a greyish-violet powder, of the formula Cr_2O_3,H_2O, whilst in a quartz tube a bright green substance of the same composition was obtained. A mixture of potassium chromate and sulphuric acid (50%) gave an insoluble crystalline substance of the formula $Cr_2(SO_4)_3,Cr_2O_3,K_2O,H_2O$, which was examined by the *X*-ray spectrograph. Potassium manganate and manganese nitrate under similar conditions gave the crystalline mineral hausmannite Mn_3O_4,H_2O. In presence of free nitric acid in a quartz tube a manganese silicate was obtained. Manganese chloride gave a hydrated oxide, MnO,H_2O, whilst manganese sulphate gave manganese sulphide.

Iron salts precipitated mixtures of iron oxide, and finally, as the pressure increased and the temperature was raised, crystalline magnetic iron oxide, Fe_3O_4. No metallic iron was obtained, even when potassium ferrocyanide was used, which on decomposition gave first formic acid and then nascent hydrogen, capable of reducing any iron oxide, owing to hydrolytic reactions. Ferric chloride gave a white, crystalline mass; ferric acetate did not react, except with water-gas, when ferrosoferric oxide was obtained; ferrous sulphate precipitated a mixture of magnetic oxide and ferrous sulphide.

III. Iron formate gave magnetic oxide; nickel formate gave metallic nickel mixed with nickel oxide, the amount of which increased with rise of temperature and pressure, owing to hydrolysis, whilst nickel cyanide gave only anhydrous, crystalline, black nickelous oxide. Ferrous cyanide, formate, and acetate gave magnetic oxide, whilst the thiocyanate gave a mixture of oxide and sulphide. With the double cyanide of potassium and manganese, crystalline manganese carbonate was obtained. In a quartz tube, manganese and zinc nitrate deposited the corresponding crystalline silicates.

IV. Free phosphoric acid and its alkali salts remained unaffected, but ferric phosphate gave a continuous series of crystalline complex phosphates of the type $Fe'''_nFe''_mPO_4,xH_2O$, depending on the conditions, identical with the naturally occurring minerals—the vivianites. Lead phosphate at 250—300 atm. and 360—400° deposited a colloidal orange oxide, Pb_2O, and hypophosphorous acid, whilst with water-gas at 400 atm., phosphine and some metallic lead were obtained. With lead hypophosphite, at high pressures, in presence of water, black, elementary phosphorus was formed. This form was also obtained by the action of water on red phosphorus at 260° and 100 atm. The salts of arsenic acid and iron oxide gave green, crystalline hydrated ferric arsenate, identical with the mineral scorodite. Further action resulted in the formation of elementary arsenic. If the action is prolonged for a few days, crystalline arsenical pyrites, Fe'''_nAs_m, is obtained. Copper arsenate gave the mineral domeite (cuprous arsenide, Cu_3As). With elementary arsenic a little arsine was evolved. Antimony sulphate formed crystals of antimony glance, Sb_2S_3, and potassium pyroantimonate formed crystalline elementary antimony. In general, antimony salts are more easily reduced than those of arsenic and phosphorus. M. ZVEGINTZOV.

Double sulphates of the copper–magnesium group and the sulphonium bases. I. P. C. RAY and N. RAY (J. Indian Chem. Soc., 1927, **4**, 37—42).—Double *sulphates* having the general formula $M''SO_4,(Et_3S)_2SO_4,10H_2O$, where M''=Fe'', Zn, Ni, Co, Cd, have been prepared by slow evaporation of triethylsulphonium sulphate (obtainable only in solution) with the appropriate metallic sulphate in the ratio 2 : 1. These compounds are hygroscopic; alcohol added to their aqueous solutions causes separation of the inorganic components. Salts of the type $2M''SO_4,(Et_3S)_2SO_4,11H_2O$ were also formed, where M''=Mg or Mn, and when trimethylsulphonium sulphate was substituted for the ethyl derivative nickel formed a salt of this type.

B. W. ANDERSON.

Reactions of active magnesium. A. P. TERENTIEV (Z. anorg. Chem., 1927, **162**, 349—352).—Active magnesium may be prepared by passing the vapour of an alcoholic solution of iodine over the powdered metal; 1 g. of iodine is sufficient to activate 24 g. of magnesium, which must be dried beforehand by strong heating. The active product must be freshly prepared for use, as it is very hygroscopic and its activity is destroyed by traces of moisture. A mixture of active magnesium and ethyl alcohol does not reduce the methyl esters of the fatty acids, but yields the ethyl esters. When heated in ammonia at 350—400°, the active metal forms a grey powder, consisting of magnesium amide. Ordinary magnesium reacts with aniline vapour at about 370°, whereas the active form reacts with the vapour at about 240° and with the liquid at 130—140°.

H. F. GILLBE.

Setting of dihydrates of calcium sulphate. P. P. BUDNIKOV.—See B., 1927, 483.

Decomposition of monocalcium phosphate by water. A. SANFOURCHE and B. FOCET (Compt. rend., 1927, **184**, 1652—1655).—The weight of salt entering into reaction and the degree of decomposition of crystalline monocalcium phosphate in aqueous solutions at 20° may be determined by titration of the acid liberated in the reaction $2CaH_4(PO_4)_2 = 2H_3PO_4 + Ca_2H_2(PO_4)_2$. The amount of salt decomposed increases (rapidly at first) with the amount present, 0·407 being decomposed in the case of a saturated solution (63%). The presence of calcium sulphate in the anhydrous form has no effect on the decomposition curve, but there is indirect evidence that when it is present as the hemihydrate a double salt is formed with the dicalcium phosphate produced during the reaction. Thus, up to a certain concentration of phosphate, depending on the amount of calcium sulphate present, the decomposition is characteristic of a normal salt. Beyond this point, it is characteristic of the decomposition of the pure phos-

phate, except that the amount decomposed increases with the concentration of calcium sulphate. J. GRANT.

New scaly variety of aluminium hydroxide. P. NEOGI and A. K. MITRA (J.C.S., 1927, 1222—1223).—The reduction of concentrated barium nitrate (or, although less satisfactory, strontium nitrate) solution with aluminium–mercury couple at 0° yields stable scales (probably isometric crystals) of $Al_2O_3,4H_2O$, d^{31} 1·5490, soluble in mineral acids, but insoluble in methylamine. One molecule of water is lost at 100°, and the last molecule, with difficulty, at red heat. Impure products are also obtained by the similar reduction of alkali bromates and iodates. S. K. TWEEDY.

Alkali and alkaline-earth hexabromostannates [Rb_2SnBr_6, Cs_2SnBr_6, and $BeSnBr_6,10H_2O$]. G. I. COSTEANU (Ber., 1927, 60, [*B*], 1312—1315).—The *hexabromostannates* of *rubidium*, *cæsium*, and *beryllium* are obtained from their components in aqueous solution or, in the case of cæsium, from the carbonate and hexabromostannic acid. The two former are more stable and less soluble than the other alkali hexabromostannates; the beryllium salt resembles the magnesium compound. H. WREN.

Nitrogen sulphide. S. A. VOSNESSENSKI (J. Russ. Phys. Chem. Soc., 1927, 59, 221—232).—Pure nitrogen sulphide is obtained by passing ammonia mixed with air into an anhydrous benzene solution (20% by weight) of sulphur dichloride. After this reaction, the mixture is filtered through flannel, the nitrogen sulphide extracted in a Soxhlet apparatus with benzene, and recrystallised from benzene. The product (yield, 20%, calculated on sulphur dichloride) had m. p. 179°; the presence of sulphur has a great influence in lowering the m. p. Near the m. p., sublimation occurs, and at higher temperatures the compound explodes. The sulphide has *d* 2·2, mol. wt. 184·3, indicating the formula N_4S_4. Decomposition occurs in a damp atmosphere and in water, hot water decomposing it violently. Data are given of its solubility in carbon disulphide, benzene, and ethyl alcohol. The reactions with water, acid, and alkali, respectively, are fully investigated. General methods for preparing the series of additive *compounds* $N_4S_4,2NH_3$, $N_4S_4,2Cl_2$, $N_4S_4,2Br_2$, $3N_4S_4,2SCl_2$, N_4S_4,SCl_2, and $N_4S_4,2SCl_2$ are given. The structural formula suggested, $S{:}S(.N{\cdot}S{:}N)_2$, agrees with (1) the equation $N_4S_4+12HCl=4NH_3+4S+12Cl$, for it may be here assumed that the sulphur and nitrogen are combined by twelve valencies, and that the atoms of nitrogen are not combined among themselves; (2) the formulation of its metallic derivatives $S{:}S\langle^{N}_{N}\rangle Pb$ and $S\langle^{N}_{N}\rangle Hg$; (3) the data obtained on hydrolysis. However, the formula does not explain the reaction $N_4S_4+Me{\cdot}COCl\longrightarrow N_3S_4Cl$ and the production of the compounds N_3S_4Br, $N_3S_4NO_3$, N_3S_4CNS, or the reaction $N_3S_4Cl+NH_3\longrightarrow N_4S_4$. J. KAYE.

Formation of ozone by electric discharge in presence of foreign gases. A. PINKUS and A. JULIARD (J. Chim. phys., 1927, 24, 370—390).—When oxygen is subjected to the silent discharge, the fraction which is ozonised is, for a given rate of flow of the gases, nearly the same for all pressures between 300 and 600 mm., this being a maximum value. Under comparable conditions of pressure and rate of flow, hydrogen and, to a less extent, silicon tetrafluoride reduce the yield of ozone. If the rate of flow is high and the voltage is small, the presence of nitrogen may cause the yield to be better than with pure oxygen under comparable conditions. With increase in the voltage and decrease in the rate of flow, however, the optimum amount of nitrogen diminishes, probably because in these circumstances more oxides of nitrogen are formed, and these exert a greater destructive action on the ozone, according to the equations $2NO+O_3=N_2O_5$, and $2NO_2+O_3=N_2O_5+O_2$. R. CUTHILL.

Oxidation with fluorine. VII. Action of fluorine on water and alkali hydroxide solutions. VIII. Unstable peroxide from sulphuric acid. IX. Action of fluorine on phosphoric acid, phosphates, and pyrophosphates. X. Action of fluorine on carbonates and borates. F. FICHTER and W. BLADERGROEN (Helv. Chim. Acta, 1927, 10, 549—552, 553—559, 559—565, 566—570; cf. this vol., 123).—VII. When fluorine is led into water, hydrogen peroxide is produced in amounts which at first increase rapidly and then decrease as the time of treatment is prolonged. The decrease is attributed to the decomposition of the peroxide by ozone, which is formed in the later stages. Fluorine forms with concentrated potassium hydroxide solution at −20° a brown, explosive compound which is probably potassium ozonide. This substance is decomposed by water with the formation of molecular oxygen and a small amount of hydrogen peroxide.

VIII. The unstable compound previously recorded (A., 1926, 925) is formed in greatest amount when cooled, 2·35*M*-sulphuric acid is treated with fluorine; it may also be obtained in almost equal amount (equivalent to 4·4% of the total sulphate when calculated as SO_4) from solutions of sulphates or hydrogen sulphates of medium concentration. The substance oxidises manganous sulphate rapidly to permanganate, precipitates silver peroxide immediately from silver nitrate solution, and also oxidises phenolphthalein to fluorescein and other hydroxylated derivatives. The substance originally obtained by Berthelot (Compt. rend., 1878, 86, 20) on subjecting a mixture of sulphur dioxide and oxygen to the discharge in an ozoniser, also gives these reactions when dissolved in sulphuric acid, and it is concluded that the peroxide produced by fluorine is probably a sulphur tetroxide (SO_4 or S_2O_8) identical with that present in Berthelot's substance.

IX. Solutions of phosphoric acid, after treatment with fluorine, immediately precipitate iodine from iodides. A slight additional precipitate occurs in one or two cases on keeping. The oxidising power is attributed principally to permonophosphoric acid, H_3PO_5; the solutions, and also permonophosphoric acid prepared by the action of hydrogen peroxide on phosphorus pentoxide, oxidised manganous sulphate to violet manganic phosphate, and not to permanganate (cf. Schmidlin and Massini, A., 1910, ii, 498).

The action of fluorine on di- or tri-alkali phosphates and on pyrophosphates produced salts of both permonophosphoric acid and perphosphoric acid, $H_4P_2O_8$ (iodine precipitated in two stages); the former is unstable, so that it was possible to obtain perphosphoric acid mixed with potassium fluoride from the solution. Possible mechanisms for the reactions involved are discussed.

X. Well-cooled solutions of sodium, potassium, or rubidium carbonate were treated with fluorine, alkali hydroxide being added from time to time to neutralise the acid formed. The resulting oxidising properties of the solutions were relatively feeble, and no percarbonate separated out. Addition of metaborate to the potassium carbonate solutions resulted in an increase of oxidising power to more than twice that recorded with carbonate alone, but no solid perborate was obtained. The presence of mutually antagonistic oxidation products was indicated by the fact that admixture of sodium metaborate solution with potassium hydroxide solution which had been treated with fluorine resulted in a decrease of oxidising power.

G. A. Elliott.

Mechanism of the deoxidation of potassium, lithium, and sodium permanganates in alkaline solution. A. A. Maximov (Z. anorg. Chem., 1927, **163**, 49—64).—The rates of formation of manganate at 100° from potassium, lithium, and sodium permanganates in presence of the corresponding hydroxide have been determined. The results support Bogorodsky's theory that the rate of deoxidation is related to the case of formation of the peroxide of the alkali metal. If hydrogen peroxide or the peroxide of the alkali metal be added in excess to a solution of the hydroxide and permanganate of sodium or potassium, no manganate is formed, but a vigorous reaction, resulting in the production of manganese dioxide, takes place. The quantities of hydrogen peroxide necessary for complete deoxidation to manganate and to manganese dioxide, respectively, are in agreement with the theory that the reaction takes place in two consecutive stages, given for potassium permanganate by the equations $2KMnO_4+H_2O_2+2KOH=2K_2MnO_4+2H_2O+O_2$, and $2K_2MnO_4+2H_2O_2=4KOH+2MnO_2+2O_2$. These equations hold only when the potassium hydroxide concentration is greater than about 0·5*N*. If it is less than about 0·05*N*, hydrated manganese dioxide is formed simultaneously with potassium manganate; rise of temperature has a similar effect. The mechanism of the reactions is discussed, and it is shown that the formation of the peroxide of the alkali metal is a necessary intermediate stage. H. F. Gillbe.

Reaction between arsenite and permanganate in sulphuric acid solutions. T. Oryng (Z. anorg. Chem., 1927, **163**, 195—205).—The reaction between sodium arsenite and potassium permanganate in dilute sulphuric acid solution is discussed. It has been shown experimentally that the final reaction products are compounds of tervalent and bivalent manganese, and that the hydrated manganese dioxide which appears as a precipitate during the course of the reaction is only an intermediate product, since it disappears as the reaction proceeds to completion.

H. F. Gillbe.

Composition and properties of the products of hydrolysis of ferric chloride. N. N. Petin and M. P. Golombick (J. Russ. Phys. Chem. Soc., 1927, **59**, 171—180).—Various quantities of alkali when added to equally concentrated ferric chloride solutions produce partial hydrolysis products of different composition. For each concentration of alkali, two salts are "precipitated." In the solution, two layers separate, a clear upper layer and a cloudy lower layer. The ratio of iron equivalent to that of chlorine is less than 1 in the upper clear layer, and greater than 1 in the lower layer. As the concentration of alkali increases, this ratio increases, and the easier it is to coagulate the ferric hydroxide. Light also increases the speed of coagulation. The stability of the sol depends on the concentration of alkali, being at a maximum when the amount of alkali present is 50—70% of that required for complete precipitation of the ferric hydroxide. E. Rothstein.

Action of pure carbon monoxide on iron at elevated temperatures. W. P. Fishel and J. F. Wooddell.—See B., 1927, 525.

Mode of formation of iron nonacarbonyl from iron pentacarbonyl. E. Speyer and H. Wolf (Ber., 1927, 60, [*B*], 1424—1425).—Iron pentacarbonyl dissolved in glacial acetic acid or acetic anhydride in a vacuum or an atmosphere of hydrogen gives iron nonacarbonyl when exposed to sunlight. In chloroform, acetone, ether, etc. the nonacarbonyl is accompanied by smeary by-products. H. Wren.

Thiosulphato-cobalt complexes and complex cobalt thiosulphates. I. P. R. Ray (*J.* Indian Chem. Soc., 1927, **4**, 64—74).—By the controlled action of ammonium or sodium thiosulphate and ammonia in varying concentration on cobalt hydroxide, chloride, or nitrate in a current of air, a number of crystalline complex thiosulphato-cobalt compounds have been prepared. They are monoacidopentammine salts in which the thiosulphate radical occupies only one co-ordination position; in solution, they hydrolyse slowly into aquo-salts. The following are described: *sulphitopentamminecobaltic thiosulphate* $[(NH_3)_5Co\cdot SO_3]_2S_2O_3$ (also with $1·5H_2O$); *hydroxytetramminecobaltic sulphite*, $[(NH_3)_4Co(OH)SO_3],2H_2O$; these two compounds are brownish-yellow and thus have a sulphur atom linked direct to the cobalt atom (cf. Duff, J.C.S., 1922, **121**, 450); *thiosulphatopentamminecobaltic chloride*, $[(NH_3)_5CoS_2O_3]Cl$, and the corresponding *bromide*, *iodide*, and *nitrate*; *thiosulphatopentamminecobaltic thiosulphate*, $[(NH_3)_5CoS_2O_3]_2S_2O_3,H_2O$; *thiosulphatopentamminecobaltic dithionate*, $[(NH_3)_5CoS_2O_3],S_2O_6$, and the corresponding *chromate*; these compounds are red, the thiosulphate radical being linked to the cobalt atom through an oxygen atom; *triethylenediaminecobaltic thiosulphate*, $[Co(C_2H_8N_2)_3]_2(S_2O_3)_3$; *hexamminecobaltic chloro-thiosulphate*, $[Co(NH_3)_6]ClS_2O_3$, and *nitropentamminecobaltic thiosulphate*, $[(NH_3)_5CoNO_2]S_2O_3$. B. W. Anderson.

Osmium. Distillation of osmium tetroxide from aqueous solution, the oxidation of osmium and its relation to the regeneration of the tetroxide. I. E. Fritzmann (Z. anorg. Chem., 1927, **163**, 165—177).—A small change in the vapour

pressure of the solvent in a ternary system exerts a large influence on the vapour pressure of osmium tetroxide; application of this principle affords a convenient method for the rapid removal of osmium tetroxide from aqueous solution. Osmium and its compounds are most rapidly and conveniently oxidised by methods in which free oxygen is liberated in the course of the reaction; chlorine and bromine, and the oxides of nitrogen and of chlorine, act much more slowly. By simultaneous oxidation and distillation from aqueous solution pure osmium tetroxide may be prepared.

Osmium tetroxide in aqueous solution in many ways resembles an organic substance such as phenol. It behaves as a weak acid and possesses a very small molecular conductivity; addition of inorganic salts produces salting out, and the tetroxide may be distilled in steam. Metallic osmium and to a smaller extent its sulphide may be oxidised by the usual methods employed in organic chemistry.

H. F. GILLBE.

Preparation of potassium sulphate by Hargreaves' process. K. HEPKE.—See B., 1927, 478.

Preparation of potassium sulphate. K. KOLICHEN.—See B., 1927, 477.

Preparation of sulphuric acid from gypsum. H. MOLITOR.—See B., 1927, 520.

Preparation of liquid nickel carbonyl. C. F. VAN DUIN (Rec. trav. chim., 1927, **46**, 381—382).—A more active form of nickel than that used by Laird (this vol., 533) for the production of nickel carbonyl may be prepared by reducing nickelous oxalate with pure hydrogen at 290—300°, purified pumice being used as a carrier. When oxygen-free carbon monoxide is passed over this nickel at 90—100°, the concentration of the exit gases is such that the carbonyl may be separated by cooling in ice and salt only. E. HOLMES.

Smooth electrodes for p_H and conductivity measurements. I. I. SHUKOV (Nature, 1927, **120**, 14).—For p_H and conductivity determinations, platinum electrodes covered electrolytically with gold and with a thin, smooth layer of platinum give excellent results. Platinum foil so coated acts catalytically on a mixture of hydrogen and oxygen, whereas iridium, rhodium, and palladium have no action, or only a slight effect. A. A. ELDRIDGE.

Determination of end-points in potentiometric titrations. F. L. HAHN and M. FROMMER (Z. physikal. Chem., 1927, **127**, 1—42).—The titrations are best carried out when the reagent is added in equal and preferably not excessively small amounts. From theoretical considerations of the potential changes to be expected in the case of a simple reaction, a method has been devised whereby the end-point be calculated from the measured potential changes on either side, within a small fraction of the unit of reagent added. The application of this method to the results of titrations of chloride with silver and *vice versa* showed that the titration was equally accurate when carried out in amounts of 0·1 c.c. of solution as with 0·025*N* solution added in drops of 0·01 c.c. The experimental data served also to determine the solubility product of silver chloride. The potential changes which occur when ferrous ammonium sulphate is titrated with permanganate solution are more complex, and would appear to be determined by unknown intermediate reactions. Nevertheless, the effective reaction is a simple one near the end-point, and accurate titration may be effected by the method described. G. A. ELLIOTT.

Simple apparatus for measuring hydrogen-ion concentration. F. EMSLANDER (Woch. Brau., 1927, **44**, 268—270).—A gas chain apparatus, in which a gold electrode coated with iridium replaces a platinum electrode, is described for use in cases of liquids containing colloidal material. A curve for computing the p_H from the millivolt reading on the bridge (*E.M.F.*) is given. W. ROBSON.

Ionometric measurement of the acidity and alkalinity of glasses by means of the Luers quinhydrone potentiometer. A. MAURI.—See B., 1927, 523.

Effect of gelatin on the titration curves of various acids. E. LITTLE (J. Amer. Pharm. Assoc., 1927, **16**, 414—417).—Curves are given showing the small effect of gelatin on the titration curves of sulphuric, butyric, and lactic acids against sodium hydroxide, and for the effect of *o*-aminobenzoic acid on the titration curves of pyrogallol, tannic acid, and hydrochloric acid with sodium hydroxide.

E. A. LUNT.

Mechanism of titration with adsorbed indicators. J. HODAKOW (Z. physikal. Chem., 1927, **127**, 43—50).—Methyl-violet is adsorbed on the surface of finely-divided silver chloride in presence of excess of chlorine ions, and this process is accompanied by a sharp colour change from blue to pink. The amount of indicator removed in this way has been studied as a function of the charge on the silver chloride particles, and the results serve to explain the Fajans and Hassel titration method (A., 1924, ii, 60). The adsorption is reversible and is a true surface effect. G. A. ELLIOTT.

Standardisation of *N*- and 0·1*N*-acid and alkali solutions. G. FAVREL (Ann. Chim. anal., 1927, [ii], **9**, 161—162).—Potassium hydrogen tartrate is a convenient and accurate standard, since it may readily be obtained pure, does not deteriorate on keeping, and may be weighed out and dissolved for titration without difficulty. S. I. LEVY.

Preservation of standard solution of oxalic acid and reading of the burette. S. ISHIMARU (Bull. Chem. Soc. Japan, 1927, **2**, 134—139).—Solutions of oxalic acid undergo slow decomposition when stored in colourless bottles, and the decomposition is not prevented, but actually accelerated, in presence of sulphuric acid. Standard solutions should be kept in bottles carefully wrapped with black paper. No precautions need be taken for the exclusion of micro-organisms. A convenient device for the reading of burettes is described. J. S. CARTER.

Manganese interference in the *o*-tolidine test for available chlorine. E. S. HOPKINS.—See B., 1927, 521.

Determination of available chlorine in bleaching powder. J. HAUSNER.—See B., 1927, 521.

Micro-reactions of the acids of chlorine, bromine, and iodine. E. M. CHAMOT and C. W. MASON (Mikrochem., 1927, 5, 85—101).—To detect chloride in presence of iodide and bromide, a small quantity of the solution is heated with 10% of its volume of nitric acid in a micro-crucible until brown fumes cease to be evolved, and a crystal of silver nitrate is added to a few drops of the solution on the slide; a fine-grained, apparently amorphous, precipitate indicates the presence of chloride. In the above test, iodides are recognised by the blue colour imparted to starch grains suspended in a drop of water on the underside of a cover-glass covering the crucible, and bromides by the characteristic needle crystals produced by the vapour in a drop of a solution of *m*-phenylenediamine placed next to the drop containing the starch. Other microchemical tests for iodides are based on the formation of characteristic precipitates with mercuric chloride, copper sulphate, palladous chloride, thallous nitrate, and lead nitrate. The formation of chromyl chloride may be used for detecting the presence of chloride if the reaction is conducted in a micro-crucible covered with a slide to which a drop of water adheres; if the water becomes yellow on warming the substance with sulphuric and chromic acids, a small crystal of silver nitrate is added, when, in presence of chlorides, a white precipitate of silver chloride surrounded by orange to red silver chromate appears. The oxy-acids of the halogens are tested for by reducing them with zinc dust and sulphuric acid and applying the above tests to the solution. A. R. POWELL.

Argentometric titration of chlorides and iodides using adsorption indicators. III. I. M. KOLTHOFF (Z. anal. Chem., 1927, **71**, 235—243; cf. this vol., 434, 435).—Indicators have been examined which will give sharp colour changes on addition of slight excess of silver nitrate to chloride and iodide solutions containing acetic acid, in order to permit of the application of the method to the halogen compounds of heavy metals and alkaloids. The most suitable indicator is metanil-yellow, but good results are obtained also with bromophenol-blue; the latter is specially suitable for titration of the alkaloid chlorides by this method. S. I. LEVY.

Identification of iodides and bromides alone and in presence of each other. J. VON MIKÓ (Arch. Pharm., 1927, **265**, 445—450).—"Chloramine" is now officially substituted for chlorine water in the tests prescribed by the German pharmacopœia, but commoner official reagents are better adapted for detecting iodides and bromides. As little as 0·00005 g. of potassium iodide in 5 c.c. can be detected by adding 5*N*-hydrochloric acid (1—5 drops) and 3% hydrogen peroxide (1 drop) or 0·1*N*-potassium permanganate solution (1 drop) and shaking with chloroform. Bromides are similarly identified, but satisfactorily only when permanganate is used. The hydrogen peroxide method, with suitable proportions of the reagents, permits iodides to be detected in presence of bromides, whilst if concentrated hydrogen peroxide and an excess of hydrochloric acid be used, bromides can be identified in presence of iodides, for on shaking, the colour due to the iodine fades and leaves only the brown colour of the bromine. W. A. SILVESTER.

Determination of sulphur in pyrites by the Lunge–Berl method. KASTNER.—See B., 1927, 480.

Titrimetric determination of hydrogen sulphide in producer gas. I. CIOCHINA.—See B., 1927, 465.

Determination of combined sulphuric and hydrochloric acids in cotton. D. A. CLIBBENS and A. GEAKE.—See B., 1927, 471.

Determination of sulphate ion as barium sulphate. V. MARJANOVIĆ (Arhiv Hemiju, 1927, **1**, 5—18).—The solution, which should contain not more than 0·3 g. of sulphate, is evaporated to dryness, 5 c.c. of 10% hydrochloric acid and 2 c.c. of saturated barium chloride solution are added to the residue, together with 100 c.c. of boiling water, and the whole is placed on a water-bath for 1 hr. The supernatant liquid is then decanted through a Gooch crucible and the precipitate treated with 1 c.c. of concentrated hydrochloric acid and 50 c.c. of cold water, and warmed on the water-bath for 10 min., after which the precipitate is filtered through the same Gooch crucible, washed, dried, and weighed. The average experimental error for the above method is 0·04% for solutions of pure sulphates; the presence of chlorides and nitrates, and of sodium, potassium, magnesium, iron, copper, aluminium, and ammonium ions does not affect the accuracy of this method. Phosphate ions lead to high values, whilst in presence of calcium ions low results are obtained.

R. TRUSZKOWSKI.

Determination of phosphorus and silicon in ferrophosphorus. W. F. POND.—See B., 1927, 488.

Sensitiveness of some test papers for gaseous phosphine. M. WILMET (Compt. rend., 1927, **184**, 1456—1458).—The technique previously developed (this vol., 221) has now been applied in the examination of the sensitiveness towards gaseous phosphine of copper sulphate, silver nitrate, mercuric chloride, potassium mercuri-iodide, HgI_2,3KI, and "sensitised" mercuric chloride (alkaline iodomercurate) impregnated on filter-paper. Copper sulphate and neutral potassium mercuri-iodide are the least sensitive. Mercuric chloride (5% solution) paper affords a means of distinguishing between phosphine and arsine, if after slight exposure to the gas the test-paper is dipped in 5% potassium iodide solution. With phosphine, the shade thus developed varies from pale yellow to reddish-orange or salmon, whereas arsine gives a reddish-brown coloration. The dynamic method allows of the approximate determination of the volume of air containing 0·5 mm.^{3} of the gas with 5% mercuric chloride papers or 0·2 mm.^{3} with silver nitrate paper (0·1*N*-solution). The odour of the gas can be recognised for concentrations above 1 : 20000; below 1 : 50000 it cannot be detected.

R. BRIGHTMAN.

Determination of tervalent arsenic. L. A. DESHUSSES and J. DESHUSSES (Helv. Chim. Acta, 1927, **10**, 517—530).—A critical study of the various

methods of determining tervalent arsenic in commercial Schweinfurth green. The Avery–Beans method gave results which were consistently too high (0·1%), owing to the effect of the presence of copper on the end-point of the titration with iodine. A modified distillation method, in which the substance was distilled in presence of methyl alcohol saturated with hydrogen chloride, is both accurate and rapid. The removal of arsenic trichloride during the distillation was favoured equally by the addition of either powdered quartz or potassium bromide.

G. A. ELLIOTT.

Iodometric determination of arsenic acid. L. ROSENTHALER (Z. anal. Chem., 1927, **71**, 190—191).—A reply to Ormont's criticism (this vol., 325) of Rosenthaler's method (A., 1926, 702). A. R. POWELL.

Determination of arsenic pentoxide as magnesium ammonium arsenate. W. M. MCNABB (J. Amer. Chem. Soc., 1927, **49**, 1451—1453).—The precipitation of monopotassium hydrogen arsenate by magnesia mixture is complete in ½ hr., and accurate results are obtained only when the precipitate of magnesium ammonium arsenate is converted into pyroarsenate by ignition to constant weight at 500—600°. S. K. TWEEDY.

Gas-volumetric micro-determination of carbon. C. GRÄNACHER (Helv. Chim. Acta, 1927, **10**, 449—471).—A detailed description is given of a method whereby the gases issuing from the combustion tube are completely collected, and the volume change which occurs when the carbon dioxide is absorbed by potassium hydroxide is measured. The gas space within the combustion tube was made as small as possible. G. A. ELLIOTT.

Conductivity method for determination of carbon dioxide. L. E. BAYLISS (Biochem. J., 1927, **21**, 662—664).—The method is based on the principle that the migration velocity of the carbonate ion is considerably smaller than that of the hydroxyl ion, and consequently the conductivity of sodium hydroxide falls as it absorbs carbon dioxide. The amount of carbonate in a sodium hydroxide–sodium carbonate mixture can thus be determined when a rapid absorption of carbon dioxide by sodium hydroxide takes place. S. S. ZILVA.

Determination of potassium in presence of iodide. F. S. HAWKINS and J. R. PARTINGTON (J.C.S., 1927, 1397—1398).—The alkali iodides are dissolved in a saturated solution of potassium perchlorate in 96% alcohol, and the potassium is precipitated by the addition of a similar saturated solution of sodium perchlorate. The mixture is boiled, cooled to 0°, and filtered; the precipitate is washed at 0° with the alcoholic potassium perchlorate and dried at 360°. The method is more accurate than the other known methods; it obviates the errors described by Smith and Ross (A., 1925, ii, 437), and is applicable to any potassium salt soluble in 96% alcohol. The s pure potassium iodide gives a purity of 99·95%. S. K. TWEEDY.

Przibylla's tartaric acid method for the etermination of potassium. E. BORSCHE.—See B., 1927, 478.

Semi-quantitative spectral analysis of calcium, strontium, barium, and lithium. K. HUKUDA (Bull. Chem. Soc. Japan, 1927, **2**, 115—121).—Dilute solutions of salts fulgurated in a special fulgurator with the electrodes reversed, *i.e.*, with the anode in the solution, are observed spectroscopically. The probable limits of detection of calcium, strontium, barium, and lithium by this method are 0·013, 0·029, 0·018, and 0·0009 mg./c.c., respectively. The procedure requires only about 0·1 c.c. of solution.

J. S. CARTER.

Analysis of hydrated lime by a thermochemical method. D. F. RICHARDSON.—See B., 1927, 477.

Volumetric determination of magnesium, zinc, aluminium, and copper. F. L. HAHN and E. HARTLEB (Z. anal. Chem., 1927, **71**, 225—235).—The errors arising in the titration of salts of the metals with alkali hydroxides, due to formation of basic salts and to the adsorption of the alkali by the precipitated hydroxide, are entirely eliminated by the addition of "oxine," 8-hydroxyquinoline, which forms insoluble compounds with the metals, precipitation being complete if the liberated acid is neutralised by addition of standard alkali. The compounds are yellow, but the end-points are quite sharp if phenol-red is used as indicator; in presence of nitrates or other oxidising materials, naphtholphthalein is employed, and the end-point is rendered very sharp by addition of carbon tetrachloride, in which 8-hydroxyquinoline and its metallic derivatives are very soluble. Whilst barium salts do not interfere, calcium must be removed from the solution before the titration. S. I. LEVY.

Separation and determination of metals by means of 8-hydroxyquinoline. III. Zinc. R. BERG (Z. anal. Chem., 1927, **71**, 171—185; cf. this vol., 436, 639).—Addition of a 2% alcoholic solution of 8-hydroxyquinoline to an alkaline or acetic acid solution of a zinc salt produces a greenish-yellow precipitate of $Zn(C_9H_6ON)_2,2H_2O$, which loses $0{\cdot}5H_2O$ at 100°, becomes anhydrous at 120—130°, and is converted by ignition into zinc oxide. The solubilities of the precipitate in sodium acetate solutions, in ammonia, and in alkaline tartrate solutions are, respectively, 1 part in 1,000,000 parts, 1 in 277,000, and 1 in 140,000. From all metals except copper, magnesium, and cadmium, zinc may be separated by carrying out the precipitation in strongly alkaline tartrate solution, and from magnesium by precipitation in dilute acetic acid solution. The precipitate may be dried at 100° or ignited to oxide for weighing, or it may be determined bromometrically in the same way as the magnesium precipitate.

A. R. POWELL.

Determination of lead as cyanide. (MLLE.) S. GRUNDT (Compt. rend., 1927, **185**, 72—73).—The so-called precipitated lead cyanide of Herz and Neukirch (A., 1923, ii, 879) is actually a mixture of lead oxycyanide and hydroxide. The latter combines with atmospheric carbon dioxide during the washing and drying processes with the production of the mixture $[Pb(CN)_2,2PbCO_3,PbO,H_2O]$. By coincidence, the percentage of lead in this is the same as in the cyanide

Attempts to produce pure lead cyanide from hydrogen cyanide and hydrated lead oxide ($3PbO,H_2O$) in absence of water were unsuccessful, and resulted in the formation of compounds the highest cyanide content of which corresponded with the formula $Pb(CN)_2,PbO$. J. GRANT.

Rapid determination of copper. G. SPAGU and J. DICK (Z. anal. Chem., 1927, **71**, 185—189).—The solution of the copper salt (75—100 c.c.) is treated drop by drop with pyridine until it becomes azure-blue, 0·5 g. of solid ammonium thiocyanate is stirred in, and the precipitate collected immediately in a porcelain filtering crucible, washed with cold water containing 3 g. of ammonium thiocyanate and 3 c.c. of pyridine per litre, then with 75 vol.-% alcohol containing 8 c.c. of pyridine and 0·5 g. of ammonium thiocyanate per litre, and finally with absolute alcohol and ether containing a little pyridine, dried in a vacuum at the ordinary temperature, and weighed as $Cu(C_5H_5N)_2(SCN)_2$ which contains 18·817% Cu. A. R. POWELL.

Determination of small quantities of copper in steel. J. D. ARMOUR.—See B., 1927, 487.

Determination of cerium. R. LESSING (Z. anal. Chem., 1927, **71**, 161—170).—Bunsen's method of determining cerium volumetrically in mixtures of rare-earth oxides by distillation with hydrochloric acid and potassium iodide yields high results if more than about 1% of praseodymia is present, and cannot therefore be used for determining ceria in the rare earths obtained from monazite. Fairly good results may be obtained by warming the oxide mixture with sulphuric acid and a standard ferrous sulphate solution, and titrating the excess of the latter with permanganate; part of the higher praseodymium oxide reacts with the ferrous salt, and the remainder decomposes with evolution of oxygen. With the monazite earths, the results for cerium are within 1% of those obtained by von Knorre's method. A. R. POWELL.

Determination and separation of the oxidisable constituents of aluminium alloys. G. JANDER and F. BAUR.—See B., 1927, 527.

Use of mercuri-amides in analytical chemistry. M. KRANJCEVIC and G. RUKONIC (Arhiv Hemiju, 1927, **1**, 18—24).—Šolaja's method for the determination of iron and aluminium (A., 1925, ii, 602) is applied to the determination of chromium, of iron in presence of calcium, and of aluminium in presence of magnesium. R. TRUSZKOWSKI.

Detection and determination of very small quantities of iron in water. F. KRÖHNKE.—See B., 1927, 542.

Reaction between ferrous salts and dimethylglyoxime. E. J. KRAUS (Z. anal. Chem., 1927, **71**, 189—190).—Under the conditions in which nickel gives a red precipitate with dimethylglyoxime, ferrous salts yield a red coloration. Filtration of the solution is therefore necessary to verify the presence of traces of nickel when the solution contains a ferrous salt. A. R. POWELL.

Use of liquid amalgams in volumetric analysis. VII. Oxidimetric determination of chromium. K. SOMEYA (Sci. Rep. Tohoku Imp. Univ., 1927, **16** 397—409).—See this vol., 333.

Gravimetric determination of chromium with mercury ammonium chloride, $HgClNH_4$. W. PUMM.—See B., 1927, 480.

Potentiometric determination of molybdenum. E. MULLER [with P. BRUN and G. UNGER] (Z. Elektrochem., 1927, **33**, 182—185).—A method of determining molybdenum (in oxidised compounds) by reducing with zinc to the tervalent condition and titrating the resulting solution with permanganate has been developed by Reissaus (Metall und Erz, 1924). Success of the method depends on complete reduction to the tervalent state and exclusion of air during the titration. In the present work, potentiometric titration of the reduced solution with permanganate was found to give a sharp end-point corresponding with complete oxidation to the sexavalent condition in absence of air, but the accuracy still depends on the efficiency of the preliminary reduction, for the bend in the titration curve corresponding with oxidation to the quadrivalent condition is not well defined, and somewhat displaced, and no bend is found corresponding with conversion into the quinquevalent state. These results are discussed with reference to the potentiometric titration of sexavalent molybdenum with tervalent titanium in which the titration curve exhibits a bend corresponding with reduction to the quinquevalent state. Running a solution of tervalent molybdenum into excess of permanganate and titrating back with ferrous sulphate gives an unsatisfactory end-point by ordinary titration, but gives good results by the potentiometric method, and has the advantage that exclusion of air is not necessary. Fricke (Diss., Dresden, 1923) has shown that an ordinary titration method in presence of air consists in running the solution of tervalent molybdenum into excess of permanganate, adding excess of ferrous sulphate, and then titrating with permanganate. H. J. T. ELLINGHAM.

Determination of molybdenum in iron and steel. E. FARBER.—See B., 1927, 526.

Use of liquid amalgams in volumetric analysis. IX. Determination of vanadium and tungsten. K. SOMEYA (Z. anorg. Chem., 1927, **163**, 206—212).—A new method is described for the volumetric determination of vanadium; vanadic acid is reduced by zinc amalgam to the vanadous state, and standardised iodine solution added. The excess of iodine is reduced with sodium arsenite solution, and the excess of arsenite titrated with iodine. Cupric sulphate may be employed in place of potassium permanganate for the quantitative volumetric oxidation of tungsten. In strongly acid solution, lead amalgam reduces vanadic acid to the vanadous condition; by adding an excess of cupric sulphate solution and titrating with potassium dichromate solution, using a diphenylamine indicator, vanadium may be accurately determined, provided that the correct acid concentration is maintained. H. F. GILLBE.

Crystallisation of silver beads and detection of the platinum metals by the microscope. C. O. BANNISTER (J. Roy. Micros. Soc., 1927, **47**, 143

144).—The presence of traces of the platinum metals in silver beads obtained by cupellation causes characteristics in the surface crystallisation which permit of the identification of the foreign metal. The bead is merely examined under the microscope. The effects are illustrated by means of plates. S. I. LEVY.

Electric furnace for gas reactions. O. SCARPA.—See B., 1927, 529.

Platinum-wound resistance furnace. E. ORTON, jun., and J. F. KREHBIEL.—See B., 1927, 529.

Flames of atomic hydrogen. I. LANGMUIR.—See B., 1927, 529.

Carbon dioxide in a mercury interrupter. G. R. PARANJPE and H. D. TENDULKAR (Nature, 1927, **120**, 117—118).—Carbon dioxide can be advantageously used instead of coal gas in mercury interrupters. When hydrogen or carbon dioxide is used, the efficiency is greater than when coal gas is used. A. A. ELDRIDGE.

Simple automatic temperature regulator without relays. A. SIMON and O. FISCHER (Z. anorg. Chem., 1927, **162**, 279—286).—A device is described for maintaining a crucible in an electric oven at a constant temperature for several months. Electric contact is made and broken between a platinum wire and a small platinum sphere floating on mercury in a glass tube. The regulator is operated by the expansion and contraction of the air contained in a double-walled, crucible-shaped glass or porcelain vessel which is fitted in the oven, and into which the crucible or substance to be heated is placed. Instead of the circuit being completely broken, part of the current is allowed to pass through a shunt circuit, the actual current to be broken being thus minimised. Further, since the spark occurs between platinum electrodes, no deposit is formed on the walls of the regulator tube or on the mercury surface. H. F. GILLBE.

Weighing powdered substances in air and in a vacuum. E. ZINTL and J. GOUBEAU (Z. anorg. Chem., 1927, **163**, 105—119).—Weighing a substance in air and reducing the value to a vacuum in the usual manner does not give consistent results for powders, on account of variable adsorption effects. For example, potassium nitrate, weighed as a powder and then melted down to a compact mass, may appear to lose up to 0·09 mg. per g. The deviation is shown not to be due to decomposition of the nitrate or to experimental error. An apparatus and a method are described for precise weighing in a vacuum. H. F. GILLBE.

Measurement of low vapour and partial pressures. H. VON HALBAN and K. SIEDENTOPF (Z. angew. Chem., 1927, **40**, 661—666).—The apparatus consists of a brass rod, mounted vertically in a glass tube through which the gas to be examined passes; the upper end of the rod is maintained at 0° by immersion in a bath of ice and water, the lower end at −76° by immersion in a bath of ether and solid carbon dioxide. The point on the rod at which liquid or solid is deposited is a measure of the concentration of the vapour in the permanent gas. The apparatus is designed for the measurement of partial pressures of water vapour in air of less than 1 mm. (1 g./m.^{3}), and is calibrated for any particular vapour and permanent gas by the employment of known mixtures. It requires only small quantities of the mixture to be examined, readings can be made very quickly, and pressures of water vapour down to 0·001 mm. can be determined under technical conditions. S. I. LEVY.

New methods of gas analysis. P. RASSFELD (Z. angew. Chem., 1927, **40**, 669—672).—An account of the methods of employment of the Haber–Lowe gas interferometer, and the principles on which the composition of gas mixtures may be determined from measurement of the refractive index. S. I. LEVY.

Ferroxyl indicator in corrosion research with special reference to the problem of local corrosion. U. R. EVANS.—See B., 1927, 487.

Mineralogical Chemistry.

Influence of plankton on the phosphate content of stored sea-water. R. GILL (J. Marine Biol. Assoc., 1927, [ii], **14**, 1057—1065).—The alteration in soluble phosphate content of untreated sea-water during storage is governed by the conditions of storage; strong illumination, favourable to growth, produces a decrease, whilst darkness, unfavourable to growth, produces an increase. Samples from the surface layers of the sea give greater increases of phosphate on storage in the dark than samples from deeper water, the extent of the increase being conditioned by the number and quantity of planktonic organisms included in the water sample. The phosphate content per cub. m. of North Sea water off the Northumberland coast increases from 13·5 mg. P_2O_5 at the surface to 34·6 mg. at a depth of 70 m. Surface values at northern stations are higher than those at southern stations, whilst inshore surface waters are richer in phosphate than offshore surface waters. W. ROBSON.

Relation of plankton to chemical and physical factors in the Clyde sea area. S. M. MARSHALL and A. P. ORR (J. Marine Biol. Assoc., 1927, [ii], **14**, 837—868).—Data obtained during 1924—1926 show that a close relation exists between the diatom increases and the changes in p_H, dissolved oxygen saturation, and phosphate content. Diatom cultures grow best away from direct sunlight, diatoms in the shade producing oxygen, whilst those in sunlight may even use it up. A fall in the water-temperature curve coincides with dips in those for p_H, dissolved oxygen saturation, and phosphate content. The proximity of rivers affects the silica, but not the phosphate content of the water, whilst the saline

content and rainfall curves are closely related. Where animal life is rich, dissolved oxygen saturation and values are low and phosphate values high. The regeneration of phosphate in the deep water of Loch Strivan is described. W. ROBSON.

Adsorption of ions from sea-water by sand. F. P. STOWELL (J. Marine Biol. Assoc., 1927, [ii], **14**, 955—966).—The adsorption of the electrolytic constituents of sea-water by sand is small. Percolation of sea-water through sand causes a slight abnormality in the concentrations of calcium and magnesium ions, due to the fact that sand is not an inert adsorbing agent, but is capable of discharging calcium ions into the water in exchange for magnesium and sodium. The extent of adsorption and exchange is insufficient to cause hydrolysis and alteration in if the volume of the sea-water is large. W. ROBSON.

Present position of the lignin theory of [the origin of] coal. W. FUCHS (Brennstoff-Chem., 1927, **8**, 187—190).—A critical review of recent work on the decomposition, under natural conditions, of cellulose and lignin. The results obtained, although complicated by the probable existence of more than one kind of lignin, support the theory that the cellulose in plants is broken down, by the action of simple organisms, to lower fatty acids, and that the lignin, which is more resistant and therefore increases in relative quantity in the decomposing vegetable matter, ultimately loses acetyl and methoxyl groups and is converted into alkali-soluble humic acids, which are further transformed into alkali-insoluble humins and finally into coal.
W. T. K. BRAUNHOLTZ.

Iodine content of the salt from Rumanian rock-salt mines. D. RADULESCU and V. GEORGESCU.—See B., 1927, 479.

Hydrated alumina of the bauxites [boehmite]. J. DE LAPPARENT (Compt. rend., 1927, **184**, 1661—1662; cf. A., 1924, ii, 269).—In certain bauxites from Cadarcet and Var in which the crystalline structure is particularly well developed, orthorhombic crystals formed by a monohydrate of alumina may be seen. Their form results from a combination of the prism *m* (110) and the base *p* (001), the acute angle of the *m* faces being 63°. The mineral has a sharp cleavage plane parallel to the direction *g'* (010), its maximum birefringence is of the order of 0·020, and the mean refractive index is a little higher than that of the surrounding hydrargillite. The author considers the mineral to be a new type of monohydrated alumina which he names *boehmite*. He discusses the possibility of its identity with Boehm's bauxite (A., 1926, 113). J. GRANT.

Thorotungstite. A mineral containing tungsten and thorium from the Federated Malay States. J. B. SCRIVENOR and J. C. SHENTON (Amer. J. Sci., 1927, [v], **13**, 487—490).—A new mineral, thorotungstite, containing honey-yellow crystals was found in the Kramat Pulai mine. The crystals were transparent, apparently orthorhombic, *d* 5·55, and contained WO_3 69·69, ThO_2 16·00, Al_2O_3 4·31, Fe_2O_3 1·35, SiO_2 0·48, ZrO_2 1·96, CaO 1·02, rare earths (chiefly ceria) 1·77%, magnesia trace, loss on ignition (H_2O) 4·18, total 100·76%. The nearest molecular formula is $(ThO_2,Ce_2O_3,ZrO_2),H_2O+2WO_3,H_2O$. C. J. SMITHELLS.

Organic Chemistry.

[Exceptional instances of stereoisomerism.] G. HAHN (Ber., 1927, **60**, [*B*], 1362—1364).—A comment on the conceptions of Senior (this vol., 226), whose idea of internal compensation is considered to be too narrow. H. WREN.

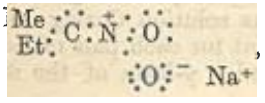
Synthesis of paraffin hydrocarbons of high mol. wt. from carbon monoxide. F. FISCHER and H. TROPSCH [with W. TER-NEDDEN] (Ber., 1927, **60**, [*B*], 1330—1334).—The reaction of water gas at an iron–copper (4 : 1) contact impregnated with potassium carbonate gives rise to solid paraffin hydrocarbons the most sparingly soluble fraction of which has m. p. 104—117°, solidifying point 109°, and appears to contain on the average about 71 carbon atoms in the molecule. Formation is attributed either to the action of hydrogen on the metallic carbide or to the production and subsequent polymerisation of methylene. H. WREN.

Addition of hydrogen bromide to allene hydrocarbons. M. BOUIS (Compt. rend., 1927, **184**, 1563—1565).—The addition of hydrogen bromide to $\Delta^{\alpha\beta}$-pentadiene yields β-bromo-Δ^{α}-pentene (cf. Lespieau, A., 1921, i, 656), β-*bromo*-Δ^{β}-*pentene*, and ββ-dibromopentane. The two first-named compounds are not isolated in a state of purity, but as a mixture, b. p. 106—115°/760 mm. These results are discussed in relation to the analogous work on dimethylallene and on diethylallene (Mokievsky, A., 1900, i, 509; Ipatiev, A., 1899, i, 657). G. A. C. GOUGH.

Tautomerism of the two erythrene dibromides. C. PREVOST (Compt. rend., 1927, **184**, 1460—1462).—Tetramethylerythrene (βε-dimethyl-$\Delta^{\beta\delta}$-hexadiene), obtained by the action of sodium in benzene at 60 on *iso*crotyl bromide, has m. p. 14·5°, b. p. 134·6°/750 mm., $d_4^{17\cdot8}$ 0·7646, $n_D^{19\cdot8}$ 1·4796, and is relatively stable when pure. With 2 mols. of bromine at −20° to −10°, it affords a liquid product which slowly solidifies. The solid product, true m. p. 72°, is regarded as βε-*dibromo*-βε-*dimethyl*-Δ^{γ}-*hexene*, and when heated slowly melts at 45—50°, undergoing transformation into the liquid isomeride, βγ-*dibromo*-βε-*dimethyl*-Δ^{δ}-*hexene*. It is suggested that in general bromination of the erythrenes affords initially the βγ-dibromo-derivative which is usually in metastable equilibrium and is transformed with slight elevation of temperature into the βε-derivative. Negative substituents in positions β and ε enhance the mobility of the ε-bromine atom but decrease that of the β-bromine. Attempts to introduce 4 atoms of bromine into di*iso*crotyl failed, halogen hydride being eliminated. R. BRIGHTMAN.

Reactions of the di*iso*crotyl dibromides. C. PRÉVOST (Compt. rend., 1927, **184**, 1561—1563).—The two isomeric di*iso*crotyl dibromides (preceding abstract) lose hydrogen bromide when heated at 100°, to yield *α-bromo-βε-dimethyl-Δ$^{\beta\delta}$-hexadiene*, b. p. 85—86°/12 mm., d_4^{18} 1·2230, n_D^{18} 1·5522. The latter, on treatment with sodium acetate or with silver acetate, yields *βε-dimethyl-Δ$^{\beta\delta}$-hexadien-α-yl acetate*, b. p. 79°/3·5 mm., d_4^{17} 0·9597, n_D^{17} 1·4890, and a *hydrocarbon*, $C_{16}H_{28}$. *βε-Dimethyl-Δ$^{\beta\delta}$-hexadien-α-ol*, b. p. 77°/3 mm., d_4^{17} 0·9197, n_D^{17} 1·5095, obtained from the acetate in the usual way, yields on hydrogenation a small amount of βε-dimethylhexan-α-ol, together with large quantities of condensation products.

G. A. C. GOUGH.

Stereochemistry of the tetrahedral carbon atom. V. Salt formation from the nitroparaffins. R. KUHN and H. ALBRECHT (Ber., 1927, 60, [*B*], 1297—1308).—The optically active *sec.*-butyl alcohols (cf. Pickard and Kenyon, J.C.S., 1913, **103**, 1937) are transformed into the corresponding iodides, which are then treated with silver nitrite at 0°. The mixture of active *sec.*-butyl nitrites and *β-nitrobutanes* is separated by fractional distillation, whereby the latter substances are obtained mixed with less than 0·2% of nitrite. The analytically homogeneous material has b. p. 35—36°/17 mm., 55—56°/47 mm., d_4^{17} 0·9854, n_D^{17} 1·4057; partial racemisation, however, occurs to a variable extent during the preparation, the most active specimen having $[\alpha]_D^{18}$ +9·14° in substance. Treatment of the active β-nitrobutanes with 5*N*-sodium hydroxide in methyl-alcoholic solution at the ordinary temperature causes complete racemisation, whereas at lower temperatures or in more dilute solution activity persists, but salt formation is incomplete. The action of the necessary quantity of sodium methoxide in methyl-alcoholic solution gives the sodium salt of *aci*-β-nitrobutane, the activity of which is about 60% of that of the nitro-compound. Addition of excess of methoxide tends to enhance the optical activity. The almost complete salt formation is established by the observations that the activity of the aqueous solutions is scarcely affected by extraction with ether, and that volumetric determination of the *aci*-form with bromine in presence of ferric chloride as indicator shows 80% of the calculated quantity when operations are very rapidly performed in strongly cooled solution. Precipitation of the sodium salt from its methyl-alcoholic solution by a large excess of ether gives a product retaining 25—30% of the original activity, whereas the residues from the ethereal liquor are optically inactive, so that unchanged nitro-compound, nitrite, or alcohol cannot be causative of the observed activity. This conclusion is confirmed by the formation of optically active β-bromo-β-nitrobutane, $[\alpha]_D$ +1·42° in substance, which can be derived only from the *aci*-form. The existence of the latter form in an optically active condition is not compatible with the customary formulation, and the electronic constitution,  , is therefore proposed, which is shown to harmonise with the general chemical properties of the compound.

H. WREN.

Ester formation in ethylene glycol. A. KAILAN and K. MELKUS (Monatsh., 1927, **48**, 9—35).—The velocity of esterification (which goes to completion) of *n*-butyric, benzoic, salicylic, and *o*- and *p*-hydroxybenzoic acids in anhydrous and wet ethylene glycol with hydrogen chloride as a catalyst has been measured at 25°, and the effects of varying concentrations of acid, water, and catalyst have been determined; intrapolation formulæ expressing the velocity constant as a function of the concentrations of the water and the catalyst are given in each case. In anhydrous glycol, the velocity is proportional to the concentration of the catalyst, but in presence of water it increases more rapidly than proportionality requires. Combining these results with those obtained by Goldschmidt and Udby (A., 1907, ii, 852) for ethyl alcohol and earlier results of Melkus for glycerol, the following conclusions are reached. For a water concentration (w) of 0·03 mol./litre, the value of the unimolecular velocity constant (k) for salicylic acid in glycol is 60% greater and for the other acids 30% smaller than in alcohol. As in ethyl alcohol, the retarding influence of water is greatest with benzoic and least with butyric acid, and is slightly less in glycol than in glycerol, and much less than in alcohol. The relative values of k for benzoic acid and its *o*-, *m*-, and *p*-hydroxy-derivatives in acid concentrations of $\frac{1}{6}$ mol./litre, and with w=0·065, are 1 : 0·073 : 1·115 : 0·39 in glycol and 1 : 0·037 : 1·17 : 0·43 in alcohol, chlorohydrin formation affecting the figures for salicylic acid. The values of k for butyric and benzoic acids in glycol are, respectively, 2·5—3 and 1·25—2 times as great (depending on the concentrations of water and the catalyst) as in glycerol.

J. W. BAKER.

Lactacidogen. V. G. EMBDEN and M. ZIMMERMANN (Z. physiol. Chem., 1927, **167**, 114—136).—A new *hexosemonophosphoric acid*, $[\alpha]_D^{20}$ +29·5°, has been isolated from fresh rabbit muscle and analysed as the crystalline *brucine* salt and the amorphous *barium* salt. The acid, like lactacidogen, leads to an increased formation of lactic and phosphoric acids by muscle juice. Although muscle juice under the influence of sodium fluoride synthesises hexosediphosphoric acid (A., 1925, i, 729), no actual proof of the presence of this acid in fresh muscle can be obtained.

A. WORMALL.

Hexosediphosphoric acid. I. α- and β-Methylhexosidediphosphoric acids. W. T. J. MORGAN (Biochem. J., 1927, **21**, 675—688).—The hexosides were prepared by Fischer's method. The changes in rotation in the process of methylation suggested the formation of two isomerides. The barium derivatives of the methylated compounds can be separated roughly by fractional precipitation of the aqueous solution with ethyl alcohol. A more complete separation was obtained by the preparation of the brucine salts, from which the barium salts were obtained, barium β-methylhexosidediphosphate, $C_6H_9O_3(OMe)(PO_4Ba)_2$, $[\alpha]_{18}^{18}$ −10·4°, free acid, −23·2°, and barium α-methylhexosidediphosphate,

$[\alpha]_{Hg}$ +8·2°. free acid. $[\alpha]^{18}_{Hg}$ +19·7°. The methyl group of the α-acid is more rapidly removed by hydrolysis than that in the corresponding β-compound. Neither hexoside is hydrolysed by emulsin. Invertase causes a partial removal of the methyl group from the α-hexoside, but not from the β-compound. Bone enzyme rapidly removes the phosphoric acid groups from the β-compound, producing a strongly lævorotatory, non-reducing substance possessing the properties of a fructoside. The methylation of hexosediphosphoric acid yielded a non-reducing syrup consisting largely of the hexamethyl-methylhexosidediphosphoric acid. S. S. ZILVA.

Aliphatic and alicyclic disulphones. A. RECSEI (Ber., 1927, 60, [*B*], 1420—1423).—The action of hydrogen chloride on a mixture of ethyl mercaptan and dipropyl ketone affords *diethylthioldi-n-propylmethane*, which could not be distilled without decomposition. It is oxidised by aqueous permanganate to *diethylsulphonyldi-n-propylmethane*, m. p. 109·5°. Similarly, *n*-propyl *iso*propyl ketone gives the corresponding *dithiol*, oxidised to *diethylsulphonyl-n-propylisopropylmethane*, m. p. 91°. *cyclo*Hexanone and ethyl mercaptan afford 1 : 1-*diethylthiol*cyclo*hexane*, b. p. 67—110°/12 mm. (partial decomp.), from which 1 : 1-*diethylsulphonyl*cyclo*hexane*, m. p. 121°, is derived. 2-*Chloro*-1 : 1-*diethylsulphonyl*cyclo*hexane*, m. p. 91°, is obtained from 2-chloro*cyclo*hexanone. Oxidation of the higher thiols is difficult. Hydrogen peroxide, chromic acid, and dilute nitric acid are ineffective; diluted Caro's acid is inferior to permanganate. The sulphones described above are much more active pharmacologically than sulphonal. H. WREN.

Preparation of pure oleic acid. S. H. BERTRAM (Rec. trav. chim., 1927, 46, 397—401).—From a comparative, quantitative study of the numerous methods available for the purification of oleic acid, the author concludes that, hitherto, oleic acid has never been obtained free from appreciable quantities both of saturated and higher unsaturated acids, and suggests that the main cause of the difficulty is the isomorphism of oleic acid and its impurities. Oleic acid containing less than 0·4—0·5% of saturated acids may be prepared by adding 100 g. of crude oleic acid to a warm mixture of 175 g. of mercuric acetate, 140 c.c. of methyl alcohol, and 35 c.c. of glacial acetic acid, and heating for 2 min. on the steam-bath. After keeping for 24 hrs., the mixture is filtered and the complex mercury compound in the filtrate decomposed by boiling with 50 c.c. of hydrochloric acid (*d* 1·19). The resulting mixture of ester and acid, after extraction with light petroleum (b. p. 40—60°), is hydrolysed. It was not found practicable to remove all higher unsaturated acids by extraction of the calcium, barium, or lithium salts with ether, benzene, light petroleum, or alcohol, but this was effected by crystallising the oleic acid from an equal volume of acetone at −10° to −15°, and washing with acetone at −20°. The resulting product consisted of colourless, transparent, needles, m. p. and s. p. 13·2°, which changed to a more stable, white modification, m. p. 16°. It then had the constants, iodine value (Hübl) 89·55, n^{20}_D 1·45823, n^{70}_D 1·44179, and contained only 0·49% of saturated acids. Elaidic and erucic acids may be purified similarly. E. HOLMES.

Acid soaps: crystalline potassium hydrogen dioleate. J. W. MCBAIN and A. STEWART (J.C.S., 1927, 1392—1394).—*Potassium hydrogen dioleate*, an anhydrous, crystalline, acid soap, has been isolated at 0° from alcoholic solutions containing oleic acid and potassium oleate in molecular proportions varying between 1 to 2 and 2 to 1, respectively. Analyses by hydrolysis with hydrochloric acid and by the determination of saponification values show good agreement, and account for 99·8% (average) of the sample taken. The compound, which may be crystallised unchanged from oleic acid, has a transition point at 43° and liquefies completely above 107°, whilst decomposition occurs when it is maintained at 55—60°. E. HOLMES.

Thermal decomposition of aryl esters of fumaric and cinnamic acids into s-diarylethylenes. R. ANSCHUTZ (Ber., 1927, 60, [*B*], 1320—1322; cf. Skraup and Beng, this vol., 560).—Thermal decomposition of phenyl fumarate affords phenyl cinnamate and ultimately stilbene. If a substituent is present in the phenyl group, the intermediate product cannot be isolated; the yields of *s*-diarylethylenes are lower, and the products are frequently uninviting resins. The following fumarates are described (cf. Wirtz, Diss., Bonn, 1887; Selden, Diss., Erlangen, 1888; Boringer, Diss., Bonn, 1919): o-*tolyl*, plates, m. p. 88—89°, or needles, m. p. 85°, b. p. 225°/12 mm.; m-*tolyl*, plates, m. p. 88°, or needles, m. p. 83°, b. p. 237°/12 mm.; p-*chlorophenyl*, m. p. 178° (and thence 4 : 4′-*dichlorostilbene*, m. p. 170°); p-*bromophenyl*, m. p. 174° (and thence 4 : 4′-dibromostilbene, m. p. 210—211°); p-*nitrophenyl*, m. p. 219—211° (decomp.). *Phenyl fumaranilate*, m. p. 214°. The following cinnamates are described: p-*chlorophenyl*, m. p. 105° (and thence p-*chlorostilbene*, m. p. 127°; *dibromide*, m. p. 190°); p-*bromophenyl*, m. p. 116° (and thence p-*bromostilbene*, m. p. 135°; *dibromide*, m. p. 199°); o-*nitrophenyl*, m. p. 84·5°; p-*nitrophenyl*, m. p. 146°; *phenyl* p-*nitrocinnamate*, m. p. 152°, from p-*nitrocinnamoyl chloride*, b. p. 205—210°, m. p. 124—125°, and phenol; p-*acetamidophenyl cinnamate*, m. p. 220°. The gaseous products of the thermal decomposition of the esters generally contain carbon monoxide in addition to carbon dioxide, and, frequently, the phenol employed in the preparation of the ester. H. WREN.

Lactones derived from simple sugars. H. D. K. DREW, E. H. GOODYEAR, and W. N. HAWORTH (J.C.S., 1927, 1237—1245).—Ten completely methylated lactones derived from normal and γ-forms of completely methylated glucose, galactose, mannose, xylose, and arabinose have been studied, with the object of establishing a comparison of the rates of hydrolysis of these lactones from the point of view of their structural relationships. Tables and comparative figures are given, together with a graph representing the percentage amount of lactone present in aqueous solution during 10 days. It is demonstrated that for each pair of lactones derived from a normal and a γ-form of the same sugar, the curve

representing the rate of formation of γ-hydroxy-acid from γ-lactone is sharply distinguished from that representing the rate of formation of δ-hydroxy-acid from δ-lactone, the latter being much the steeper. Between the two extremes are found two less steep δ-lactone curves (trimethyl-δ-xylono- and tetramethyl-δ-mannono-lactones) and two less flat γ-lactone curves (trimethyl-γ-arabono- and trimethyl-γ-glucono-lactones), this phenomenon being the subject of further investigation. These results confirm the earlier findings of Charlton, Haworth, and Peat (A., 1926, 273) as to the structure of the constituent sugars. E. HOLMES.

Condensation of pyruvic acid with paraformaldehyde in presence of sulphuric acid. V. V. THEOPHILAKTOV (J. Russ. Phys. Chem. Soc., 1926, **58**, 759—766).—The products obtained by condensing pyruvic acid with formaldehyde in presence of sulphuric acid comprise a solid *acid*, $C_9H_8O_6$ (and not $C_8H_8O_6$, as described by O. Kaltwasser), m. p. 234°, and a *lactone*, m. p. 140—144°, which loses water when slowly heated to 90°, giving a viscous liquid, which sets to a glassy mass. The alkali salts of the acid did not crystallise, whilst the silver salts lost water on keeping for 15 min., to give a viscous mass. Phenylhydrazine gave an amorphous, yellow, very unstable precipitate, whilst hydroxylamine hydrochloride gave an *oxime*, m. p. 192—194° (decomp.). On oxidation with 3% hydrogen peroxide, a *lactone-acid*, m. p. 112—113°, was obtained. Acetic anhydride gave an *acetyl* derivative, m. p. 193°, with loss of a molecule of water. On reduction of the lactone with hydrogen in presence of platinum-black, two neutral isomeric *solids*, m. p. 219° and 234—235°, differing in crystalline form, were obtained. With tin and hydrochloric acid, only the isomeride of m. p. 219° was formed. The lactone did not give a coloration with ferric chloride. M. ZVEGINTZOV.

Transformation of acetaldehyde into its enolic form. S. A. SCHOU (Compt. rend., 1927, **184**, 1452—1454).—The absorption curves in ultra-violet light of acetaldehyde solutions show marked maxima at λ 2215 in 0·01*N*-sodium hydroxide and at λ 2205 in dilute hydrochloric acid, and minima at λ 2475 and 2465 Å., respectively. A solution of paracetaldehyde in dilute hydrochloric acid gives an absorption curve showing a maximum at λ 2205 and a minimum at λ 2465 Å. These maxima and minima indicate the presence of the enolic form of acetaldehyde, $CH_2{:}CH{\cdot}OH$, and in the proportion calculated from the curves of 1 in 335 in sodium hydroxide solution, 1 in 830 in hydrochloric acid solution, and 1 in 1045 for paracetaldehyde in hydrochloric acid solution. R. BRIGHTMAN.

α-Bromo-aldehydes. A. KIRRMANN (Compt. rend., 1927, **184**, 1463—1465).—Addition of magnesium ethyl bromide to excess of α-bromovaleraldehyde at −10° affords the expected bromohydrin in small yield, the main product being an *olefine*, C_{18}, b. p. 144°, d^{21} 0·742, n^{21} 1·4259. Similarly, bromoheptaldehyde and magnesium methyl bromide afford a little *γ-bromo-β-octanol*, b. p. 106—107°/d^{16} 1·207, n^{16} 1·4751, together with methyl hexyl ketone, b. p. 64°/12 mm., 173°/760 mm., d^{16} 0·823, n^{16} 1·4196 (Moureu and Delange, A., 1903, i, 399), a tertiary *alcohol*, b. p. 79—80°/12 mm., d^{19} 0·823, n^{19} 1·4299, probably β-methyloctan-β-ol, and an *olefine*, C_9H_{18}, b. p. 146°, d^{16} 0·738, n^{16} 1·4243, resulting from dehydration of the tertiary alcohol (cf. Henry, A., 1907, i, 744). Since the action of lead hydroxide on α-bromoheptaldehyde affords heptoic acid, and not the expected aldehyde-alcohol, it is probable that the ketone is formed by molecular transposition in the action of magnesium methyl bromide, and not through the ethylene oxide, as suggested by Henry (*loc. cit.*). α-Halogeno-aldehydes thus behave in some respects as acyl halides. R. BRIGHTMAN.

Mono- and di-thiotriacetaldehydes. S. W. LEBEDEV and M. S. PLATONOV (J. Russ. Phys. Chem. Soc., 1926, **58**, 705—711).—The products of the polymerisation of acetaldehyde by hydrogen sulphide in acid solution contain a triple *polymeride*, $CHMe\langle^{O\cdot CHMe}_{O\cdot CHMe}\rangle S$, m. p. 53·5—54°, b. p. 160° (decomp.). Acid potassium permanganate gives a colourless *sulphone*, m. p. 150—152°. Further action of hydrogen sulphide gives a mixture of the monothiotriacetaldehyde with *dithiotriacetaldehyde*, $CHMe\langle^{S\cdot CHMe}_{S\cdot CHMe}\rangle O$ m. p. 70—72°, which can be separated by fractionation. It does not react with phenylhydrazine or semicarbazide. Acid potassium permanganate oxidises it to a disulphone, decomp. 215°. Of the theoretically possible five optical and geometrical isomerides for each compound, only one, probably the stable racemic *trans*-form, was obtained. M. ZVEGINTZOV.

New, unsaturated anhydro-sugar. K. MAURER and H. MAHN (Ber., 1927, **60**, [*B*], 1316—1320; cf. A., 1926, 602).—The action of diethylamine on acetobromoglucose in presence of benzene affords diethylammonium bromide and a *tetra-acetyl* compound, $C_{14}H_{18}O_9$, m. p. 61—62°, $[\alpha]_D^{18}$ −16·87° in ethyl alcohol. The compound reduces Fehling's solution, is readily decomposed by concentrated mineral acids, and is not converted into dextrose by 0·1*N*-hydrochloric acid. It is decomposed by hydrogen bromide in glacial acetic acid. It does not appear to react with phenylhydrazine. It takes up halogen with evolution of halogen acid; the *bromo*-derivative is very unstable, the *chloro*-compound relatively stable. Hydrolysis with methyl-alcoholic ammonia converts the tetra-acetate into an amorphous *powder*, m. p. about 94°, decomp. 134°, analyses of which do not agree well with results required for the expected anhydro-sugar, $C_6H_{10}O_5$; re-acetylation of the amorphous product does not give the original tetra-acetate.

Acetobromogalactose and diethylamine similarly yield a crystalline *tetra-acetate*, $C_{14}H_{18}O_9$, m. p. 110°, $[\alpha]_D$ +4·69° in ethyl alcohol. H. WREN.

Reactivity of the methylated sugars. I. Action of alkaline hydrogen peroxide solution on tetramethyl-*d*-glucose. E. L. GUSTUS and W. L. LEWIS (J. Amer. Chem. Soc., 1927, **49**, 1512—1521).—Oxidation of βγδζ-tetramethylglucose (100 g.) with alkaline hydrogen peroxide yields carbon dioxide (13·42 g.), formic acid (33·78 g.), *dimethyl*-d-

arabonolactone (17·24 g.), m. p. 77°, $\alpha=1\cdot475$, $\gamma=1\cdot526$, $[\alpha]^{20}$ +89° in water, falling to +71·8° in 237 hrs. (p-*bromophenylhydrazide*), demethylated hexonic and pentonic acids (3·59 g.), and methyl esters of methylated tetronic acids (6·7 g.) containing probably methyl mono- and di-methyl *d*-erythronates. These results indicate the oxidation of an αβ-enediol, together with some total destruction of the sugar molecule. This, and the known stability of the methylated sugars, are explained if enolisation is effected by keto–enol tautomerisation rather than by selective addition and loss of water.

F. G. Willson.

Sugar carbonates. III. Derivatives of γ-methylfructoside, γ-ethylfructoside, and normal methylfructoside. C. F. Allpress, W. N. Haworth, and J. J. Inkster (J.C.S., 1927, 1233—1236).—The condensation of γ-methylfructoside with methyl chloroformate in chloroform containing pyridine yields *tetracarbomethoxy-γ-methylfructoside*, b. p. 226—227°/0·1 mm., $[\alpha]_D$ +19·8° in acetone, whilst the corresponding *tetracarbethoxy-γ-methylfructoside* has b. p. 235—238°/0·07 mm., $[\alpha]_D$ +22·5°. *γ-Ethylfructoside*, $[\alpha]_D$ +28°, condenses with ethyl chloroformate to give *tetracarbethoxy-γ-ethylfructoside*, b. p. 228°/0·05 mm., $[\alpha]_D$ +27·5° in ethyl alcohol. These products retain the structure of the original methyl- and ethyl-fructosides, but the fructosidic methyl and ethyl groups lose much of their labile character. Methylation of the normal forms of tetracarbomethoxyfructose and tetracarbethoxyfructose, previously prepared by Allpress and Haworth (A., 1924, i, 943), has resulted in the preparation of *tetracarbomethoxymethylfructoside*, m. p. 107°, $[\alpha]_D$ −126·1° in chloroform, and *tetracarbethoxymethylfructoside*, $[\alpha]_D$ −90·9° in acetone, neither of which reduces Fehling's solution. E. Holmes.

Hydrazine compounds of α-glucoheptose. E. Glaser and N. Zuckermann (Z. physiol. Chem., 1927, **167**, 37—69).—The following compounds have been prepared: α-*glucoheptose*-p-*nitrophenylhydrazone*, m. p. 199°, $[\alpha]_D^6$ −39°; α-*glucoheptose*-p-*nitrophenylosazone*, m. p. 243°; α-*glucoheptose*-o-*nitrophenylhydrazone*, m. p. 172°; α-*glucoheptose*-o-*nitrophenylosazone*, m. p. 220°; α-*glucoheptose*-2 : 4-*dinitrophenylhydrazone*, m. p. 180°, $[\alpha]_D^{17}$ −28°; α-*glucoheptose*-2 : 4-*dinitrophenylosazone*, m. p. 231°; α-*glucoheptose*-o-*tolylosazone*, m. p. 177°, $[\alpha]_D^{16}$ −9°; α-*glucoheptose*-m-*tolylosazone*, m. p. 186°, $[\alpha]_D^{17}$ −31°; α-*glucoheptose*-p-*tolylosazone*, m. p. 215°, $[\alpha]_D^{17}$ ±0°; α-*glucoheptosephenylbenzylhydrazone*, m. p. 156—157°; α-*glucoheptosephenylbenzylosazone*, m. p. 216—218°, $[\alpha]_D^{18}$ −44°; α-*glucoheptosephenylmethylosazone*, m. p. 173°, $[\alpha]_D$ −204°; α-*glucoheptosephenylethylhydrazone*, m. p. 145°, $[\alpha]_D^{16}$ −23°, and α-*glucoheptose*-β-*naphthylhydrazone*, m. p. 182°, $[\alpha]_D^{17}$ −13°. The preparation and properties of d-*glucose*-2 : 4-*dinitrophenylhydrazone*, m. p. 118—122°, $[\alpha]_D^{18}$ +12°, and d-*glucose*-2 : 4-*dinitrophenylosazone*, m. p. 256—257°, $[\alpha]_D^{18}$ −133°, are described. All are well crystalline except the second-named above, and these compounds can be prepared easily except α-glucoheptosebenzylphenylosazone, the formation of which requires 2—3 weeks. The crystalline form, solubility, m. p., and optical rotation of these compounds and those of the corresponding compounds of *d*-glucose and *l*-xylose, where known, are tabulated. The α-glucoheptose compounds are all lævorotatory or inactive in pyridine–methyl alcohol solution; the corresponding *l*-xylose compounds behave similarly, but of the *d*-glucose compounds examined about half are dextrorotatory and about half lævorotatory

For the detection of α-glucoheptose, the preparation of the hydrazones and osazones with *p*-nitrophenylhydrazine and 2 : 4-dinitrophenylhydrazine is recommended. For micro-chemical purposes, the compounds with phenylbenzylhydrazine and phenylethylhydrazine are most suitable, on account of their characteristic crystalline forms. In the purification of α-glucoheptose, the phenylbenzylhydrazone is prepared and decomposed with formaldehyde, whilst for the separation from dextrose, the insolubility of α-glucoheptose-2 : 4-dinitrophenylhydrazone in cold ethyl alcohol compared with the corresponding glucose compound is utilised. A. Wormall.

Degradation of reducing bioses. VI. *d*-Galacto-*d*-arabinose obtained by degradation of lactose. G. Zemplén (Ber., 1927, **60**, [*B*], 1309—1312; cf. A., 1926, 1229).—After being preserved during several months, *d*-galacto-*d*-arabinose yields crystals, m. p. 166—168° (decomp.), $[\alpha]_D^{20}$ −50·3° to −63·1° in water after 25 hrs. The identity of the product with that derived from the oxidative degradation of calcium lactobionate is established.

H. Wren.

Synthesis of maltose. A. Pictet and H. Vogel (Compt. rend., 1927, **184**, 1512—1514).—*Maltose*, in the form of the octa-acetyl derivative, is isolated from the product obtained by heating equal molecules of α- and β-glucose at 160° in a vacuum. The identity of the sugar is established by the preparation of maltose, together with its osazone and nitrate, from the synthetic acetyl compound.

G. A. C. Gough.

Third component sugar of scammonine. E. Votoček and F. Valentin (Arhiv Hemiju, 1927, **1**, 3—5).—Scammonic acid yields on hydrolysis with 10% sulphuric acid not only dextrose and rhodeose, but also *l*-rhamnose. R. Truszkowski.

Ruberythric acid. E. Glaser and O. Kahler (Ber., 1927, **60**, [*B*], 1349—1356).—Alizarin is converted by acetobromoglucose in alkaline solution into the corresponding 2-*tetra*-*acetylgluco*-derivative, $C_{14}H_6O_2(OH)\cdot O\cdot C_6H_7O_5Ac_4$, m. p. 203°, $[\alpha]_D^{17}$ −6·9 in acetone; the second hydroxy-group of alizarin is not attacked by a large excess of acetobromoglucose. It is converted by acetic anhydride and pyridine into the *acetyl* compound, $C_{30}H_{28}O_{14}$, m. p. 192—193°. The non-acetylated glucoside is decomposed by methyl-alcoholic ammonia into alizarin and the 1 : 2-*diglucosido*-derivative,

$C_6H_4<C(OH)(NH_2)^2>C_6H_2(O\cdot C_6H_{11}O_5)_2$, m. p. 193—194°, which is hydrolysed by emulsin to 9 : 10-*diamino*-1 : 2 : 9 : 10-*tetrahydroxy*-9 : 10-*dihydroanthracene*, m. p. 193—194°. The diglucosido-compound is converted by cold, concentrated hydrochloric acid into 1 : 2-*diglucoalizarin*, $C_{14}H_6O_2(O\cdot C_6H_{11}O_5)_2$, m. p.

213—214°, which is not identical with ruberythric acid. The acid is probably an alizarinmaltoside.

H. WREN.

Structure of starch. II. E. PEISER (Z. physiol. Chem., 1927, **167**, 88—90).—Acetylated starch (cf. this vol., 136), suspended in toluene and chlorinated with phosphorus pentachloride at 105°, yields a colourless substance, $C_{48}H_{56}O_{42}ClAc_{25}$. Attempts to remove the chlorine atom without the simultaneous removal of the acetyl groups have been unsuccessful. It is concluded that starch contains, in the middle of the monosaccharide chain, an aldehydic group which is not as firmly attached as the others, and that the adjacent alcohol group is not free, but is concerned in the chain formation. A. WORMALL.

Cryoscopic behaviour of glycogen acetate. K. HESS and R. STAHN (Annalen, 1927, **455**, 115—122).—The cryoscopic behaviour of glycogen acetate (Pringsheim and Lassmann, A., 1922, i, 634) in acetic acid in absence of air resembles that of cellulose and inulin acetates (cf. following abstracts), although a value of the mol. wt. corresponding with a dextrose anhydride unit is not reached, the initial value in dilute solutions being midway between that of a glucosan triacetate and a biosan hexa-acetate. Hence the latter cannot be regarded as the fundamental unit. The recovered material at the end of the experiment is identical with the starting material.

J. W. BAKER.

Cryoscopic behaviour of inulin acetate. K. HESS and R. STAHN (Annalen, 1927, **455**, 104—114).—Inulin triacetate, $[\alpha]_D^{19}$ −40·5° in acetic acid, prepared by the method of Bergmann and Knehe (A., 1926, 1230) from commercial inulin or chicory inulin, exhibits a similar irregular variation of its mol. wt. with time to that shown by cellulose acetates when the determination is carried out by the cryoscopic method in absence of air (cf. following abstract). In low concentrations, the value of the mol. wt. falls to that of a lævulose anhydride triacetate, before increasing slowly to infinity. In presence of air, the mol. wt. is almost a linear function of the concentration of the solution. J. W. BAKER.

Cellulose. XXV. Cryoscopic behaviour of cellulose acetates. K. HESS and G. SCHULTZE (Annalen, 1927, **455**, 81—103).—When amorphous cellulose triacetate (obtained by acetylation of cellulose with acetic anhydride and zinc chloride) is treated with acetic acid at 18—20°, only a small proportion goes into solution, and when this soluble portion is recovered and again treated with acetic acid, the same phenomenon is observed, and the process may be repeated until the whole of the sample is insoluble. The same observation is made at 45° and 60°, but at higher temperatures (90° and 100°) the sample is completely soluble. The various fractions separated in this manner have the same acetyl content and the same specific rotatory power, the varying solubility not being due to difference in chemical constitution. It may be due either to presence of impurities produced by acetolysis, or to variation in the size of the cells, the solution formed being a colloidal one. A specimen thus fractionated and completely insoluble in cold acetic acid was dissolved in warm acetic acid (90°) and reprecipitated with ether, and the variation of its mol. wt. with time determined by the cryoscopic method in 0·1—0·6% solution in acetic acid in an evacuated apparatus as previously described (Hess and Schultze, A., 1926, 715), and found to be identical with that of the crystalline triacetate, an initial decrease to the value for dextrose anhydride triacetate being followed by a continuous increase to infinity (*loc. cit.*). The substance isolated at the end of the experiment is identical with the starting material. A similar variation in the mol. wt. is exhibited by the triacetate obtained from ramie fibre and by a purified specimen of cellulose triacetate *A*, decomp. 280—285°, $[\alpha]_D^{20}$ −19·52° in chloroform (cf. Hess, Weltzien, and Messmer, A., 1924, i, 142), and with the diacetate. These observations support the view, previously given, concerning the constitution of cellulose and its acetates.

J. W. BAKER.

Lignin acetals. I. E. HAGGLUND and H. URBAN (Cellulosechem., 1927, **8**, 69—71).—By treating finely-divided wood with amyl-alcoholic hydrogen chloride, more than half the material was dissolved. From the solution, a light brown *lignin semiacetal*, probably $C_{16}H_{10}O_5(OMe)\cdot OC_5H_{11}$, was isolated. The residue apparently contained a lignin acetal with two amyloxy-groups in the molecule. Similar extraction with butyl-alcoholic hydrogen chloride yielded the corresponding *semiacetal* $C_{16}H_7O_2(OH)_2(OMe)\cdot OBu$. From these experiments, it appears that lignin has M=about 315, and contains one carbonyl, one methoxyl, and three hydroxyl groups.

B. W. ANDERSON.

Residual affinity and co-ordination. XXIX. Cupric salts stabilised by ethylenediamine. G. T. MORGAN and F. H. BURSTALL (J.C.S., 1927, 1259—1269).—Cupric salts of the weaker acids are known to decompose readily, and in view of the enhanced stability of these salts when they contain ethylenediamine as addenda of crystallisation exemplified by the iodide (A., 1926, 1027), further researches have been carried out to demonstrate this effect. Interaction between the requisite silver salts and bisethylenediaminocupric iodide led to the isolation of *bisaquobisethylenediaminocupric carbonate*, $[Cu,2\,en]CO_3,2H_2O$, m. p. 135° (decomp.), and *bisethylenediaminocupric nitrite*, $[Cu,2\,en](NO_2)_2$, m. p. 128° (rapid decomp.), as stable, well-defined salts. Two derivatives of cupric sulphite were obtained, depending on the method of preparation: (1) *monoaquoethylenediaminocupric sulphite*, $[Cu,en,H_2O]SO_3$, blackens at 100°, turning brown later, and (2) *bisethylenediaminocupric sulphite*, $[Cu,2\,en]SO_3$, decomp. 190—200°, this latter being the more stable. The reaction between bisethylenediaminocupric sulphate and the requisite barium salt in aqueous solution was used for the preparation of *bisethylenediaminocupric hypophosphite*, $[Cu,2\,en](H_2PO_2)_2$, decomp. 115—118°, and *thiosulphate*, $[Cu,2\,en]S_2O_3$, decomp. 150—155°. Other salts which have been prepared are *bisethylenediaminocupric dithionate*, $[Cu,2\,en]S_2O_6$, decomp. 260°; *trithionate*, $[Cu,2\,en]S_3O_6$, decomp. 170—175°; *tetrathionate*, $[Cu,2\,en]S_4O_6$, decomp. 160°; *persulphate*, $[Cu,2\,en]S_2O_8$, decomposes with explosive violence and detonates on percussion, and *seleno-*

cyanate, [Cu,2 en](CNSe)$_2$, m. p. 159—160°, this last furnishing a noteworthy example of the stabilising effect of ethylenediamine on a cupric salt. The co-ordination numbers of bivalent copper are discussed, and it is shown that, on the evidence adduced, the value 4 gives the type most conducive to molecular stability. E. HOLMES.

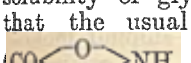
Tetrachloro(triaminopropane-γ-monohydrochloride)platinum, an optically active complex salt of a new type. F. G. MANN (J.C.S., 1927, 1224—1232).—In tetrachloro(triaminopropanemonohydrochloride)platinum, previously described (A., 1926, 1234), two of the amino-groups of the triaminopropane are implicated in the co-ordination complex, the third being free for normal salt formation with acids. Such a compound might exist in two forms, depending on the inclusion of the αβ- or the αγ-diamino-groups in the ring structure, *i.e.*, (I) [Cl$_4$PtNH$_2$·CH$_2$·CH(NH$_2$)·CH$_2$·NH$_2$·HCl] or (II) [Cl$_4$PtNH$_2$·CH$_2$·CH(NH$_2$·HCl)·CH$_2$·NH$_2$]. In (I), asymmetry is induced in the central carbon atom of the triaminopropane molecule by the disposition of the co-ordination linkings, this compound becoming capable of resolution into optically active forms, whilst (II) should not be so resolvable. The former has been proved to be correct, since fractional crystallisation of the camphorsulphonates has given the optically pure l-*tetrachloro(triaminopropanemono*-d-*camphor*-β-*sulphonate)platinum hemihydrate*, $[M]_{5461}$ —426°, m. p. 270—285° after darkening at 260°, and d-*tetrachloro(triaminopropanemono*-l-*camphor*-β-*sulphonate)platinum hemihydrate*, +424°. Treatment of these compounds with calcium chloride gave, respectively, l-*tetrachloro(triaminopropanemonohydrochloride)platinum*, —502°, m. p. 277—278° (decomp.) after darkening at 260—265°, and d-*tetrachloro(triaminopropanemonohydrochloride)platinum*, +501°, m. p. (decomp.) 277—278° after darkening at 260—265°. This, therefore, is the first recorded case of a carbon atom owing its asymmetry to the operation of auxiliary valencies. The following compounds are also described: *tetrachloro(triaminopropanemono*-d-α-*bromocamphor*-π-*sulphonate)platinum*, $[M]_{5461}$ +346°, m. p. 271—273° (decomp.); *trichlorotriaminopropaneplatinic chloride*, m. p. 242—243° (decomp.) after darkening at 210°; *tetrachloro(triaminopropanehydrogenoxalate)platinum*, m. p. 248—251° (decomp.), and *monochloromono-oxalatotriaminopropaneplatinic chloride*, decomp. 200—210°. E. HOLMES.

Substituted *o*-alkylhydroxylamines chemically related to medicinally valuable amines. L. W. JONES and R. T. MAJOR (J. Amer. Chem. Soc., 1927, **49**, 1527—1540).—Treatment of *ON*-dimethylhydroxylamine with ethylene oxide yields ON-*dimethyl*-N-*hydroxyethylhydroxylamine*, b. p. 57—58°/23 mm. (*hydrochloride*, m. p. 71—72°; *chloroplatinate*, m. p. 112—113°). When treated with methyl iodide, this affords *methoxydimethylhydroxyethylammonium iodide*, m. p. 57—58°, deliquescent, darkening on exposure to light, from which the corresponding *hydroxide* is obtained in solution by treatment with silver oxide. The corresponding *hydrochloride*, liquid, and *chloroplatinate*, m. p. 183° (decomp.), were prepared. Treatment of diethylaminoethanol in benzene with acetyl or benzoyl chloride yields, respectively, the *acetate*, b. p. 80°/20 mm. (*chloroplatinate*, m. p. 147°), or *benzoate*, b. p. 156—158°/19 mm. (*chloroplatinate*, m. p. 161°), and these, on treatment with ethyl iodide, afford, respectively, *triethylacetoxyethylammonium iodide*, m. p. 113°, and *triethylbenzoxyethylammonium iodide*, m. p. 134°. Treatment of diethylaminoethanol with aqueous 3% hydrogen peroxide affords *diethylhydroxyethylamine oxide*, liquid [*chloroplatinate*, m. p. 191° (decomp.)]. *Ethylethoxyaminoethyl* p-*aminobenzoate*, b. p. 217°/11 mm., is obtained by heating *ON*-diethylhydroxylamine with chloroethyl *p*-aminobenzoate in a sealed tube for 24 hrs. at 100°. *Ethylethoxyaminoethyl benzoate*, b. p. 152—153°/10 mm., is obtained by heating benzoyl chloride with *ON*-diethyl-*N*-hydroxyethylhydroxylamine, but could not be prepared from β-*chloroethyl benzoate*, b. p. 256—257°/752 mm., and *ON*-diethylhydroxylamine. *Ethylethoxyaminoethyl* p-*nitrobenzoate*, m. p. 180—190°, is obtained analogously. β-*Iodoethyl* p-*nitrobenzoate*, m. p. 68—69°, and β-*hydroxyethyl* p-*nitrobenzoate*, m. p. 77—78°, are described. *p*-Nitrobenzoyl chloride and *ON*-dimethyl-*N*-hydroxyethylhydroxylamine in benzene afford *methylmethoxyaminoethyl* p-*nitrobenzoate*, m. p. 51·4°. *Methoxycarbamide*, m. p. 84·5°, and *ethoxycarbamide*, m. p. 91·5°, are obtained by treating the appropriate *O*-alkylhydroxylamine hydrochlorides with aqueous potassium cyanate. When heated with diethylmalonyl chloride in benzene at 110° for 30 hrs., ethoxycarbamide yields N-*ethoxy*-CC-*diethylbarbituric acid*, m. p. 70°. NN'-*Dimethoxydiethylmalonamide*, m. p. 130°, and NN'-*diethoxydiethylmalonamide*, m. p. 117—118°, are obtained by treating the respective *O*-alkylhydroxylamines with diethylmalonyl chloride in ether, in presence of potassium carbonate. Condensation of phenylcarbimide in benzene with *O*-methyl- and *O*-ethylhydroxylamines yields, respectively, β-*methoxy*-α-*phenyl*-, m. p. 115°, and β-*ethoxy*-α-*phenyl-carbamide*, m. p. 106—108°, whilst β'-*methoxy*-α-*phenyl*-β-*methylcarbamide*, m. p. 61°, and β'-*ethoxy*-α-*phenyl*-β-*ethylcarbamide*, m. p. 63°, are obtained similarly from the corresponding *ON*-dialkylhydroxylamines. β-*Methoxy*-α-*propylthiocarbamide*, m. p. 37°, is obtained by treating *O*-methylhydroxylamine with propylthiocarbimide in benzene. The pharmacological action of the substituted *O*-alkylhydroxylamines appears to differ only in degree from that of the corresponding amines. F. G. WILLSON.

New compound obtained by the catalytic decomposition of collagen. W. S. SADIKOV (J. Russ. Phys. Chem. Soc., 1926, **58**, 775—778).—The products of the decomposition of collagen by 1% hydrochloric acid were extracted with non-aqueous solvents. The amyl alcohol extract gave, on treatment with copper carbonate, a green solution, from which acetone precipitated a green *powder*, $C_{17}H_{28}O_{12}N_4Cu_2$, probably

$$CH_2\Big[[CH\cdot OH]_2\cdot C(NH_2)<\begin{matrix}CH_2—CH_2—C\cdot NH_2\\ \qquad\qquad\quad\ \ \cdot O\cdot CO\end{matrix}\Big]$$

Such a type of compound occurs also in the amyl alcohol fraction of the decomposition products of goose feathers, and in bilirubin. M. ZVEGINTZOV.

Kinetics of the reaction of formation of glycine from monochloroacetic acid and the influence of neutral salts. I. V. SAPOJNIKOVA (J. Russ. Phys. Chem. Soc., 1927, 59, 125—136).—Ammonium chloroacetate reacts slowly with ammonia at 25°, the reaction being bimolecular. Increase in concentration, or the presence of ammonium salts, increases the speed of reaction, unlike that between ethyl chloroacetate or ethyl acetate and ammonia. Barium and potassium salts also increase the speed of reaction. Alcohol, on the other hand, reduces the speed of reaction by about 59%, probably due to the sparing solubility of glycine in alcohol. It follows, then, that the usual ring formula for the substance  is incorrect, and that it exists in the form of ions and consists of complexes of the type $^{+}NH_3{\cdot}CH_2{\cdot}CO^{-}$ $^{+}NH_3{\cdot}CH_2{\cdot}CO_2^{-}$ $^{-}CO_2{\cdot}CH_2{\cdot}NH_3^{+}$ $^{-}CO_2{\cdot}CH_2{\cdot}NH_3^{+}$. E. ROTHSTEIN.

Synthesis of dipeptides containing arginine. Isomeric phenylalanylarginines and their conversion into phenylalanylornithine. M. BERGMANN and H. KOSTER (Z. physiol. Chem., 1927, **167**, 91—113).—The azlactone of α-acetamidocinnamic acid, $CHPh{:}C\langle^{CO\cdot O}_{N=}{}^{|}_{M}$, reacts with free *d*-arginine in a water–acetone solution to form an acetylated unsaturated peptide. This compound takes up 2 atoms of hydrogen in presence of palladium-black to form the saturated acetyldipeptide, from which the free dipeptide is obtained by treatment with cold acetic anhydride followed by heating with *N*-hydrochloric acid. The following compounds have been prepared: 2-*acetamidocinnamoyl*-d-*arginine*, m. p. 192—193° (corr.), $[\alpha]^{23}$ −18·0°; N-*acetylphenylalanyl*-d-*arginine*, m. p. about 178°; optically inactive N-*acetylphenylalanylarginine*, m. p. 216° (corr.), and its *dihydrate*, m. p. 216° (corr.); d-*phenylalanyl*-d-*arginine* and its o-*hydroxybenzylidene* compound, m. p. 199° (corr.), *picrate*, m. p. 95—97°, and *dihydrochloride*, m. p. 192—193° (corr.); inactive *phenylalanylarginine*, m. p. 236° (corr.), and its o-*hydroxybenzylidene* compound, m. p. 162—163° (corr.), and a second *modification*, m. p. 237° (corr.), and *dihydrochloride*, m. p. 130° (corr.); *acetylphenylalanyldiacetylanhydroarginine*, m. p. 201° (corr.); *acetylphenylalanylanhydro-ornithine*, m. p. 245° (corr.), and in a second modification with similar properties but lower m. p.; and *phenylalanylornithine*, m. p. 149° (corr.). A. WORMALL.

Ethyl cyanoacetate [W. A. Noyes' method of preparation]. Y. URUSHIBARA (Bull. Chem. Soc. Japan, 1927, **2**, 143—145).—The product of the interaction of ethyl chloroacetate and potassium cyanide in methyl-alcoholic solution, according to the method of Noyes, is shown by chemical and physical means to be a mixture of about equal parts of the methyl and ethyl esters. Methyl cyanoacetate has d_4^{17} 1·133, as compared with d_4^{17} 1·114 for the ester prepared by Noyes' method, whilst pure ethyl cyanoacetate, prepared in ethyl-alcoholic solution, has d_4^{20} 1·063, against d_4^{20} 1·110 for the mixed esters. When the mixed esters react in ethyl-alcoholic solution they do so as the ethyl ester only. E. HOLMES.

Selective action of organo-magnesium compounds and ethyl diethyloxamate. A. MCKENZIE and G. K. DUFF (Ber., 1927, **60**, [*B*], 1335—1341; cf. Barré, this vol., 447).—The action of an excess of hot Grignard's reagent on ethyl diethyloxamate affects only the carbethoxy-group, leaving the diethylcarboxylamide group unattacked. A general method of preparing the diethylamides of α-hydroxy-acids is thus afforded, but the compounds are remarkably stable towards hydrolytic agents, so that their transformation into α-hydroxy-acids is difficult. *Benzildiethylamide*, m. p. 95—96°, prepared from ethyl diethyloxamate and magnesium phenyl bromide (but not from methyl benzilate and diethylamine), is reduced by stannous chloride to *diphenylacetdiethylamide*, prisms, m. p. 67—68°, or needles, m. p. 64—65°, which is readily obtained from diphenylacetyl chloride and diethylamine in presence of light petroleum. *Di-α-naphthylglycolldiethylamide*, m. p. 196—197° (and thence *di-α-naphthylacetdiethylamide*, m. p. 204—205°), *di*-p-*tolylglycolldiethylamide*, m. p. 118—119°, *di*-o-*tolylglycolldiethylamide*, m. p. 140—141°, diethylglycolldiethylamide, m. p. 122—123°, and *dibenzylglycolldiethylamide*, m. p. 120·5—121·5°, are similarly obtained. Oxalic acid and magnesium phenyl bromide yield benzoylformic acid in traces, whereas oxamide is very stable towards the reagent. Triphenylcarbinol is obtained by the action of magnesium phenyl bromide on oxamethane or ethyl cyanoformate. H. WREN.

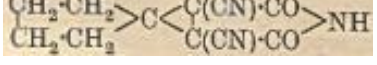
Additive compounds of allylthiocarbamide with silver halides. S. E. SHEPPARD and H. HUDSON (Phot. J., 1927, **67**, 331—335, and J. Amer. Chem. Soc., 1927, **49**, 1814—1819).—By the action of dilute aqueous allylthiocarbamide on fused silver bromide, crystals of *allylthiocarbamide silver bromide*, $AgBr,C_4H_8N_2S$, were obtained. Silver nitrate added to a solution of allylthiocarbamide and potassium iodide precipitated a non-crystallisable mass of *allylthiocarbamide silver iodide* (?). The corresponding silver chloride compound was similarly prepared. These compounds with their low solubilities (the silver iodide compound being the least soluble) are of interest in their bearing on photographic sensitisation. Their constitution according to co-ordination theories is discussed. B. W. ANDERSON.

Mechanism of hydrolysis of guanidines. H. LECHER and G. DEMMLER (Z. physiol. Chem., 1927, **167**, 163—176).—Earlier results and conclusions (Lecher and Graf, A., 1924, i, 1051) are discussed in the light of more recent publications. It is considered impossible to apply Werner's scheme for the hydrolysis of carbamide to guanidines. The scheme of hydrolysis of "kreatinol" suggested by Schotte (Z. angew. Chem., 1926, **39**, 677), in which is postulated the formation of a diguanidide as an intermediate compound, is not valid for *as*-diethylguanidine, which is used as a typical compound. Quantitative examination of the products of hydrolysis gives inconclusive results, but the scheme is impossible, since *as*-diethylguanidine and diethylcyanamide do not react. Schenck's preparation of *s*-tetramethylguanidine from cyanogen iodide and dimethylamine has been repeated with diethylamine.

Tetraethylguanidine is formed, but, in addition, some diethylcyanamide was isolated from the reaction mixture, and is regarded as a secondary and not as an intermediate product. This opposes Schenck's scheme for the reaction, which postulates the intermediate formation of dimethylcyanamide. An alternative scheme for this reaction is given. The following compounds are prepared: the *anhydro-base*, m. p. 88—89°, the *hydrochloride*, m. p. 148—149° (corr.), and the *picrate*, m. p. 221—224°, of as-*diethylguanidine*; *s*-tetraethylguanidine, b. p. 83·5° (corr.)/10 mm., and 92° (corr.)/13 mm., and its *picrate* and *chloroplatinate*, m. p. 203—207° (corr.). A. WORMALL.

Influence of groups and associated rings on the stability of heterocyclic systems. II. Substituted succinimides. III. Substituted paraconic acids. S. S. G. SIRCAR (J.C.S., 1927, 1252—1256, 1257—1259; cf. this vol., 451).—II. The rates of hydrolysis of various substituted succinimides show that, in the ascending series, H, H; Me, H; Et, H; Me, Me; Me, Et; Et, Et; *cyclo*pentane and *cyclo*hexane, the steady increase in stability anticipated in accordance with Thorpe and Ingold's modified strain theory is found in all but the first two members. The methyl group produces an abnormal increase in the stability of the ring, and the unsubstituted succinimide is also unusually stable. The velocities of hydrolysis of a number of imide systems in which the hetero-ring is attached to a carbocyclic ring by two carbon atoms show much-decreased stability compared with the corresponding *spiro*-systems. A possible explanation is offered. The following are described: as-*methylethylsuccinimide*, m. p. 64—65°; as-*diethylsuccinimide*, m. p. 85—86°; cyclo*pentane*spiro*succinimide*, m. p. 124°; cyclo*hexane*spiro-*succinimide*, m. p. 145°; trans-*hexahydrophthalimide*, m. p. 163—164°; trans-*hexahydrohomophthalimide*, m. p. 185°. *Ethyl* Δ^1-cyclo*pentenecarboxylate*, b. p. 92°/25 mm., prepared by treating ethyl *cyclo*pentan-1-ol-1-carboxylate with phosphorus pentachloride and heating the product with diethylaniline, condenses with ethyl cyanoacetate in presence of sodium ethoxide to give an additive *compound*, b.p. 185—186°/17 mm. Hydrolysis with concentrated hydrochloric acid gives trans-cyclo*pentane*-1-*carboxy*-2-*acetic acid*, m. p. 158°, yielding an *imide*, m. p. 184—185°.

III. The rates of hydrolysis of various substituted paraconic acids show that, in the ascending series, H, H; Me, H; Et, H; Me, Me; Me, Et; Et, Et; *cyclo*pentane and *cyclo*hexane, there is a steady increase in stability, in accordance with Thorpe and Ingold's modified strain theory. The influence of two ethyl groups is, however, greater than that of the *cyclo*pentane or *cyclo*hexane group. The following are described: the *imide*, $CMeEt<^{C(CN)\cdot CO}_{(CN)\ CO}>NH$, m. p. 225—227° (cf. Birch, Gough, and Kon, J.C.S., 1921, **119**, 1320); 2 : 3-*dicyano*-1-*methyl*-1-*ethyl*cyclo*propane*-2-*carboxylamide*, m. p. 127—128°; *γ-lactone* of β-*hydroxy*-β-*ethylbutane*-γδδ-*tricarboxylic acid*, m. p. 157—158° (decomp.); *methylethylparaconic acid*, m. p. 131—132° (*silver* salt); the *imide*,



m. p. 202—203°; cyclo*pentane*spiro-2 : 3-*dicyano*cyclo*propane*-2-*carboxylamide*, m. p. 126°; *γ-lactone* of 1-*hydroxy*cyclo*pentylethane*-αββ-*tricarboxylic acid*, m. p. 175—177° (decomp.); cyclo*pentane*spiro*paraconic acid*, m. p. 127° (*silver* salt). M. CLARK.

Behaviour of cyanogen bromide towards metallic salts. F. OBERHAUSER (Ber., 1927, **60**, [*B*], 1434—1439).—Antimony tribromide, when heated with cyanogen bromide at 180° and subsequently at 120°, gives the additive *compound*, $2SbBr_3,3BrCN$; the *compounds* $SbCl_3,2BrCN$, $AsBr_3,2BrCN$, and $AsCl_3,2BrCN$ are analogously prepared. Antimony pentachloride and cyanogen bromide in carbon disulphide afford sulphur monochloride. Tin tetrabromide yields the *compound* $SnBr_4,2BrCN$. Additive compounds could not be obtained from aluminium halides. Titanium tetrachloride readily yields the *product* $3TiCl_4,2BrCN$. Cuprous and ferrous bromides yield the corresponding cupric and ferric salts. Compounds of metallic halides or hydrogen cyanide with cyanogen chloride have been prepared. H. WREN.

Phosphinocarboxylic acids. A. E. ARBUSOV (J. Russ. Phys. Chem. Soc., 1927, **59**, 239—245; cf. A., 1914, i, 653).—Priority is claimed over the work of Nylen (A., 1925, i, 1134). Contrary to Nylen, the action of halogen-substituted esters on triethyl phosphite appears the most general method for the preparation of phosphinocarboxylic esters, and is applicable to α-bromo- and β-iodo-propionic and α-bromobutyric esters. Results of hydrolyses of ethyl phosphinoacetate, α- and β-phosphinopropionates, and phosphinoformate agree, in general, with those of Nylen. J. KAYE.

Cacodylic acid from trimethylarsine. A. VALEUR and P. GAILLIOT (Compt. rend., 1927, **184**, 1559—1561).—*Trimethylarsine dichloride*, prepared by the passage of chlorine over the surface of a benzene solution of trimethylarsine, decomposes into chloroform and cacodyl chloride (90% yield) when heated at 180°. From the latter, cacodylic acid is obtained by oxidation. The two additive *compounds*, $AsMe_3,AsCl_3$ and $AsMe_3,AsMeCl_2$, are also described. G. A. C. GOUGH.

Electrolysis of Grignard solutions. L. W. GADDUM and H. E. FRENCH (J. Amer. Chem. Soc., 1927, **49**, 1295—1299).—Electrolysis of ethereal magnesium benzyl chloride (110—130 volts, 0·02 amp.) yields metallic magnesium, magnesium chloride, and dibenzyl in approximately equimolecular amounts. Results obtained analogously with magnesium phenyl bromide were indefinite, possibly owing to side reactions brought about by the solubility of magnesium bromide in ether. During the electrolysis of magnesium phenyl bromide, marked anodic luminescence was observed. The deposited magnesium reacted with cold water with evolution of heat, and violently with halogen compounds under Grignard conditions. F. G. WILLSON.

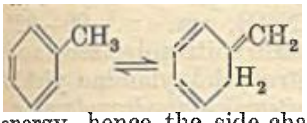
Substitution in the benzene nucleus. M. V. IONESCU (Bul. Soc. Chim. Romania, 1926, **8**, 25—28).—An account of Wieland's work on the reaction between ethylene and nitric acid (A., 1919, i, 307;

1920, i, 280) and the application of the results to the problem of substitution in the benzene nucleus (cf. Holleman, Chem. Reviews, 1925, **1**, 192).

The experiments of Datta (A., 1917, i, 15, 332; 1919, i, 153) on the halogenation of benzene hydrocarbons in presence of nitric acid are criticised.

H. Burton.

Tautomeric forms of toluene. P. P. Schorigin (J. Russ. Phys. Chem. Soc., 1926, **58**, 767—774).—Theoretical. The physical and chemical properties of toluene and its derivatives are reviewed and the existence of an "active" form (annexed formula) is



suggested. The amount of "active" modification is assumed to increase by addition of external energy, hence the side-chain reactions of toluene in strong light and on heating. The mechanisms of halogenation, oxidation with potassium permanganate, nitration, and some migration reactions are explained on this hypothesis. The "active" form should, theoretically, give an exaltation of molecular refractivity, and it is shown that for toluene and benzyl alcohol the refractivity increases rapidly with rise of temperature, owing to the increase of the "active" constituent.

M. Zvegintzov.

Nitration of mixed dihalogen derivatives of benzene. I and II. T. van Hove (Bull. Acad. roy. Belg., 1926, [v], **12**, 801—823, 823—835).—I. In contrast to *p*-chlorofluorobenzene, the nitration of *p*-bromofluorobenzene yields a preponderance of the compound nitrated *ortho* to the fluorine (cf. A., 1916, i, 133). The constitutions of the two possible isomerides are determined by synthesis, and the relative proportions produced in the nitration estimated. 5-*Bromo*-o-*fluoronitrobenzene*, b. p. 145—147°/13 mm., m. p. 19°, obtained from 4-fluoro-*m*-nitroaniline, is easily attacked by alkalis (including sodium carbonate) to give 4-bromo-*o*-nitrophenol. With sodium methoxide, it yields 4-bromo-*o*-nitroanisole, and with ammonia 4-bromo-*o*-nitroaniline. 6-*Bromo*-m-*fluoronitrobenzene*, b. p. 140°/30 mm., m. p. 38·5°, prepared similarly from 4-fluoro-*m*-nitroaniline, is only slowly attacked by alkalis (bromine eliminated).

Nitration of *p*-bromofluorobenzene with a mixture of nitric and sulphuric acids, and with a mixture of nitric and fuming sulphuric acids (30% SO_3), yields 43·5% and 40·6% of 5-bromo-*o*-fluoronitrobenzene, respectively. The percentages are calculated on the total mononitrated product from the proportion attacked by sodium methoxide; small amounts of 4-bromo-*o*-nitrophenol and of 2 : 4-dinitrophenol are formed at the same time. By a study of the m. p. of mixtures of the two isomerides, similar results are obtained.

II. Nitration of *p*-iodofluorobenzene with potassium nitrate and sulphuric acid at −10° yields *p*-fluoronitrobenzene, together with a tri-iodofluorobenzene and iodofluoronitrobenzenes in small amounts. Similarly, *p*-chloroiodobenzene yields *p*-chloronitrobenzene, a chlorodi-iodonitrobenzene, and small amounts of chloroiodonitrobenzenes. 6-*Iodo*-m-*fluoronitrobenzene*, b. p. 162—163°/35 mm., m. p. 22·5°, and 5-*iodo*-o-*fluoronitrobenzene*, b. p. 174—176°/45 mm., m. p. 35°, are obtained from the corresponding fluoronitroanilines. The latter is easily attacked by sodium methoxide and by ammonia to give 4-iodo-*o*-nitroanisole and 4-iodo-*o*-nitroaniline, respectively.

G. A. C. Gough.

Aromatic sulphonyl disulphides. L. G. S. Brooker, R. Child, and S. Smiles (J.C.S., 1927, 1384—1388).—The following sulphonyl disulphides, having the general formula $R{\cdot}SO_2{\cdot}S{\cdot}S{\cdot}R'$, have been prepared by the interaction of the appropriate aryl thiosulphonates with the aryl sulphur chlorides: 4-*toluenesulphonyl* 2-*nitrophenyl disulphide*, m. p. 141°; 4-*acetamidobenzenesulphonyl* 2-*nitrophenyl disulphide*, m. p. 171° (decomp.); 4-*toluenesulphonyl* 4-*chloro*-2-*nitrophenyl disulphide*, m. p. 114°; 4-*toluenesulphonyl* 2 : 5-*dichlorophenyl disulphide*, m. p. 95—96°; 4-*methoxytoluene*-3-*sulphonyl* 2-*nitrophenyl disulphide*, m. p. 115—116°; 4-*chlorobenzenesulphonyl* 2-*nitrophenyl disulphide*, m. p. 147° after softening at 130°. The behaviour of these compounds with such reagents as sodium 2-naphthoxide, sodium acetylacetone, and mercaptans has been studied, and the following products are described: 2 : 5-*dibromophenyl trisulphide*, m. p. 167—168°; 2 : 5-*dibromophenyl* 2-*nitrophenyl disulphide*, m. p. 138°; 2 : 5-*dichlorophenyl* 2-*nitrophenyl disulphide*, m. p. 138°, and 2 : 5-*dichlorophenyl trisulphide*, m. p. 140°. Alternative methods of synthesis have been devised and used in the identification of these products.

E. Holmes.

Constitution of mixed magnesium organic compounds. A. P. Terentiev (J. Russ. Phys. Chem. Soc., 1927, **58**, 1252—1264).—See A., 1926, 1130.

Action of *m*- and *p*-nitroaniline on 2 : 3 : 4 : 6-tetranitrophenylmethylnitroamine. C. F. van Duin and D. R. Koolhaas (Rec. trav. chim., 1927, **46**, 378—380).—In continuation of earlier work (van Duin and Roeters van Lennep, A., 1920, i, 155), it is shown that besides 2 : 4 : 6 : 4′-tetranitro-5-methylnitroaminodiphenylamine, the main product of the interaction of *p*-nitroaniline and 2 : 3 : 4 : 6-tetranitrophenylmethylnitroamine in saturated benzene solution, there is also formed in smaller amount 4 : 4′-dinitrodiazoaminobenzene. In the case of *m*-nitroaniline no such secondary product is obtained.

E. Holmes.

Reduction of aromatic nitro-derivatives by hydrogen in presence of platinum-black. V. Vesely and E. Rein (Arhiv Hemiju, 1927, **1**, 55—61).—Hydrogen in presence of platinum-black acts selectively on one of the nitro-groups of dinitroaryl compounds. Thus *m*-dinitrobenzene yields *m*-nitroaniline, 1 : 2-, 1 : 3-, and 1 : 8-dinitronaphthalenes yield 2-, 3-, and 8-nitronaphthylamines, whilst 5 : 6-dinitrotetralin yields mainly 5-nitro-6-aminotetralin, together with a small quantity of 6-nitro-5-aminotetralin. Similarly are obtained *o*-nitro-*p*-toluidine, 6-nitro-*o*-toluidine, and 1-*nitro*-2-*methyl*-8-*naphthylamine*, m. p. 106—107° (*acetyl* derivative, m. p. 191—193°), the position of the amino-group of which was determined by conversion through the diazo-derivative into 1-nitro-2-methylnaphthalene, or into

8-bromo-1-nitro-2-methylnaphthalene, m. p. 113°, yielding on reduction *8-bromo-2-methyl-1-naphthylamine*, m. p. 84—85°. A mixture of 1 : 5- and 1 : 8-dinitro-2-methylnaphthalenes yields on catalytic reduction only the 8-amino-derivative, thus affording a method for the separation of these isomerides.

R. TRUSZKOWSKI.

Condensation of nitriles with thioamides. III. Nitriles with thioanilides and thionaphthalides. S. ISHIKAWA (Mem. Coll. Sci. Kyoto, 1927, **10**, 191—198).—From a study of the condensation of acetonitrile and benzonitrile with thioformanilide, thioacetanilide, and thiobenzanilide, and of benzonitrile with α- and β-thioacetonaphthalides and α- and β-thiobenzonaphthalides, in ethereal hydrogen chloride solution, it is concluded that iminosulphides are produced thus: $NR''{:}CR{\cdot}SH+NCR'' \longrightarrow NR''{:}CR{\cdot}S{\cdot}CR''{:}NH$. When isolated, the iminosulphides are unstable, yellow substances, which become red in moist air, and then decompose. When no iminosulphide was isolated, its hydrolytic decomposition products (thioamide+anilide), or other condensation products (imino*iso*thioamide, cf. A., 1921, i, 728), were obtained.

H. BURTON.

Interaction of sulphuryl chloride with substances containing the reactive methylene group. K. G. NAIK and M. L. SHAH (J. Indian Chem. Soc., 1927, **4**, 11—21).—In the reaction of sulphuryl chloride with various mono- and di-substituted amides of malonic and methylmalonic acids, the methylene group is completely chlorinated in the compounds malondiphenylamide, malondibenzylamide, malondi-*o*-tolylamide, malondi-*p*-tolylamide, malondipropylamide, and malon-*p*-tolylamide, which are converted, respectively, into *dichloromalondiphenylamide*, m. p. 127°; *dichloromalondibenzylamide*, m. p. 170—171°; *dichloromalondi-o-tolylamide*, m. p. 140—141°; *dichloromalondi-p-tolylamide*, m. p. 145—146°; *dichloromalondipropylamide*, m. p. 108—109°, and *dichloromalon-p-tolylamide*, m. p. 145—146°. In the case of *malondi-m-tolylamide*, m. p. 152°, malonanilide, and malondi-β-naphthylamide, chlorination of the nucleus takes place in addition, with formation of *dichloromalondi-m-tolylamide dichloride*, m. p. 164°; *dichloromalonchlorophenylamide*, m. p. 136°; and *dichloromalondi-β-naphthylamide dichloride*, m. p. 183°, respectively. Malondimethylphenylamide is converted into *chloromalondimethylphenylamide*, m. p. 187°, and malondi-α-naphthylamide into *chloromalondi-α-naphthylamide dichloride*, m. p. 182°. Methylmalondiphenylamide, methylmalondi-*o*-tolylamide, and methylmalondi-*p*-tolylamide after chlorination form *chloromethylchloromalondiphenylamide*, m. p. 128°, *chloromethylchloromalondi-o-tolylamide*, m. p. 130°, and *chloromethylchloromalondi-p-tolylamide*, m. p. 138°, respectively, the course of the latter reactions apparently being due to the enolisation of the terminal methyl groups.

B. W. ANDERSON.

Phenyl-o-nitrobenzyldimethylammonium chloride. H. BAW (J.C.S., 1927, 1398).—*o*-Nitrobenzyl chloride and dimethylaniline, when mixed in equivalent proportions, combine slowly to form yellow rhombs of *phenyl-o-nitrobenzyldimethylammonium chloride*, m. p. 99·5°.

G. A. C. GOUGH.

Formation of nitrosoarylhydroxylamines. D. BIGIAVI and F. FRANCESCHI (Gazzetta, 1927, **57**, 362—383).—The action of hydroxylamine on *p*-nitro-β-azoxybenzene, $NPh{:}NO{\cdot}C_6H_4{\cdot}NO_2$, in presence of sodium ethoxide yields *p*-nitroazobenzene, and the *nitrosohydroxylamine*, $NPh{:}NO{\cdot}C_6H_4{\cdot}NO{:}NOH$, orange scales, m. p. 97—98° (decomp.), which forms salts with *phenylhydrazine*, $C_{12}H_{10}O_3N_4{,}NHPh{\cdot}NH_2$, m. p. 117° (decomp.), *hydroxylamine*, m. p. 200—204° (decomp.), various metals, and ammonium. Similarly, hydroxylamine and *p*-nitro-α-azoxybenzene, $O{:}NPh{:}N{\cdot}C_6H_4{\cdot}NO_2$, give the orange *nitrosohydroxylamine*, $O{:}NPh{:}N{\cdot}C_6H_4{\cdot}NO{:}NOH$, m. p. 90—92° (decomp.). Interaction of *p*-nitronitrosobenzene and the sodium derivative of nitrohydroxylamine yields the *sodium* salt of *nitroso-p-nitrophenylhydroxylamine*, $NO_2{\cdot}C_6H_4{\cdot}NO{:}NONa{,}5H_2O$; free *nitroso-p-nitrophenylhydroxylamine*, m. p. 75° (decomp.), readily decomposes with formation of *p*-nitronitrosobenzene, and forms a sparingly soluble *phenylhydrazine* salt, m. p. 140°; an *ammonium* salt (*p-nitrocupferron*), m. p. 145° (decomp.); a *silver* salt; a *barium* salt ($+3H_2O$); a *ferric* salt, m. p. 202° (decomp.); a *copper* salt, m. p. 250° (decomp.); a *nickel* salt, m. p. 249° (decomp.), and a *cobalt* salt, m. p. 222° (decomp.).

As regards the analogy between the reactions of nitrohydroxylaminic acid (nitroxyl) with nitroso-derivatives and with aldehydes, the nitrosoarylhydroxylamines and the hydroxamic acids formed in the two cases both yield complex metallic salts. In the latter reaction, the formation of the hydroxamic acid is preceded by the appearance of a greenish-blue coloration owing to the formation of the nitroso-alcohol, $OH{\cdot}CHR{\cdot}NO$; similarly, the transitory deep red coloration sometimes observed on mixing solutions of *p*-nitronitrosobenzene and the sodium salt of nitrohydroxylamine may appertain to a labile form represented by the old formula, $OH{\cdot}NR{\cdot}NO$, ascribed to the nitrosoarylhydroxylamines by Bamberger.

Not only the nitroso-group, but also the nitro-group of aromatic derivatives is transformed by nitroxyl into the grouping of the nitrosoarylhydroxylamines $R{\cdot}NO_2 \longrightarrow O{:}NR{:}NOH$. In this way nitrosohydroxylamines have been obtained from nitrobenzene, *p*-nitrotoluene, *m*- and *p*-dinitrobenzenes, and *pp'*-dinitroazobenzene. Thus, *m*-dinitrobenzene gives, as *sodium* salt, *nitroso-m-nitrophenylhydroxylamine*, $C_6H_5O_4N_3$, m. p. 75—76°, and *p*-dinitrobenzene gives, first, the sodium salt of nitroso-*p*-nitrophenylhydroxylamine (see above), and then the *sodium* salt ($+1H_2O$) of *p-dinitrosophenylenedihydroxylamine*, $NOH{:}NO{\cdot}C_6H_4{\cdot}NO{:}NOH$, which begins to blacken at 85°, yields *p*-dinitrosobenzene, possibly identical with that obtained by Nietzki and Kehrmann (A., 1887, 575), when heated with dilute mineral acid, and forms complex metallic salts.

Various azoxy-derivatives are reduced by nitrohydroxylaminic acid. Thus, azoxybenzene is converted into azobenzene and an orange sodium salt, possibly $NONa{:}NPh{:}NPh$; *pp'*-dinitroazoxybenzene gives *pp'*-dinitroazobenzene and a sodium salt of a nitrosohydroxylamine (?); *p*-nitroazoxybenzene gives *p*-nitroazobenzene.

The reduction of nitro- to azoxy-derivatives by alcoholic potassium hydroxide sometimes proceeds

further. Thus, trisazoxybenzene and monoazoxybisazobenzene are reduced to *trisazobenzene*, m. p. 235°. T. H. POPE.

Nitration of aromatic compounds with metallic nitrates. G. BACHARACH (J. Amer. Chem. Soc., 1927, 49, 1522—1527).—Treatment of *p*-toluidine with cupric, ferric, manganese, nickel, or cobalt nitrate in a mixture of acetic anhydride and glacial acetic acid, or with mercurous nitrate in glacial acetic acid, or with lithium nitrate in boiling acetic anhydride, affords *m*-nitroaceto-*p*-toluidide. Aniline and lithium nitrate yield, similarly, *p*-nitroacetanilide. In acetic anhydride at 100°, cupric nitrate is without action on benzoic acid, benzaldehyde, and nitrobenzene. The nitrating action of metallic nitrates is thus selective, and the structure of the nitro-derivative produced depends on the particular nitrate applied (cf. Menke, A., 1925, i, 655; Spiegel and Haymann, A., 1926, 390). F. G. WILLSON.

Preparation of pharmacologically valuable amines. K. KINDLER [with F. BURGHARD, P. KORDING, O. GIESE, F. HESSE, F. FINNDORF, and H. CHRISTLIEB] (Arch. Pharm., 1927, 265, 389—415).—The author's recent work (A., 1923, i, 568; 1924, i, 731 etc.) is reviewed and amplified, the practical value of the electrolytic reduction processes being emphasised. In general, the electrolyte is alcoholic hydrochloric or sulphuric acid; a specially prepared lead cathode is used and the current density is high. The yields (given below in parentheses in % of theory) are much higher than those obtainable by other methods. In the following list of results obtained, m. p. or b. p. are given only when they differ from those recorded by earlier workers, and in all cases the figures are corrected. β-Arylethylamines are easily prepared from aldehydes (cf. Kindler, *loc. cit.*, 1923); thus, benzaldehyde, through acetylthiomandeloylamide (Albert, A., 1915, i, 8), yields β-phenylethylamine, and piperonal is similarly converted into homopiperonylamine. The following are obtained by the reduction of the corresponding acid amide: benzylamine (74%) and benzyl alcohol (23%); *o*-tolylmethylamine (83%) and *o*-methylbenzyl alcohol (11%); *m*-tolylmethylamine (53%) and *m*-methylbenzyl alcohol (35%); *p*-tolylmethylamine (79%) and *p*-methylbenzyl alcohol (18%); *p*-anisylmethylamine (73%) and *p*-methoxybenzyl alcohol (22%); m-*bromobenzylamine*, b. p. 244—245° (*hydrochloride*, m. p. 218·5°; *chloroplatinate*, m. p. 250·5—251·5°, decomp.) (64%), and *m*-bromobenzyl alcohol (19%); *p*-bromobenzylamine, b. p. 249·5—251·5° (67%)—some bromine is split off during this reduction; *p*-chlorobenzylamine, b. p. 229—230·5° (carbonate, m. p. 121—121·5°; hydrochloride, m. p. 261·5°; benzoyl derivative, m. p. 142·5°) (65%); ω-α-naphthylmethylamine (55%). Benzomethylamide and phenylacetmethylamide are also reduced to benzylmethylamine and β-phenylethylmethylamine, respectively, but, in general, secondary amines are more readily obtained from the amides as described below. p-*Anisoyldimethylamide* (from the chloride), b. p. 196°/16 mm., yields on reduction *p*-methoxybenzyldimethylamine, b. p. 108°/11 mm. *N*-Benzoylpiperidine similarly gives N-benzylpiperidine (57%); phenylacetdimethylamide gives β-phenylethyldimethylamine (76%); phenylacetdiethylamide gives β-phenylethyldiethylamine, b. p. 97—99°/8 mm. (80%); *phenylacetdipropylamide*, b. p. 183—184°/16 mm., prepared from the chloride, gives β-*phenylethyldipropylamine*, b. p. 268—269° (89%); *phenylacetpiperidide*, b. p. 201—202°/18 mm., gives N-β-*phenylethylpiperidine*, b. p. 272°, *hydrochloride*, m. p. 223° (63%); hydrocinnamodimethylamide gives γ-phenylpropyldimethylamine (70%); p-*methoxyhydrocinnamodimethylamide*, b. p. 200°/17 mm., obtained by heating the dimethylammonium salt of the acid at 200°, gives on reduction γ-p-*methoxyphenylpropyldimethylamine*, b. p. 260° (*picrate*, m. p. 92°), which affords homohordenine, m. p. 111—111·5° (von Braun and Deutsch, A., 1912, i, 845), quantitatively on demethylation. Details, which were omitted in earlier papers, are now given for the preparation of *N*-alkylthioamides: the aldehyde or ketone is mixed with sulphur and the amine (in 10% excess); the mixture is heated in a closed tube fitted with an inner vessel containing potassium hydroxide to take up the water as fast as it is formed. The interaction is complete, at 140—150° and 3—4 atm. pressure, in about 4 hrs. In this way, benzaldehyde yields thiobenzdimethylamide (80%); acetophenone yields phenylthioacetdimethylamide (70%); *p*-tolyl methyl ketone yields p-*tolylthioacetdimethylamide*, m. p. 72° (80%); *p*-ethylphenyl methyl ketone yields p-*ethylphenylthioacetdimethylamide*, b. p. 224—225°/20 mm. (40%); *p*-anisyl methyl ketone gives *p*-methoxyphenylthioacetdimethylamide (75%); 3 : 4-dimethoxyphenyl methyl ketone gives 3 : 4-*dimethoxyphenylthioacetdimethylamide*, m. p. 118° (68%), and phenyl ethyl ketone gives β-*phenylthiopropiondimethylamide*, m. p. 55—56° (58%). When aldehydes or ketones are heated with sulphur and a monoalkylamine, poor yields are obtained, but *N*-methylaldimines and *N*-methylketimines are smoothly converted into thioamides. *N*-Methylbenzaldimine thus affords, when heated with sulphur, thiobenzmethylamide (80%); N-*methyl*-p-*methoxybenzaldimine*, b. p. 129—130°/18 mm., gives *p*-methoxythiobenzmethylamide (40%); *N*-methylacetophenoneimine gives phenylthioacetmethylamide (30%), and its 3 : 4-dimethoxy-analogue gives 3 : 4-dimethoxyphenylthioacetmethylamide (45%). All these compounds are smoothly reduced by the electrolytic method in alcoholic hydrochloric or sulphuric acid; thus, thiobenzmethylamide gives benzylmethylamine (79%); similarly are obtained *p*-methoxybenzylmethylamine (84%), β-phenylethylmethylamine (83%), benzyldimethylamine (100%), β-phenylethyldimethylamine (100%), β-p-*tolylethyldimethylamine*, b. p. 226·5° (88%), β-*p*-ethylphenylethyldimethylamine (74%), and γ-phenylpropyldimethylamine (73%). The production of *N*-methylhomopiperonylamine, available for the synthesis of hydrastinine, by similar methods is described (cf. also *loc. cit.*, 1923), and further details are given for preparing hordenine and certain analogues. Thus, *p*-nitrophenylacetdimethylamide (*loc. cit.*, 1923) is smoothly reduced electrolytically to β-p-*aminophenylethyldimethylamine*, m. p. 41—42°, b. p. 150°/18 mm., which is easily converted into hordenine by decomposition of its diazonium derivative. Hordenine is also obtained from anisole as

follows: anisole is converted into *p*-methoxyacetophenone, and the *p*-methoxyphenylthioacetdimethylamide obtained thence is electrolytically reduced (yield 92%) to β-p-*methoxyphenylethyldimethylamine*, b. p. 253—254°, readily demethylated by hydrobromic acid and red phosphorus to hordenine. Similarly, 3 : 4-dimethoxyphenylthioacetdimethylamide, described above, yields (80%) β-3 : 4-*dimethoxyphenylethyldimethylamine*, b. p. 168—170°/19 mm. (*picrate*, m. p. 126°, *methiodide*, m. p. 232°), which on demethylation affords (90%) β-3 : 4-*dihydroxyphenylethyldimethylamine*, m. p. 156° (*picrate*, m. p. 169°; *methiodide*, m. p. 205°). *p*-Methoxyacetophenone, sulphur, and piperidine at 165° yield N-p-*methoxyphenylthioacetopiperidide*, m. p. 65°, which is successively converted into N-β-p-*methoxyphenylethylpiperidine*, b. p. 175—176°, and N-β-p-*hydroxyphenylethylpiperidine*, m. p. 163°. W. A. SILVESTER.

Influence of the sulphonic group on the isomeric naphthylaminesulphonic acids. G. G. VENDELSTEIN (J. Russ. Phys. Chem. Soc., 1927, **59**, 146—157).—The relative speeds of diazotisation of α-naphthylamine and the seven isomeric monosulphonic acids derived from it, and the relative rates of coupling and of decomposition of the diazo-compounds have been measured. The reactions in the first two instances were bimolecular, and in the last case unimolecular. The presence of a sulphonic acid group in α-naphthylamine decreases the stability of the amino-group towards nitrous acid. The isomeric naphthylaminesulphonic acids divide themselves into three groups, the 1 : 3-, 1 : 6-, and 1 : 7-naphthylaminesulphonic acids have much the same speeds of diazotisation; the 1 : 5- and 1 : 8-acids are much more stable than these, and their diazo-compounds form derivatives much less readily. The remaining two, the 1 : 4- and 1 : 2-acids, show the greatest tendency to form diazo-derivatives. The speeds of decomposition of the isomeric diazo-compounds are of much the same order in every case.

E. ROTHSTEIN.

Preparation of *o*-chloro-*p*-aminoacetanilide. S. C. NIYOGY (J. Indian Chem. Soc., 1927, **4**, 80—83).—Cain's method (J.C.S., 1909, **95**, 716) having proved unsatisfactory, the following preparation of *o*-chloro-*p*-aminoacetanilide was devised. *p*-Nitroaniline is dissolved in water containing hydrochloric and acetic acids and a slow current of chlorine passed at 10—15°; after boiling, adding alcohol, and filtering rapidly, a good yield of *o*-chloro-*p*-nitroaniline separates from the diluted filtrate. This is dissolved in acetic acid, acetylated in presence of sulphuric acid, and reduced with iron dust and acetic acid. *o*-Chloro-*p*-aminoacetanilide has m. p. 134—135° (Cain, *loc. cit.*, gave m. p. 111°). B. W. ANDERSON.

Action of nitrous acid on substituted *p*-phenylenediamines. I. *as*-Benzyl-*n*-butyl-*p*-phenylenediamine. J. REILLY and P. J. DRUMM (J.C.S., 1927, 1395—1397).—The study of the influence of substitution on the diazo-reaction is extended, and it is found that *benzyl*-n-*butyl*-p-*phenylenediamine*, $NH_2 \cdot C_6H_4 \cdot NBu \cdot CH_2Ph$, like *n*-butyl-*p*-phenylenediamine (J.C.S., 1917, **111**, 1034), yields a stable diazo-solution. Whilst methyl-*p*-phenylenediamine cannot be diazotised in hydrochloric acid solution, it yields a stable diazo-solution in dilute sulphuric acid.

Benzyl-*n*-butylaniline (see this vol., 553; *picrate*, m. p. 129°; *chloroplatinate*, m. p. 185—186°), also obtained by the interaction of *n*-butyl iodide and benzylaniline in alcohol at 100°, yields with nitrous acid, followed by treatment of the product with hydrogen chloride in benzene, p-*nitrosobenzyl*-n-*butylaniline hydrochloride*, m. p. 138° (with previous darkening). The corresponding *base*, m. p. 48—49°, on reduction with zinc dust and sulphuric acid, gives *benzyl*-n-*butyl*-p-*phenylenediamine*, b. p. 220—224°/12 mm. (*sulphate*, *hydrochloride*, and *benzoyl* compound, m. p. 131°, described).

4-p-*Sulphobenzeneazobenzyl*-n-*butylaniline*, obtained by the action of *p*-diazobenzenesulphonic acid on an acetic acid solution of benzyl-*n*-butylaniline, yields, on reduction with ammonium sulphide, benzyl-*n*-butyl-*p*-phenylenediamine identical with that described above. The last-named base, when diazotised and coupled with β-naphthol, gives p-*benzyl*-n-*butylaminobenzeneazo*-β-*naphthol*, m. p. 133—134°.

G. A. C. GOUGH.

Diacyl derivatives of benzidine and *p*-phenylenediamine. F. J. A. BROGAN (J.C.S., 1927, 1381—1384).—The ascending homologous series of normal diacyl derivatives of benzidine and of *p*-phenylenediamine show no alternation in m. p. such as that existing in the corresponding series of normal fatty acids (cf. Robertson, J.C.S., 1908, **93**, 1033; 1919, **115**, 1210). Both m.-p. curves fall sharply at first, and then more slowly with increasing mol. wt., without attaining a minimum at either eighteenth member. In connexion with these results, an explanation of the alternation of the m. p. of the dibasic acids, founded on considerations of polarity, is suggested.

The diacyl derivatives were prepared by Cain's method (J.C.S., 1909, **95**, 714), and of them the following are new. Benzidine derivatives: *dipropionyl*, m. p. 317°; *dibutyryl*, m. p. 310°; *divaleryl*, m. p. 301°; *dihexoyl*, m. p. 283°; *diheptoyl*, m. p. 274°; *dioctoyl*, m. p. 268°; *didecoyl*, m. p. 256°; *diundecoyl*, m. p. 250°; *dilauryl*, m. p. 247°; *ditridecoyl*, m. p. 243°; *dimyristyl*, m. p. 241°; *dipalmityl*, m. p. 233°; *distearyl*, m. p. 231°. *p*-Phenylenediamine derivatives: *divaleryl*, m. p. 225°; *dihexoyl*, m. p. 215°; *diheptoyl*, m. p. 211°; *dioctoyl*, m. p. 208°; *dinonoyl*, m. p. 205°; *didecoyl*, m. p. 202°; *diundecoyl*, m. p. 199°; *dilauryl*, m. p. 194°; *ditridecoyl*, m. p. 190°; *dimyristyl*, m. p. 187°; *dipalmityl*, m. p. 182°; *distearyl*, m. p. 178°. G. A. C. GOUGH.

Benzidine. H. H. HODGSON (J. Soc. Dyers Col., 1927, **43**, 185—189).—Mainly a discussion of work already published (A., 1926, 945, 1133). In addition to Cain's 4″ : 4‴-dichlorotetranitro-*pp*′-diphenyldiphenyl, m. p. 203° (J.C.S., 1912, **101**, 2298; 1913, **103**, 2074), treatment of tetrazotised 3 : 5′-dinitrobenzidine with cuprous chloride affords an *isomeride*, orange-red, m. p. 300°, probably 4″ : 4‴-*dichloro*-2 : 2′ : 3″ : 3‴-*tetranitro*-pp′-*diphenyldiphenyl*, together with a crystalline substance, m. p. 170—180°, containing chlorine. If the tetrazo-solution is saturated with sodium chloride before treating with cuprous

chloride, orange-red products soluble in alcohol are obtained, of lower m. p. and higher chlorine content, probably formed by displacement of nitro-groups by chlorine. In the preparation of 4 : 4′-dichloro-3 : 5′-dinitrodiphenyl from 4-chloro-3-nitro-aniline, a yellowish-white substance, $C_{12}H_6O_4N_2Cl$, m. p. 160—170°, is also obtained, which is probably a mixture of 4 : 4′-dichloro-3 : 5′-dinitrodiphenyl with either 4 : 4′-dichloro-2 : 2′-dinitrodiphenyl or 4 : 4′-dichloro-3 : 3′-dinitrodiphenyl. R. BRIGHTMAN.

Derivatives of benzeneazopyrogallol. D. BIGIAVI and G. GRECHI (Gazzetta, 1927, **57**, 355—361).—For benzeneazopyrogallol (cf. Stebbins, A., 1880, 880), m. p. 198° (decomp.), the structure indicated by Ghosh and Watson (J.C.S., 1917, **111**, 816) is preferred, as the triacetyl and tribenzoyl derivatives of this compound are only slowly oxidised to the corresponding azoxy-compounds by peracetic acid. Benzeneazopyrogallol forms the following derivatives: *diacetyl*, m. p. 126—128°; *triacetyl*, m. p. 108—110°; *tribenzoyl*, m. p. 125°. *Benzeneazoxypyrogallol*-A, O:NPh:N·$C_6H_2(OH)_3$, m. p. 146—147°, forms a *tribenzoyl* compound, m. p. 161—163°. *Benzeneazoxypyrogallol*-B, NPh:NO·$C_6H_2(OH)_3$, has m. p. 109—112°. T. H. POPE.

Addition of amino- and hydrazino-bases to nitrostyrene. D. E. WORRALL (J. Amer. Chem. Soc., 1927, **49**, 1598—1605).—β-Nitrostyrene reacts with certain amines and hydrazines, with formation of the corresponding derivatives of α-nitro-β-amino-β-phenylethane. The applicability of the reaction is limited on account of the ease with which the nitrostyrene polymerises and hydrolyses, so that the additive reaction is prevented in many cases by steric hindrance under the mild conditions which have to be employed. The products are amphoteric. The following derivatives of α-nitroethane are described: β-*anilino*-, m. p. 86—87° (*hydrochloride*, m. p. 126—127°; *hydrobromide*, m. p. 113—114°; *nitrate*, m. p. 113—114°; *sodium* salt, unstable, m. p. indefinite); β-p-*toluidino*-, m. p. 82—84° (*hydrochloride*, m. p. 132°; *sodium* and *potassium* salts); β-p-*aminodiphenylamino*-, m. p. 113° (decomp.); β-*phenylhydrazino*-, m. p. 75° (*hydrochloride*, m. p. 135—136°; *nitrate*, m. p. 77°); β-*diphenylhydrazino*-, m. p. 81—82°; β-(β-*naphthyl*)*hydrazino*-, m. p. 117—118°; β-p-*tolylhydrazino*-, yellow, m. p. 86—87°; α-*semicarbazido*-, m. p. 131—132°; β-*thiosemicarbazido*-, m. p. 128—129°; and α-*nitro*-β-*piperidino*-β-*phenylethane*, m. p. 71—72°. ββ′-*Dinitro*-αα-*dipnenyldiethylamine*, m. p. 122—123°, is obtained by passing ammonia into a benzene solution of β-nitrostyrene. *p*-Phenylenediamine in alcohol affords similarly ββ′-*dinitro*-αα′-*diphenyl*-s-*diethyl*-p-*phenylenediamine*, yellow, m. p. 146—149° (*hydrochloride*, p. indefinite; *sodium* salt), whilst benzidine yields 3,3′-*nitro*-αα′-*diphenyldiethylbenzidine*, yellow, m. p. 162°. F. G. WILLSON.

Action of *cyclo*hexyl bromide on arylhydrazines. II. Decomposition of phenylhydrazine in presence of its salts. M. BUSCH [with A. BECKER] (J. pr. Chem., 1927, [ii], **116**, 34—). In correction of previous work (this vol., 455) it is now found that *cyclo*hexyl bromide and *o*-tolylhydrazine give only *cyclo*hexene and *o*-tolylhydrazine hydrobromide. The compound described as *cyclo*hexyl-*o*-tolylhydrazine was *o*-toluidine formed by catalytic decomposition (see below) of the hydrazine, and the supposed hydrazones were Schiff's bases, C_7H_7·N:CHR. Attempts to prepare *cyclo*hexyltolylhydrazine from sodium *o*-tolylhydrazine and *cyclo*hexyl bromide were also unsuccessful. Other *o*-substituted phenylhydrazines, viz., 2 : 4-dimethyl-, *o*-methoxy-, *o*-chloro-, and *o*-bromo-phenylhydrazine, and also *p*-bromophenylhydrazine, react similarly, yielding in each case the corresponding amine and *cyclo*hexene, whilst α-naphthylhydrazine gives resinous products. With *p*-chlorophenylhydrazine, however, at 120—135°, *cyclo*hexyl bromide gives the *hydrobromide* of as-cyclo*hexyl*-p-*chlorophenylhydrazine*, m. p. 57—58° [*hydrochloride*, m. p. 185° (decomp.); *benzoyl* derivative, m. p. 221°], and with β-naphthylhydrazine, the *hydrobromide* of as-cyclo*hexyl*-β-*naphthylhydrazine*, m. p. 106° (*hydrochloride*, m. p. 184—185°, softening at 180°), from which *benzaldehyde*cyclo*hexyl*-β-*naphthylhydrazone*, m. p. 102°, is obtained.

When phenylhydrazine is heated in contact with its hydrochloride, it is catalytically decomposed (cf. Arbusov and Tichwinsky, A., 1910, i, 776) as follows: (*a*) $3NHPh·NH_2+HCl \longrightarrow 3NH_2Ph+N_2+NH_4Cl$; (*b*) $2NHPh·NH_2+HCl \longrightarrow NH_2Ph+C_6H_6+N_2+NH_4Cl$. At 100—135° the reaction proceeds slowly, and only according to (*a*), but above 160° the secondary reaction, (*b*), sets in, with vigorous decomposition, the proportion of benzene formed increasing with rising temperature. H. E. F. NOTTON.

Dehydration of *cyclo*hexanols to ethers. A. LACOURT (Bull. Soc. chim. Belg., 1927, **36**, 346—358).—Di*cyclo*hexyl ether, b. p. 115·8°/15 mm., 242·2°/758·9 mm., d_4^{20} 0·9227, is obtained in 7·6% yield by heating *cyclo*hexanol in an autoclave with toluene-*p*-sulphonic acid at 170°. Lower yields are obtained by heating the alcohol with other catalysts at atmospheric pressure, the main product being *cyclo*hexene. By heating mixtures of *cyclo*hexanol and *cyclo*hexene in presence of toluene-*p*-sulphonic acid, up to 20% of the ether is obtained. Refractive indices and dispersions of the ether for several wave-lengths are given. Hydrolysis of di*cyclo*hexyl ether by hydriodic acid and red phosphorus yields mainly iodo*cyclo*hexane. Treatment of the mixtures of geometrical isomerides of the methyl*cyclo*hexanols with toluene-*p*-sulphonic acid gives, in addition to the corresponding hexenes, *di*-4-*methyl*cyclo*hexyl ether*, b. p. 135·3—141·6°/16 mm., *di*-3-*methyl*cyclo*hexyl ether*, b. p. 131·8—138°/16 mm., and *di*-2-*methyl*cyclo*hexyl ether*, b. p. 116—123°/13 mm. A mixture of *cis*- and *trans*-3-methyl*cyclo*hexanols was separated by distillation with the addition of phenetole into isomerides, b. p. 171—171·4°/760 mm., $d_4^{19\cdot4}$ 0·920 and b. p. 173·6—174·6°/760 mm., $d_4^{19\cdot4}$ 0·9139. The corresponding *allophanates* have m. p. 141·6° and 178·8° (cf. Gough, Hunter, and Kenyon, A., 1926, 1032). L. M. CLARK.

***cis*–*trans*-Isomerism and steric hindrance. V. (I). 4-*iso*Propyl*cyclo*hexanols.** G. VAVON and A. CALLIER (Bull. Soc. chim., 1927, [iv], **41**, 677—687; cf. this vol., 455).—The influence of the *iso*-

propyl group is less marked in the *para*- than in the *ortho*-position, and the difference in reaction velocities between the *cis*- and *trans*-forms of *p-iso*propyl*cyclo*hexanol is considerably smaller than between the *cis*- and *trans*-forms of 2-*iso*propyl*cyclo*hexanol (*loc. cit.*). *p*-Nitro*iso*propylbenzene is reduced by hydrogen more rapidly than the *o*-isomeride, affording an 80% yield of *p-iso*propylaniline, b. p. 100—101°/10 mm., 226—227°/745 mm., converted by the diazo-reaction into *p-iso*propylphenol, b. p. 109—111°/10 mm., m. p. 61° (yield 65%). Hydrogenation of the phenol in acetic acid in presence of platinum-black is also more rapid than with the *o*-isomeride, and affords a mixture consisting of 1 part of *iso*propyl*cyclo*hexane and 2 parts of a mixture of the *cis*- and *trans*-forms of 4-*iso*propyl*cyclo*hexanol in approximately equal proportions. The same mixture of alcohols (b. p. 100—102°/12 mm., d^{18} 0·919, n_D^{18} 1·4665) is obtained by hydrogenation of 4-*iso*propyl*cyclo*hexanone, b. p. 85—86°/10 mm., d^{23} 0·915, n_D^{23} 1·4563 [*oxime*, b. p. 129—130°/12 mm., m. p. 33—35° (affording, on hydrogenation in dilute hydrochloric acid in presence of platinum-black, β-4-iso*propyl*cyclo*hexylhydroxylamine*, m. p. 61°); the semicarbazone, m. p. 187—188°, similarly affords 4-iso*propyl*cyclo*hexylsemicarbazide*, m. p. 159—160°], in ether or acetic acid in presence of platinum-black. Hydrogenation of the ketone in acetic acid containing hydrochloric acid affords a mixture in which the cis-4-iso*propyl*cyclo*hexanol*, m. p. 36—37°, b. p. 89°/8 mm., $n^{11·5}$ 1·4690, $d^{11·5}$ 0·926 (*hydrogen phthalate*, m. p. 129—130°; *hydrogen succinate*, m. p. 32—33°; *phenylurethane*, m. p. 88—89°), preponderates, the influence of the medium being thus manifested when steric hindrance is less marked. Reduction of 4-*iso*propyl*cyclo*hexanone with sodium and absolute alcohol affords mainly trans-4-iso*propyl*cyclo*hexanol*, m. p. 5—6°, b. p. 94°/10 mm., $d^{11·5}$ 0·920, $n^{11·5}$ 1·4696 (*hydrogen phthalate*, m. p. 114—115°; *hydrogen succinate*, m. p. 66—67°; *phenylurethane*, m. p. 112—113°), the *trans*-alcohol also being obtained by heating the sodium derivative of the *cis*-form at 160° for 2 hrs. *trans*-4-*iso*Propyl*cyclo*hexanol is esterified more rapidly than the *cis*-isomeride, the difference being more marked at a low temperature and in presence of a catalyst. Similarly, the *trans*-hydrogen phthalate is hydrolysed more rapidly than the *cis*-phthalate, the ratio of the velocity constants in 75% alcohol being 2·6 : 1 at 68° and 2·5 : 1 at 39°. With the hydrogen succinates, the ratio of the velocity constants for the *trans*- and *cis*-forms is 4 : 1 in water at 0°. The hydrogen phthalate of *cis*-4-*iso*propyl*cyclo*hexanol is hydrolysed fifty times as fast in 75% alcohol at 68° as that of the corresponding *cis*-2-isomeride; the corresponding ratio for the hydrogen succinates in water at 0° is 175 : 1.

R. BRIGHTMAN.

Action of *cyclo*hexene oxide on alkali and ammonium halides. H. K. SEN and C. BARAT (J. Indian Chem. Soc., 1927, 4, 22).—Neutral solutions of potassium halides treated with a few drops of *cyclo*hexene oxide quickly doveloped alkalinity in the order: iodide, bromide, chloride. Ammonium chloride behaves similarly. An explanation is tentatively suggested. B. W. ANDERSON.

Interaction of phenol and methyl alcohol at high temperatures and pressures. V. IPATIEV, N. ORLOV, and A. PETROV (J. Russ. Phys. Chem. Soc., 1927, **59**, 181—186).—The reaction of phenol with methyl alcohol has already been described (A., 1926, 281). When anisole and aluminium oxide were heated for 36 hrs. at 440° in an atmosphere of hydrogen at a maximum pressure of 200 atm., ethylene and *o*-cresol were formed. Phenol and *o*-cresol with aluminium oxide at 440—450° under 125 atm. gave a 2% yield of xanthen in 10 hrs. Phenol with aluminium oxide at 480—500° and a maximum pressure of 200 atm. yielded hydrogen, diphenylene oxide, and diphenyl ether. In addition to the above products, in every case a small quantity of a solid of low m. p. was obtained which dissolved in sodium hydroxide, giving a deep blue colour, and in alcohol with a deep green fluorescence. E. ROTHSTEIN.

Nature of the alternating effect in carbon chains. XIX. Mechanism of certain aromatic migrations. C. K. INGOLD, E. W. SMITH, and C. C. N. VASS (J.C.S., 1927, 1245—1250).—The hypothesis that the migration reactions of aryl iodide dichlorides are really substitutions in one molecule of chlorine derived from another, is tested by investigation of the apparent exception of *o*-iodoanisole dichloride (Jannasch and Hinterskirch, A., 1898, *i*, 575). The main product of the migration reaction of the latter is shown to be, not 5-chloro-2-iodoanisole (as stated by the previous workers), but 4-chloro-2-iodoanisole. The hypothesis is further confirmed by the chlorination of acetanilide to *p*-chloroacetanilide by means of 4-*chloro*-2-*iodoanisole dichloride*.

4-Chloro-2-iodoanisole, m. p. 48°, is synthesised from *p*-chloroanisole by nitration to 4-chloro-2-nitroanisole, followed by reduction to the amine and replacement of the amino-group by iodine. This product is found to be identical with that obtained by the rearrangement of *o*-iodoanisole dichloride. During the preparation of the latter, a *dichloroiodoanisole*, m. p. 37°, is also obtained.

4-*Chloro*-2-*iodoanisole dichloride*, m. p. 76° (decomp.), spontaneously decomposes in chloroform solution to give the *dichloroiodoanisole*, m. p. 37°, and 4-*chloro*-2-*iodoanisole*. The 5-chloro-2-iodophenetole described by Jannasch and Naphtali (A., 1898, i, 576) is really 4-*chloro*-2-*iodophenetole*. G. A. C. GOUGH.

***p*-Methylaminophenyl acetate.** L. GALATIS (Ber., 1927, **60**, [*B*], 1399—1402).—*p*-Benzylideneaminophenyl acetate is converted by methyl sulphate at 80—85° into the corresponding *methosulphate*, which, at a higher temperature and with excess of the reagent, evolves methyl acetate and forms the *compound*, $SO_3Me{\cdot}C_6H_4{\cdot}NMe(:CHPh){\cdot}O{\cdot}SO_3Me$. An analogous reaction is observed with the diacetyl derivative of *p*-aminophenol and methyl sulphate, ethyl sulphate, or sodium ethyl sulphate. The methosulphate of *p*-benzylideneaminophenyl acetate is converted by water into benzaldehyde and p-*methylaminophenyl acetate*, b. p. 168·5° (corr.)/9 mm., m. p. 43°; the corresponding *hydrochloride*, m. p. 200°, *oxalate*, and *picrate*, m. p. 157·5° (corr.), are described. p-*Aminophenyl acetate picrate* has m. p. 189° (corr.). *p*-Benzylideneaminophenol is

transformed by ethyl sulphate at 100—105° and treatment of the product with water into benzaldehyde and p-*ethylaminophenol*, m. p. 103—104° (*monoacetyl* derivative, m. p. 187°). *p*-Benzylidenecaminophenylacetate gives only small yields of the corresponding quaternary compound with ethyl sulphate or ethyl iodide. H. WREN.

New derivatives of phenacetin. M. T. BOGERT and W. H. TAYLOR (J. Amer. Chem. Soc., 1927, 49, 1578—1583).—When heated with alcoholic ammonia for 10—12 hrs. at 110—120°, 2 : 3-dinitrophenacetin affords 3-*nitro*-2-*amino*-4-*acetamidophenetole*, (I), golden-orange, m. p. 160° (*acetyl* derivative, yellow, m. p. 258°), which, on hydrolysis with concentrated sulphuric acid yields 3-*nitro*-2 : 4-*diaminophenetole*, dark purple, m. p. 95°, whilst elimination of the amino-group yields 3-nitro-4-acetamidophenetole. The formation of this nitroamine is contrary to the conclusions of Reverdin and Roethlisberger (A., 1922, i, 537). Reduction of (I) affords 4-*amino*-5-*ethoxy*-2-*methylbenziminazole*, m. p. 147°, whilst treatment according to the method of Bogert and Hand (A., 1903, i, 292) yields 2-*nitro*-3-*acetamido*-6-*ethoxybenzonitrile*, (II), m. p. 219°, and this, on treatment with concentrated sulphuric acid at 100°, affords 2-*nitro*-3-*amino*-6-*ethoxybenzamide*, yellow, m. p. 199°. Treatment of the latter with acetic anhydride yields 2-*nitro*-3-*amino*-6-*ethoxybenzonitrile*, m. p. 201°. Reduction of (II) with tin and glacial acetic acid affords 2-*amino*-3-*acetamido*-6-*ethoxybenzonitrile*, m. p. 250°. F. G. WILLSON.

Chloro- and bromo-derivatives of *o*- and *m*-cresol. E. BURES (Chem. Listy, 1927, 21, 221—227, 261—265; cf. this vol., 554).—The following substances were prepared: 3 : 5-*dibromo*-2-*methoxytoluene*, m. p. 33·5°, b. p. 265°; 3 : 5-dibromo-2-ethoxytoluene; *bismuth* and *mercuric* 3 : 5-*dibromo*-o-*tolyloxide*; *basic mercuric* 3 : 5-*dibromo*-o-*tolyloxide*; : 6-*trichloro*-3-*methoxytoluene*, m. p. 46°, b. p. 258°, and the corresponding *ethoxy*- and *phenoxy*-derivatives, m. p. 35·5° and 103°, b. p. 266° and 234°, respectively; *antimony*, *bismuth*, and *mercuric* 2 . 4 : 6-*trichloro*-m-*tolyloxides*; *basic mercuric* 2 : 4 : 6-*trichloro*-m-*tolyloxide*; *di*- and *tri*-2 : 4 : 6-*trichloro*-m-*tolyl phosphates*, m. p. 94·5° and 230°, respectively; 2 : 4 : 6-*tribromo*-m-*cresol*, m. p. 81·6—81·9°, the corresponding *methoxy*- and *ethoxy*-derivatives, m. p. 97° and 47·5°, respectively, and *bismuth*, *mercuric*, and *basic mercuric* 2 : 4 : 6-*tribromo*-m-*tolyloxides*; 2 : 4 : 6-tribromo-*m*-toluidine, m. p. 101° (*acetyl* derivative, p. 155°), and 2 : 4 : 5 : 6-*tetrabromo*-3-*ethoxytoluene*, p. 108°. Bromination of *m*-cresol in sunlight yields, not 2 : 4 : 6-tribromocresol, but a tetrabromo-derivative, m. p. 115—125° (decomp.), which appears to be either 2 : 4 : 6 : 6-tetrabromo-1-methyl-$\Delta^{1:3}$-*cyclo*hexadien-5-one, 2 : 4 : 6 : 6-tetrabromo-1-methyl-*cyclo*hexadien-3-one, or 2 : 4 : 4 : 6-tetrabromo-methyl-$\Delta^{1:5}$-*cyclo*hexadien-3-one. Chloro- or bromo-substitution of *o*- or *m*-cresol follows the same rules as for amino- or hydroxy-derivatives of benzene. In halogen derivatives of *o*-cresol, the halogen atom in the *ortho*-position to the hydroxyl group and in derivatives those in the positions 4 and 6 to the hydroxyl group are the most labile. Bromine is more easily displaced by other substituents from the benzene nucleus than chlorine. R. TRUSZKOWSKI.

Reduction products of some nitrodi-*p*-tolyl ethers. J. REILLY and H. S. B. BARRETT (J.C.S., 1927, 1399—1400; cf. this vol., 239).—3-*Nitrodi*-p-*tolyl ether*, b. p. 206°/11 mm., prepared from potassium *p*-tolyloxide and 4-bromo-2-nitrotoluene in presence of copper bronze and *p*-cresol, yields, on reduction with stannous chloride, 3-*aminodi*-p-*tolyl ether*, m. p. 76° (*hydrochloride*, m. p. 190—195°, *chloroaurate*, *benzoyl* compound, m. p. 107°, and *azo*-β-*naphthol* compound, m. p. 149°, described).

2-*Aminodi*-p-*tolyl ether*, prepared similarly from the corresponding nitro-compound, has b. p. 196—198°/13 mm. (*hydrochloride*, m. p. 180—184°; *sulphate*, m. p. 160—162°). Addition of the 2-diazonium chloride solution to boiling sulphuric acid (50%) yields di-*p*-tolylene ether, m. p. 165°, and (?) 2-chlorodi-*p*-tolyl ether, m. p. 70°. Partial reduction of 2 : 6-dinitrodi-*p*-tolyl ether at 50—60° with stannous chloride gives 6-*nitro*-2-*aminodi*-p-*tolyl ether*, m. p. 120—122° (*hydrochloride*, m. p. 206—210°; *azo*-β-*naphthol* compound, m. p. 190—200°). The diazonium solutions of this nitroamine are less stable than those described above. Nitration of 2-nitrodi-*p*-tolyl ether gives mainly 3 : 5-dinitro-*p*-cresol, together with 2 : 2′-dinitrodi-*p*-tolyl ether, m. p. 126°. G. A. C. GOUGH.

Development of chromogenic properties in cholesterol by the action of heat. T. MOORE and S. G. WILLIMOTT (Biochem. J., 1927, 21, 585—588).—Brown, resinous substances are produced if cholesterol is melted or heated in aqueous colloidal solution. At the same time, chromogenic properties similar to those of "oxycholesterol" are acquired. Robertson's observation (A. 1925, i, 1119) on the stability of cholesterol towards "oxidation" when aerated as an aqueous colloidal solution at the b. p. in absence of brain extract as a catalyst, *i.e.*, without the production of chromogenic substances, is not confirmed. S. S. ZILVA.

Preparation of aromatic carboxylic esters of alkoxy- and dialkoxy-aryldialkylaminopropyl alcohols. C. MANNICH.—See B., 1927, 507.

Photo-oxidation of adrenaline. T. VACEK (Biochem. J., 1927, 21, 457—459).—Pure adrenaline dissolved in distilled water takes up only minute quantities of oxygen in the dark. On the other hand, when exposed to visible light, and much more so when exposed to ultra-violet radiation, it takes up oxygen freely. The compound turns pink in the process of oxidation, the intensity of the colour being commensurate with the amount of oxygen taken up Different preparations of adrenaline show different tendencies to oxidation, pure adrenaline in distilled water being more oxidisable than adrenaline hydrochloride. S. S. ZILVA.

Relation between *as*-phenylmethylethylene glycol and its corresponding anhydrous derivatives. S. DANILOV and (MME.) E. VENUS-DANILOVA (J. Russ. Phys. Chem. Soc., 1927, 59, 187—216).—See this vol., 661.

Absorption spectra of di- and tri-phenylmethane, their carbinols, and triphenylmethyl

chloride. W. R. ORNDORFF, R. C. GIBBS, (Miss) S. A. MCNULTY, and C. V. SHAPIRO (J. Amer. Chem. Soc., 1927, 49, 1541—1545; cf. A., 1926, 733).—The absorption spectra of diphenylmethane, diphenylcarbinol, triphenylmethane, triphenylcarbinol, and triphenylmethyl chloride were measured in neutral, absolute-alcoholic solution. The absorption spectrum of diphenylmethane is similar to that of benzene, but the intensity of absorption is much greater. Diphenylcarbinol shows a similar absorption spectrum, but the bands are displaced slightly towards the ultra-violet. The absorption spectrum of triphenylmethane is again similar, the intensity being greater than in the case of diphenylmethane. Triphenylcarbinol shows absorption similar to that of triphenylmethane, but the intensity is less except in the extreme ultra-violet, and the bands are shifted towards the shorter wave-lengths. The absorption of triphenylmethyl chloride is again similar, and the bands, intermediate in intensity between those of triphenylmethane and triphenylcarbinol, are shifted in the normal manner towards lower frequencies.

F. G. WILLSON.

Absorption spectra of fuchsone, benzaurin, and aurin. W. R. ORNDORFF, R. C. GIBBS, (Miss) S. A. MCNULTY, and C. V. SHAPIRO (J. Amer. Chem. Soc., 1927, 49, 1545—1556; cf. preceding abstract).—The absorption spectra of fuchsone, benzaurin, aurin, and *p*-hydroxytriphenylcarbinol have been determined in freshly-prepared, neutral alcoholic solution. The first three compounds appear to be present initially in quinonoid form, subsequently changing to an equilibrium mixture of quinonoid hydrate and carbinol, a conclusion supported by the changes in the absorption spectra of solutions of the two forms of *p*-hydroxytriphenylcarbinol. When hydrogen chloride is added to alcoholic solutions of fuchsone and aurin, salt formation takes place first, and is followed, in more concentrated acid solutions, by more or less complete reduction. In concentrated sulphuric acid solution, the absorption spectra confirm the carbonium salt formation in the case of triphenylcarbinol (Baeyer, A., 1905, i, 281, 358) as distinct from the oxonium salts of fuchsone and aurin. The addition of successive hydroxyl groups results in the appearance of more absorption bands; thus, fuchsone has four, benzaurin five, and aurin six. In presence of potassium hydroxide, fuchsone changes in alcoholic solution to the carbinol form, with formation of the potassium salt. The type of absorption spectrum obtained from aurin in alcohol in presence of potassium hydroxide depends on whether the latter is added to a solution of aurin of the required concentration, or whether this concentration is reached by dilution of a more concentrated solution to which the alkali has been added previously. In the first case, the spectrum is similar to that which is consistently obtained in presence of higher concentrations of potassium hydroxide, whilst in the second case other bands appear. In concentrated aqueous potassium hydroxide, aurin is present as a tripotassium salt of the carbinol form.

F. G. WILLSON.

Auxochromes and antiauxochromes. I. Tetraphenylethane dyes. R. WIZINGER [with J. FONTAINE] (Ber., 1927, 60, [*B*], 1377—1389).—In extension of Dilthey's chromophore theory, it i proposed to subdivide auxochromes in the following manner: (i) positive auxochromes, including those groups previously considered auxochromic and alkyls, which favour the electro-positive condition, facilitate oxidation and analogous reactions, and deepen the colour in positive ions; (ii) negative auxochromes (groups, ·NO, ·NO_2, quinoid systems, :CO, ·N:N–, ·C:N·, etc.) which favour the electro-negative condition and the addition of positive residues and analogous reactions, and deepen the colour in negative ions; (iii) amphoteric auxochromes (aryls and the group >C:C<) which favour ionisation in the positive and negative sense, facilitate the substitution of hydrogen by metals or negative groups, and deepen the colour in positive and negative ions. From this point of view, it is shown that the introduction of positive auxochromes into tetraphenylethylene, in itself possessing limited additive ability and yielding the colourless, homopolar dichlorotetraphenylethane only under peculiar conditions, gives compounds with negative residues which are heteropolar and coloured. Thus octamethyltetra-aminotetraphenylethylene, m. p. 295—300°, is converted by cautious treatment with chlorine in carbon tetrachloride solution into the coloured *chloride*, $[(NMe_2\cdot C_6H_4)_2\dot{C}\cdot\dot{C}(C_6H_4\cdot NMe_2)_2]^{++}Cl_2^{--}$, and by bromine and iodine under similar conditions into the *perhalides*, $C_{34}H_{40}N_4Br_6$ and $C_{34}H_{40}N_4I_6$. Salts are also prepared by treatment of the ethylenic compound with acids and various oxidising agents (air, hydrogen peroxide, lead tetra-acetate) and by double decomposition from the halides; the *nitrate*, *sulphate*, *phosphate*, *oxalate*, *acetate*, *perchlorate*, *chloroaurate*, *chloroplatinate*, and *iodide* are described. Substitution of other auxochromes for the dimethylamino-group shows that the stability of the salts is increased by the number and strength of such groups. Thus tetramethyldiaminotetraphenylethylene yields the *chloride*, $C_{30}H_{30}N_2Cl_2$, *iodide*, $C_{30}H_{30}N_2I_6$, *perchlorate*, $C_{30}H_{30}O_8N_2Cl_2$, *chloroaurate*, $C_{30}H_{30}N_2Cl_8Au_2$, *sulphate*, and *nitrate*. *Tetra-p-aminophenylethylene*, m. p. 250°, prepared by reduction of diaminobenzophenone or tetra-*p*-nitrophenylethylene, affords the *periodide*, $C_{26}H_{24}N_4I_6$, and *chloroaurate*, $C_{26}H_{24}N_4Cl_8Au_2$. The coloured halide salts are converted into the ethylenes by treatment with copper powder. Tetrahydroxyphenylethylene gives a bluish-black *perchlorate*, $[(OH\cdot C_6H_4)_2\dot{C}\cdot\dot{C}(C_6H_4\cdot OH)_2]^{++}(ClO_4)_2^{--}$ converted by water into the anhydro-glycol, $OH\cdot C_6H_4\cdot C(:C_6H_4:O)\cdot C(:C_6H_4:O)\cdot C_6H_4\cdot OH$. Tetramethoxyphenylethylene yields still more unstable salts, among which the *perchlorate* is described. The carbinol bases corresponding with the dyes are the substituted benzpinacols. Octamethyltetra-aminotetraphenylethylene glycol and tetramethyldiaminotetraphenylethylene glycol yield the corresponding violet and red dyes; in the tetrahydroxy- and tetramethoxy-series, however, the anhydro-compounds, $OH\cdot C_6H_4\cdot C(:C_6H_4:O)\cdot C(:C_6H_4:O)\cdot C_6H_4\cdot OH$ and $(OMe\cdot C_6H_4)_2C{<}\begin{matrix}C(C_6H_4\cdot OMe)_2\\ \diagdown\!O\!\diagup\end{matrix}$, are obtained. Evidence in favour of the predicted behaviour of antiauxochromes is derived from the literature. Thus, tetraphenylethylene yields an unstable,

yellowish-red sodium salt, whereas dianthrone, derived from tetraphenylethylene by introduction of the antiauxochrome, C:O, gives a corresponding, completely stable compound.

In the stilbene series a new group of dye salts, $[OMe{\cdot}C_{10}H_6{\cdot}CH{\cdot}CH{\cdot}C_{10}H_6{\cdot}OMe]^{++}X_2$ and $[NH_2{\cdot}C_6H_4{\cdot}CH{\cdot}CH{\cdot}C_6H_4{\cdot}NH_2]^{++}X_2$, has been isolated.

H. WREN.

Reactions of 1-anilino*cyclo*hexane-1-carboxylic acid. Synthesis of ψ-indoxyl*spirocyclo*hexane. R. L. BETTS, R. MUSPRATT, and S. G. P. PLANT (J.C.S., 1927, 1310—1314).—The similarity of the properties of 1-*anilino*cyclo*hexane*-1-*carboxylic acid* to those of 1-anilino*cyclo*pentane-1-carboxylic acid (A., 1925, i, 1271) confirms the constitution assigned to the latter. 1-Anilino-1-cyano*cyclo*hexane (Walther and Hübner, A., 1916, i, 560), on keeping with concentrated sulphuric acid, gives 1-*anilino*cyclo*hexane*-1-*carboxylamide*, m. p. 148° (*hydrochloride* and *nitrosoamine*, m. p. 172°, described), which in turn yields 1-*anilino*cyclo*hexane*-1-*carboxylic acid*, m. p. 142° (*nitrosoamine*, m. p. 70°). This acid decomposes when heated to give Δ^1-*cyclo*hexene-1-carboxylic acid, which combines additively with bromine to produce 1:2-dibromo*cyclo*hexane-1-carboxylic acid.

ψ-*Indoxyl*spirocyclo*hexane*, m. p. 124°, is prepared by the fusion of 1-anilino*cyclo*hexane-1-carboxylic acid with potassium hydroxide at 340—350° for ½ hr. The crude product is acetylated and the purified 7-*acetyl*-ψ-*indoxyl*spirocyclo*hexane*, m. p. 105°, hydrolysed to give pure ψ-*indoxyl*spirocyclo*hexane*. This compound is unaffected by boiling dilute hydrochloric acid or dilute sodium hydroxide solution, but when heated with an excess of the latter at 200°, it gives a *sodium* derivative. Attempts to prepare the nitrosoamine and the semicarbazone were unsuccessful. With boiling dilute nitric acid, it gives 10-*nitro*-ψ-*indoxyl*spirocyclo*hexane*, pink, m. p. 177—178°, which yields a yellow *sodium* derivative and a 7-*methyl* derivative, m. p. 129°, by methylation with methyl sulphate. That the methyl group is attached to nitrogen is shown by the fact that no methyl iodide is produced under the conditions of the Zeisel experiment.

G. A. C. GOUGH.

α-Imino- and α-amino-acids from amines and carbonyl compounds. A. SKITA and C. WULFF (Annalen, 1927, **455**, 17—40; cf. this vol., 559).—Condensation of pyruvic acid with Schiff's bases of the type CHAr:NR (Ar=aryl, R=aliphatic radical) yields, intermediately, α-imino-acids of the type ArR.CHMe·CO_2H, with liberation of the aryl aldehyde, and these further condense to yield α-imino-unsaturated acids of the type CHAr:CH·C(:NR)·CO_2H, which are the first isolated products. The latter, on catalytic reduction with colloidal platinum in acetic acid, yield the corresponding substituted α-aminobutyric acids, $CH_2Ar{\cdot}CH_2{\cdot}CH(NHR){\cdot}CO_2H$, which on decarboxylation yield the corresponding secondary amines $CH_2Ar{\cdot}[CH_2]_2{\cdot}NHR$. Thus the compound $_{16}H_{19}O_2N$, obtained by the action of benzylidene-*y* onexylamine on pyruvic acid (this vol., 157), is *ylimino*-β-*benzylidenepropionic acid* (Ar= Ph, C_6H_{11}), which on reduction yields α-*cyclo*- l amino-γ-phenylbutyric acid (*loc. cit.*; *methyl* er, b. p. 215—217°/12 mm.; *hydrochloride* of methyl ester, m. p. 148°; *nitroso*-derivative of methyl ester, m. p. 63°), which is synthesised by heating *cyclo*hexylamine and α-bromo-γ-phenylbutyric acid in alcohol at 130° for 6 hrs. On decarboxylation by heating in quinoline, this amino-acid yields cyclo*hexyl*-γ-*phenylpropylamine*, b. p. 169—171°/12 mm. (*hydrochloride*, m. p. 217—218°; *nitrobenzoyl* derivative, m. p. 106—107°; *picrolonate*, m. p. 217—218°), which is also obtained by the reduction, with colloidal platinum in acetic acid, of *cinnamylidene*cyclo*hexylamine*, b. p. 180—185°/12 mm. (obtained by the condensation of cinnamaldehyde with *cyclo*hexylamine). On reduction in acetic acid suspension with hydrogen at 45°/3 at. in presence of colloidal platinum, α-*cyclo*hexylamino-γ-phenylbutyric acid yields α-cyclo*hexylamino*-γ-cyclo*hexylbutyric acid*, m. p. 265° (*ethyl* ester, b. p. 198—199°/11 mm.). The action of benzaldehyde on the condensation product of pyruvic acid with propylidene*cyclo*hexylamine also yields the same parent compound, $C_{16}H_{19}O_2N$. Benzylidene-ethylamine and pyruvic acid similarly yield α-*ethylimino*-β-*benzylidenepropionic acid*, m. p. 133—134°, which when heated in glycerol suspension at 140° for 1 hr. yields cinnamaldehyde, and on hydrolysis with dilute hydrochloric acid yields benzylidenepyruvic acid and ethylamine. On similar treatment in glycerol, the corresponding β-anisylidene-acid yields *p*-methoxycinnamaldehyde, and on hydrolysis with dilute hydrochloric acid, α-*cyclo*hexylimino- and α-amylimino-β-benzylidenepropionic acids yield benzylidenepyruvic acid, α-ethylimino-β-anisylidenepropionic acid yields anisylidenepyruvic acid, and α-amylimino-β-piperonylidenepropionic acid yields piperonylidenepyruvic acid. On reduction, α-ethylimino-β-benzylidenepropionic acid yields α-*ethylamino*-γ-*phenylbutyric acid*, m. p. 250° (*hydrochloride*, m. p. 198—199°), which on decarboxylation yields γ-phenylpropylethylamine, which is also obtained by the reduction of cinnamylidene-ethylamine. Condensation of benzylidenepyruvic acid with *cyclo*hexylamine, however, yields a *substance*, m. p. 122°, to which the constitution $NH{\cdot}C_6H_{11}{\cdot}CHPh{\cdot}CH_2{\cdot}CO{\cdot}CO_2H$ is assigned, whilst with aniline it yields 2:3-*diketo*-1:5-*diphenylpyrrolidine*, m. p. 163°. Phenylpyruvic acid and benzylidene*cyclo*hexylamine condense to yield γ-*hydroxy*-α-*keto*-βγ-*diphenylbutyro*cyclo*hexylamide*, $CHPh(OH){\cdot}CHPh{\cdot}CO{\cdot}CO{\cdot}NH{\cdot}C_6H_{11}$, m. p. 114—115°, which when heated with dilute hydrochloric acid yields 2:3-*diketo*-4:5-*diphenyl*-1-cyclo*hexylpyrrolidine*, m. p. 234—235°, the *dipotassium* salt of which with ethyl iodide yields 2:3-*diethoxy*-4:5-*diphenyl*-1-cyclo*hexylpyrrole*, m. p. 155—156°. By similar condensations with pyruvic acid and the appropriate Schiff's bases and subsequent treatment as above are obtained: α-*amylimino*-β-*benzylidenepropionic acid*, m. p. 136°; α-*amylamino*-γ-*phenylbutyric acid*, m. p. 216—218°; γ-*phenylpropylamylamine hydrochloride*, m. p. 215°; p-*tolylideneamylamine*, b. p. 134°/12 mm.; α-*amylimino*-β-p-*tolylidenepropionic acid*, m. p. 130°; α-*amylamino*-γ-p-*tolylbutyric acid*, m. p. 232°; γ-p-*tolylpropylamylamine*, b. p. 153—154°/13 mm. (*hydrochloride*, m. p. 213°; *nitrobenzoyl* derivative, m. p. 225°); p-*tolylidenepyruvic acid*, m. p. 123°; α-*ethylimino*-β-*anisylidenepropionic acid*, m. p. 122° (decomp.); α-*ethylamino*-γ-

anisylbutyric acid, m. p. 225°; *piperonylideneamylamine*, m. p. 36°, b. p. 210—215°/25 mm.; *α-amylimino-β-piperonylidenepropionic acid*, m. p. 135° (decomp.); *α-amylamino-γ-piperonylbutyric acid*, m. p. 230—231°; *γ*-piperonylpropylamylamine, b. p. 196°/12 mm. (*hydrochloride*, m. p. 203°; *picrate*, m. p. 128°). Similar compounds are obtained from the Schiff's bases derived from cinnamaldehyde, and thus are obtained: *α-amylimino-*, m. p. 136—138°; *α-ethylimino-*, m. p. 151—152°; and α-cyclo*hexylimino-*, m. p. 145°, *-β-cinnamylidenepropionic acids*. Partial reduction of the α-amylimino-acid yields *α-amylamino-ε-phenylhexenoic acid*, m. p. 213°, which on further reduction yields *α-amylamino-ε-phenylhexoic acid*, m. p. 214—216°; *α-ethylamino-*, m. p. 222—223°, and α-cyclo*hexylamino-*, m. p. 242°, *-ε-phenylhexoic acids* are obtained similarly. Decarboxylation yields, respectively, *ε-phenylamyleneamylamine hydrochloride*, m. p. 215°; *ε-phenyldiamylamine*, b. p. 310° (*hydrochloride*, m. p. 184—186°); *ε-phenylamylethylamine*, b. p. 295° (*hydrochloride*, m. p. 144°), and cyclo*hexyl-ε-phenylamylamine*, b. p. 315° (*hydrochloride*, m. p. 246°). J. W. Baker.

New way of utilising carbon monoxide. H. Dieterle and W. Eschenbach (Arch. Pharm., 1927, **265**, 187—195).—That carbon monoxide yields carbonyl compounds with many elements has been shown particularly by Manchot (A., 1925, ii, 232 and earlier papers), whilst that, *e.g.*, acid amides are "decarbonylated" by certain catalysts has been demonstrated by Mailhe (A., 1926, 54). Details of an apparatus, but none of the particular catalysts employed, are given for carrying out on the laboratory scale processes based on the above facts. These processes, covered by patent applications, are outlined as follows. Chlorobenzene and carbon monoxide yield benzoic acid; *p*-chlorotoluene similarly gives *p*-toluic acid. *o*-Dichlorobenzene also yields benzoic acid, and phthalic acid as an intermediate stage has not yet been detected. Chlorobenzene with carbon monoxide and ammonia yields aniline, presumably by carbonylation followed by decarbonylation, and *p*-chlorotoluene similarly gives *p*-toluidine.

W. A. Silvester.

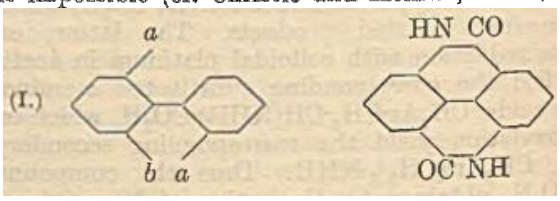
Aminobenzoate of thiodiglycol [ββ′-dihydroxydiethyl sulphide] and its sulphone. New higher homologue of ββ′-dihydroxydiethyl sulphide. R. T. Major (Bull. Soc. chim., 1927, [iv], **41**, 634—637).—To obtain anæsthetics for administration by external application, the author has prepared *ββ′-di-p-aminobenzoyloxydiethyl sulphide*, m. p. 184·5° (yield 70%), by reduction of *ββ′-di-p-nitrobenzoyloxydiethyl sulphide*, m. p. 107·7° (obtained by Fromm and Kohn's method, A., 1921, i, 242). Neither the sulphide nor the corresponding sulphone possesses any anæsthetic action by external application, probably in consequence of their slight solubility in most solvents. *ββ′-Di-p-nitrobenzoyloxydiethyl sulphone*, m. p. 153°, obtained by oxidation of the sulphide in acetic acid with potassium permanganate and sulphuric acid, on reduction by Einhorn's method (A., 1910, i, 170) affords *ββ′-di-p-aminobenzoyloxydiethyl sulphone*, m. p. 149—150°. Hydrolysis of ββ′-di-*p*-aminobenzoyloxydiethyl sulphide with alcoholic potassium hydroxide affords ethyl *p*-aminobenzoate and sulphur dioxide. *ββ′-Dihydroxy-ββ′-dimethyl di-n-butyl sulphide*, b. p. 148·5—149°/11 mm., obtained in 45% yield by the action of sodium sulphide on β-chloromethyl-*n*-butan-β-ol in alcoholic solution, has an intense soporific action on mice, and slight toxicity.

R. Brightman.

Union of benzoylacetonitrile with organic bases in presence of salicylaldehyde. I. P. Krishnamurti and B. B. Dey (J.C.S., 1927, 1349—1351).—Benzoylacetonitrile combines with piperidine in presence of traces of salicylaldehyde to yield a mono-acid *base*, $C_{10}H_{18}ON_2$, m. p. 173° [*hydrochloride*, m. p. 235—242°, *picrate*, m. p. 138° (losing alcohol of crystallisation at 98°), and *chloroplatinate* described]. When the base is oxidised with alkaline potassium permanganate, benzoic acid and piperidine are produced. Piperidine and benzoylacetonitrile are formed when the base is heated above its m. p. The action of nitrous acid on the hydrochloride of the base yields a *nitroso-hydrochloride*, m. p. 258° (decomp.), which in turn yields an *iso*nitroso-compound, $C_{14}H_{17}O_2N_3$, m. p. 183° (decomp.) [*diacetyl* derivative, m. p. 180—181° (decomp.), and *dibenzoyl* derivative, m. p. 148°]. *N*-Alkylpiperidines do not give this reaction. The alternative constitutions $CH_2Bz{\cdot}C{:}NH{\cdot}NC_5H_{10}$ and $CH_2Bz{\cdot}C(:NH){\cdot}NC_5H_{10}$ are proposed for the base, and in consideration of its stability to alkalis and its instability to acids, the former is favoured. The *iso*nitroso-derivative is represented $OH{\cdot}N{:}CBz{\cdot}C{:}NH{\cdot}NC_5H_{10}$.

G. A. C. Gough.

Stereochemistry of diphenyl. J. Meisenheimer and M. Höring (Ber., 1927, **60**, [*B*], 1425—1433).—The possibility that the existence of substituted diphenic acids in optically active forms may be due in some manner to the carboxy-groups is discounted by the impossibility of resolving *o*-nitrobenzoic, 8-nitronaphthoic, or 5-nitronaphthoic acid into optical isomerides. 6 : 6′-Dinitrodi-*o*-tolyl, obtained by the action of copper powder on 2-iodo-3-nitrotoluene, is reduced by stannous chloride to 6 : 6-diaminodi-*o*-tolyl, which is resolved into its optically active forms by the alternate use of *d*- and *l*-tartaric acids in absolute alcoholic solution. *1-6 : 6′-Diamino-di-o-tolyl* has m. p. 156°, $[\alpha]_D$ −34·8° in *N*-hydrochloric acid; the properties of the d-*base* are similar. The compounds are not prone to racemisation. The only possible explanation of the stereoisomerism appears to lie in the assumption that with a particular type of substitution (I) free rotation of the two rings is impossible (cf. Christie and Kenner, J.C.S., 19—,



121, 615). Consideration of the distances between the groups as shown by Röntgen spectrography indicates that the proximity of the methyl and amino-groups to one another may easily be such as to inhibit free rotation of the benzene nuclei around the

common axis and to permit only vibratory motion. If this explanation be accepted, isomerism must disappear when the substituting groups are mutually attractive or actually react chemically with one another. The active 6 : 6′-*diaminodi-o-tolyls* are therefore transformed (without considerable racemisation) into the corresponding *diacetyl* derivatives, m. p. 229°, $[\alpha]_D$ −131° (+133°), which are oxidised by boiling, neutral potassium permanganate solution to largely racemised 6 : 6′-diacetamidodiphenic acids. [The *quinine* salt of *d*-diacetamidodiphenic acid has m. p. 187°, $[\alpha]_D$ −92·2° in methyl-alcoholic solution ($c = 2{\cdot}489$); the rotation of optically homogeneous *sodium* d-*diacetamidodiphenate* is calculated to be $[\alpha]_D$ −211·6°.] If the active diacetamido-acids are hydrolysed under as mild conditions as possible (contact with dilute sulphuric acid at the atmospheric temperature), the acetyl groups are removed and the completely racemised *dilactam* (II), m. p. above 330°, is produced.

The resolution of 6 : 6′-diaminodi-*o*-tolyl cannot readily be effected by π-bromocamphorsulphonic acid.

The following salts are described incidentally: *brucine o-nitrobenzoate*, m. p. about 120° (decomp.); *brucine* 8-*nitronaphthoate*, decomp. 155—165°, m. p. 242° (decomp.); *brucine* 5-*nitronaphthoates*, m. p. 212° and decomp. about 170°, which probably differ from one another in their content of solvent of crystallisation. H. WREN.

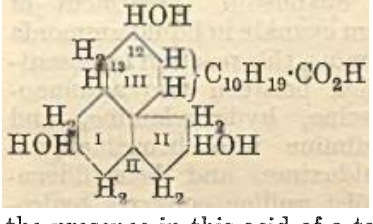
Hydrocaffeic acid a constituent of spores of *Lycopodium clavatum*. F. ZETZSCHE and K. HUGGLER (Helv. Chim. Acta, 1927, **10**, 472—474).—The acidified alkali extract of spores of *Lycopodium clavatum* is extracted with ether and the oil so obtained is freed from lycopodium oil with chloroform or light petroleum, giving a 5% yield of crude hydrocaffeic acid (β-3 : 4-dihydroxyphenylpropionic acid), from which the pure acid, m. p. 139° (dimethyl ether, m. p. 97°), is obtained by crystallisation from xylene. The dimethyl ether is oxidised by alkaline permanganate to veratric acid, m. p. 179—180°.

C. HOLLINS.

Derivatives of cumidic and pyromellitic acids. H. DE DIESBACH and M. GUHL (Helv. Chim. Acta, 1927, **10**, 442—449; cf. de Diesbach and Zurbriggen, A., 1925, i, 1427).—By the action of chlorine on β-cumidyl chloride at 150° and finally at 180—190°, there is obtained 1 : 4-*bisdichloromethylbenzene*-2 : 5-*dicarboxyl chloride*, m. p. 110—111°. The corresponding *acid*, m. p. 270°, and *ethyl* ester, m. p. 127·5°, are described. The ethyl ester is converted at 190°, with elimination of 2 mols. of ethyl chloride, into *chloro-p-pyromellitide* [*dilactone* of 1 : 4-*bis*(*chlorohydroxymethyl*)*benzene*-2 : 5-*dicarboxylic acid*], m. p. 282°. If the temperature of chlorination does not exceed 150° the product is impure 1 : 4-*bischloromethylbenzene*-2 : 5-*dicarboxyl chloride* [free *acid* decomp. 325° without melting; *ethyl* ester, m. p. 132° (decomp.)]. By continuing chlorination at 265°, there is obtained the symmetrical octachloride of pyromellitic acid, *dianhydro*-1 : 2 : 4 : 5-*tetrakis*(*dichlorohydroxy*)*benzene*, m. p. 267—268°, which is not hydrolysed by formic or acetic acid, but gives pyromellitic acid when boiled with concentrated alkali. Chlorination above 265° gives decarboxylated products. The octachloride is formed directly at 150° (better 200°) when α-cumidic acid is used, and also from *m*- or *p*-pyromellitide, pyromellitic acid, its chloride or anhydride, by action of phosphorus pentachloride in a sealed tube at 200—210°. The normal chloride of pyromellitic acid is converted by aluminium chloride at all temperatures between 80° and 180° into the as(2 : 5)-*chloride*, $O<\begin{matrix}CO\\CCl\end{matrix}>C_6H_2<\begin{matrix}CCl_2\\CO\end{matrix}>O$, m. p. 225—227° (with regeneration of the normal chloride), reducible by zinc and acetic acid to *p*-pyromellitide without any trace of *m*-pyromellitide. Of the three di-imides of pyromellitic acid described by Meyer and Steiner (A., 1914, i, 841), the so-called *as*-di-imide, prepared by sublimation in a vacuum, could not be obtained. A benzene solution of the *as*-acid chloride gives with dry ammonia the *p*-diamide, $C_6H_2(CO_2H)_2(CO{\cdot}NH_2)_2$, which is converted at 200° into the normal di-imide.

C. HOLLINS.

Bile acids. XXVII. Constitution of acids resulting from the breakdown of cholic acid. H. WIELAND (Z. physiol. Chem., 1927, **167**, 70—75).—The results of Windaus and van Schoor (A., 1926, 169; this vol., 56) and Borsche and Frank (A., 1926, 1140) are regarded as establishing definitely the position of the hydroxyl group in ring III in cholic acid, this group being attached to the carbon atom 12 instead of 13. The statement of the latter authors, that the liberation of carbon monoxide when choloidanic acid is heated with concentrated sulphuric acid proves the presence in this acid of a tertiary-bound carboxyl group, is regarded as erroneous. The production of carbon monoxide from choloidanic acid under such stringent conditions, resulting in the production of a black fused mass and the evolution of appreciable amounts of sulphur dioxide, is not satisfactory evidence of this fact. Similarly, Borsche's formula for solanellic acid, where this acid is regarded as a derivative of malonic acid, is incorrect, since this substance loses only one third of the theoretical amount of carbon dioxide at 210—215°.



A. WORMALL.

Application of the Perkin reaction to phenolic aldehydes. S. OGAWA (Sci. Rep. Tôhoku Imp. Univ., 1927, **16**, 383—396).—See this vol., 359.

Hydrobenzamide and benzaldimine as ammono-aldehydes. H. H. STRAIN (J. Amer. Chem. Soc., 1927, **49**, 1558—1571).—In extension of Franklin's conception of nitrogen compounds (A., 1924, ii, 850) as acids, bases, or salts of ammonia, analogy is drawn between certain organic oxygen and nitrogen derivatives. Thus primary and secondary amines are the nitrogen analogues of the alcohols, and tertiary amines those of the ethers. Similarly, the acid amidines (carbazylic acids) are the ammonia analogues of the carboxylic acids, and as the latter lose water with formation of the acid anhydrides,

so the acid amidines lose ammonia with formation of the corresponding acid anammonides, the nitriles, whilst the pyrogenic decomposition of an acid salt of an amidine, with formation of a hydrocarbon and cyanamide, is analogous to the decomposition of the sodium salts of the carboxylic acids with formation of hydrocarbons and carbon dioxide. Certain more complex analogies are similarly formulated.

Hydrobenzamide dissolves slowly in liquid ammonia, and the solution deposits *benzaldimine*, the formation of which is accelerated in presence of ammonium chloride. Benzaldimine loses ammonia when kept or heated, with formation of hydrobenzamide. On reduction with sodium and liquid ammonia, it yields benzylamine. It dissolves sodium and potassium amides in liquid ammonia solution, with formation of *sodium* and *potassium* salts. When heated at 210° with potassamide and liquid ammonia, it yields potassium benzamidine and benzylamine, a reaction analogous to the Cannizzaro reaction with benzaldehyde and potassium hydroxide. At the same time, about 60% of the benzaldimine is converted into amarine, which in turn is converted into lophine by the action of the potassamide. Treatment of benzaldimine with iodine in liquid ammonia at −39° affords cyaphenin (20%) and benzamidine (40%), together, probably, with a trace of benzonitrile, whilst amarine yields similarly lophine, and this, on further treatment with iodine in boiling liquid ammonia, yields cyaphenin. Treatment of cyaphenin with ammonium cyanide in liquid ammonia affords benzylidenecyanamine, this reaction representing an aldol condensation between two ammonoaldehydes. Phenylhydrazine, hydroxylamine, and aniline convert benzaldimine into benzaldehydephenylhydrazone, benzaldoxime, and benzylideneaniline, respectively, whilst aniline converts hydrobenzamide into benzylideneaniline and ammonia. Hydrobenzamide does not combine with dry sulphur dioxide in absolute alcohol, Otto's product (Annalen, 1859, **112**, 305) being precipitated on addition of the necessary proportion of water. Treatment of hydrobenzamide in benzene with sulphurous acid affords the *compound* $[CHPh(SO_2\cdot OH)\cdot NH]_2CHPh$, and this is hydrolysed by water with formation of benzaldehyde and Otto's compound, to which the formula $CHPh<^{NH_2}_{SO_2}>O$ is ascribed. F. G. Willson.

Influence of substituents on the stability of Schiff's bases. I. Hydrolysis of nitro- and methoxy-benzylideneanilines. (Miss) E. M. Langman, W. Healy, and P. K. Dutt (J. Indian Chem. Soc., 1927, **4**, 75—79).—The *o*-, *m*-, and *p*-nitro- and *o*-, *m*-, and *p*-methoxy-benzylideneanilines were prepared, and equivalent quantities separately hydrolysed with hydrochloric acid. The percentages of anils hydrolysed were determined at intervals in each case until equilibrium was reached. In the light of the results thus obtained, the influence of general polar effect, induced polar effect, mass, steric effects, conjugation, and constitutional changes on the equilibrium points and initial velocities of reaction in the hydrolysis of the anils is discussed.

B. W. Anderson.

Bromination of anisaldehydephenylhydrazone. I. M. Vanghelovitch (Bul. Soc. Chim. Romania, 1926, **8**, 20—25; cf. Chattaway and Walker, A., 1925, i, 929).—Bromination of anisaldehydephenylhydrazone in cold glacial acetic acid in absence of light yields *ω-bromoanisaldehyde-2 : 4-dibromophenylhydrazone*, m. p. 129—130°, which is converted by alcoholic potassium cyanide into *ω-cyanoanisaldehyde-2 : 4-dibromophenylhydrazone*, m. p. 182°. Bromination in sunlight gives *1 : 4-di-p-bromophenyl-3 : 6-di-p-methoxyphenyl-1 : 4-dihydro-1 : 2 : 4 : 5-tetrazine*, m. p. 150°, formed by elimination of 2 mols. of hydrogen bromide from 2 mols. of ω-bromoanisaldehyde-*p*-bromophenylhydrazone. H. Burton.

Constitution and derivatives of 4 : 6- and 2 : 6-dinitro-3-methoxybenzaldehyde. J. Troger and C. Eicker (J. pr. Chem., 1927, [ii], **116**, 17—33).—The two isomeric dinitromethoxybenzaldehydes obtained by direct nitration of *m*-methoxybenzaldehyde (Tiemann and Ludwig, A., 1883, 188) are both converted by boiling 5% sodium hydroxide into a mixture of 2 : 4-dinitroanisole and 2 : 4-dinitrophenol [*sodium* $(+H_2O)$ and other salts are described]. Of the two possible compounds from which these substances could be derived, that of m. p. 110° must be *4 : 6-dinitro-3-methoxybenzaldehyde* (*phenylhydrazone*, m. p. 210°; *semicarbazone*, m. p. 247°; *oxime*, m. p. 117°), since it is oxidised by hot aqueous permanganate to 4 : 6-dinitro-3-methoxybenzoic acid (*potassium* and *silver* salts; *acid chloride*, m. p. 85°; *amide*, m. p. 215°; *anilide*, m. p. 215°). The aldehyde condenses with acetone in alkaline solution to amorphous *6 : 6′-dinitro-5 : 5′-dimethoxyindigotin*, and with sodium phenylacetate in presence of acetic anhydride to *4 : 6-dinitro-3-methoxy-α-phenylcinnamic acid*, m. p. 160° (*barium* salt); with aqueous ammonia, it gives 2 : 4-dinitroanisole. The second isomeride, m. p. 156°, must be *2 : 6-dinitro-3-methoxybenzaldehyde* (*phenylhydrazone*, m. p. 185°; *semicarbazone*, m. p. 225°; *oxime*, m. p. 165°); this is confirmed by the formation with acetone and alkali of amorphous *4 : 4′-dinitro-5 : 5′(? 7 : 7′)-dimethoxyindigotin*. It condenses with sodium phenylacetate, giving *2 : 6-dinitro-3-methoxy-α-phenylcinnamic acid*, m. p. 255 (*silver* salt), and is oxidised by permanganate to *2 : 6-dinitro-3-methoxybenzoic acid*, m. p. 195° (*potassium* and *silver* salts; *acid chloride*, m. p. 85°; *amide*, m. p. 222°; *anilide*, m. p. 243°), which yields 2 : 4-dinitroanisole when heated with soda-lime at 185—190°. Attempts to obtain amino-derivatives from the aldehydes by reduction or heating with alcoholic ammonia, or from the dinitromethoxyphenylcinnamic acids by reduction, were unsuccessful. H. E. F. Notton.

New derivatives of vanillin and some of their reactions. L. C. Raiford and G. C. Hilman (J. Amer. Chem. Soc., 1927, **49**, 1571—1577; cf. this vol., 564).—The following derivatives of 5-bromovanillin are described: *phenylhydrazone*, m. p. 111°, *p-bromophenylhydrazone*, m. p. 153°; *semicarbazone*, m. p. 185—186°; *5-bromovanillylidene-aniline*, m. p. 124°; *-p-toluidine*, m. p. 159—160°, and *-toluene*, m. p. 184—185°. *5 : 6-Dibromovanillylideneaniline* m. p. 147°, is obtained by boiling the aldehyde and aniline together in pyridine; *p*-toluidine yields

similarly 5 : 6-*dibromovanillylidene*-p-*toluidine*, purple, becoming yellow below 100°, m. p. 150°. *Di*-5 : 6-*dibromovanillylidenebenzidine*, m. p. not below 350°, is described, as well as the aldehyde *phenylhydrazone*, m. p. 102° after softening at 94°, *semicarbazone* ($+C_5H_5N$), m. p. (solvent-free) 224°, and *oxime*, m. p. 187°. No stereoisomeride of the latter could be obtained, the oxime of dibromoprotocatechualdehyde being obtained when the dibromovanillin was heated with alcohol, hydroxylamine hydrochloride, and hydrochloric acid at 160—170°. When boiled with acetic anhydride, the oxime yields 5 : 6-*dibromo*-4-*acetoxy*-3-*methoxybenzonitrile*, m. p. 169°, which, on hydrolysis with alkali, yields 5 : 6-*dibromo*-4-*hydroxy*-3-*methoxybenzonitrile*, m. p. 179° (*benzoyl* derivative, m. p. 215° after softening at 212°). The cyano-group of this nitrile is particularly resistant to hydrolysis. F. G. WILLSON.

Mechanism of the formation of ketones during the dry distillation of salts of organic acids. C. DOSIOS and G. LEUCADITIS (Compt. rend., 1927, **184**, 1458—1460).—The formation of mixed ketones by dry distillation of a mixture of the salts of different organic acids is explained on the assumption that anhydrides are primarily formed, $(R\cdot CO_2)_2Ca \longrightarrow (R\cdot CO)_2O+CaO$, and that interchange of groups occurs between the anhydrides prior to the decomposition, $(R\cdot CO)_2O+CaO \longrightarrow R\cdot CO\cdot R+CaCO_3$. This assumption is supported by the presence of traces of anhydrides among the reaction products, *e.g.* calcium benzoate affords a little benzoic anhydride, and crude acetone from calcium acetate always contains a little acetic acid. Further support is found in the observations that under 1 mm., calcium benzoate affords benzophenone at 420° in place of at 550° under 760 mm.; that mixed ketones are obtained by passing the vapours of anhydrides over heated calcium carbonate (Sabatier and Mailhe, A., 1914, i, 168), and that, whilst benzoic acid vapour passed over calcium carbonate at 550° affords only decomposition products, ketones containing the benzoyl group are obtained at much lower temperatures by the use of a suitable vapour mixture. The decomposition temperature of the intermediate mixed anhydride is evidently lower than that of benzoic anhydride. R. BRIGHTMAN.

Relative affinity of the *p*-tolyl radical. M. TIFFENEAU and (MLLE.) J. LÉVY (Compt. rend., 1927, **184**, 1465—1467).—In the addition of hypoiodous acid to α-*p*-tolyl-β-methyl-Δ^{α}-propylene, the *p*-tolyl group behaves as the anisyl radical, and not as the phenyl group, affording β-*iodo*-α-p-*tolyl*-β-*methyl*-n-*propyl alcohol*, converted by dry potassium hydroxide into α-*p*-tolyl-α-methylpropaldehyde, b. p. 129°/ mm. (*semicarbazone*, m. p. 172°). Similarly, the isomerisation of α-p-*tolyl*-β-*methylpropylene oxide*, p. 120—125°/27 mm., obtained by oxidation of e perbenzoic acid, affords α-*p*-tolylethyl methyl ketone, showing that the affinity of the *p*-o yl radical, like that of the anisyl group, is greater an that of the phenyl radical. On the other hand, e ydration of α-*p*-tolyl-β-methylpropane-αβ-diol with phuric acid affords α-*p*-tolyl-α-methylpropaldehyd , the *p*-tolyl group, like the phenyl group, gra ing to the carbon atom carrying the methyl groups. β-*Phenyl*-α-p-*tolylethylene oxide*, m. p. 59—60°, obtained by oxidising *p*-methylstilbene with perbenzoic acid, when heated in presence of zinc chloride, affords phenyl-*p*-tolylacetaldehyde, b. p. 190—192°/22 mm. (semicarbazone, m. p. 153—154°), isomerisation of α-*p*-tolyl-α-phenylethylene oxide affording the same product. R. BRIGHTMAN.

Thiosemicarbazone series. P. K. BOSE and D. R. CHAUDHURY (J. Indian Chem. Soc., 1927, **4**, 84—88).—Since cinnamylidenephenylhydrazone and some similar compounds are known to undergo ring-closure readily, forming pyrazolines, it was thought that the thiosemicarbazones of unsaturated aldehydes or ketones which contain the same system, –C:CH·CH:N·NH–, might also undergo conversion into pyrazolines. Several cinnamylidene- and styryl methyl ketone thiosemicarbazones were prepared, but did not undergo conversion, the compounds probably existing in the form CHPh:CH·CH:N·N:C(SH)·NHR, where the necessary imino-hydrogen atom has migrated to the sulphur atom. The following are described: *cinnamylidene-thiosemicarbazone*, m. p. 134—135°; *cinnamylidene*-4-*methyl*-, -4-*ethyl*-, -4-p-*tolyl*-, -4-o-*tolyl*-, -4-m-*tolyl*-, and -4-β-*naphthyl-thiosemicarbazones*, m. p. 170°, 166—167°, 194°, 207°, 146°, and 213°, respectively; *styryl methyl ketone thiosemicarbazone*, m. p. 147—148°, and the corresponding 4-*methyl*-, 4-o-*tolyl*-, 4-α-*naphthyl*-, and 4-*phenyl-thiosemicarbazones*, m. p. 149°, 185°, 189°, and 163—164°, respectively; *cinnamylidenebenzyldithiocarbazinate*, m. p. 183°, and *styryl methyl ketone benzyldithiocarbazinate*, m. p. 130—131°. Cinnamylidene-4-phenylthiosemicarbazone has m. p. 182—183°. B. W. ANDERSON.

Interaction of ketones and alcohols under the influence of light. J. BÖESEKEN, W. D. COHEN, and S. L. LANGEDIJK. II. Explanation of some photochemical discrepancies by the theory of the interior filter. S. L. LANGEDIJK (Rec. trav. chim., 1927, **46**, 383—396).—By using various aromatic ketones in alcoholic solution as exterior light filters for the transformation of benzophenone into benzpinacone, under the influence of light, it has been found possible to measure their relative "extinction coefficients." The various ketones examined have values of the same order as that of benzophenone, which was taken as the standard, with the exception of fluorenone and phenyl α-naphthyl ketone, which gave abnormally high figures, whilst the maximum effect is noticeable, not at 4050—4080 Å., corresponding with the maximum absorption, but nearer the ultra-violet end of the spectrum, at approximately 3850 Å. The theory of the interior light filter (A., 1925, i, 408), applied to the mutual action of mixed organic liquids on their photochemical reactions, is now shown to explain the discrepancies noticed by Cohen (A., 1920, i, 393) in the photochemical behaviour of mixtures of aromatic ketones in alcoholic solution. This theory accounts satisfactorily also for the observed phenomena when oxygen is bubbled into alcoholic solutions of these ketones subjected to photochemical action, except in the two cases already mentioned, to explain which an ingenious theory is advanced. E. HOLMES.

Transformation of phenyl acetate into *p*-hydroxyacetophenone. W. J. MINAEV (J. Russ. Phys. Chem. Soc., 1926, **58**, 729—736).—The preparation of *p*-hydroxyacetophenone from phenol and acetyl chloride by Friedel and Crafts' method was investigated, with a view of elucidating the mechanism of the reaction, which always gives low yields. The hypothesis that the *p*-hydroxyacetophenone is a product of the migration of the acetyl group of the previously formed phenyl acetate under the influence of the metallic chloride to the nucleus was tested by adding dry aluminium chloride to phenyl acetate saturated with dry hydrogen chloride: a 28·8% yield of *p*-hydroxyacetophenone was obtained, indicating that the migration to the nucleus was probably a stage in the Friedel and Crafts reaction.

M. ZVEGINTZOV.

Reactivity of positive hydrogen atoms. I. Diphenacyl sulphide. W. DILTHEY [with A. LACHS] (Ber., 1927, **60**, [*B*], 1403—1405).—The methylene hydrogen atoms of diphenacyl sulphide can be proved to react readily with aldehyde if piperidine is used as condensing agent, since the products are stabilised by the production of additive compounds with the base, in which the latter is so firmly attached that it is not removed when the adduct is crystallised from indifferent media. Presumably, the piperidine molecule is attached to the sulphur atom. Condensation occurs also in presence of ammonia, methylamine, sodium methoxide, aniline, dimethylaniline, or pyridine, but crystalline products could not be isolated. The following derivatives of diphenacyl sulphide are described: *dibenzylidene*-$[COPh{\cdot}C(:CHPh)]_2S$, m. p. 139—140° (also $+2C_5H_{11}N$, m. p. 167—169°); *di*-p-*anisylidene*- ($+C_5H_{11}N$), m. p. 157—159°; *disalicylidene*- ($+C_5H_{11}N$), m. p. 167—169° (decomp.); *di*-p-*dimethylaminobenzylidene*- ($+C_5H_{11}N$), m. p. about 153—154°. H. WREN.

Pungent principles of ginger. IV. H. NOMURA and S. TSURUMI (Proc. Imp. Acad. Tokyo, 1927, **3**, 159—161).—Assuming that shogaol is β-4-hydroxy-3-methoxyphenylethyl *n*-heptenyl ketone, the authors have synthesised this substance by the condensation of zingerone with *n*-hexaldehyde. An oil with a pungent taste similar to natural shogaol was obtained, b. p. 201—203°/2—2·5 mm., n_D^{25} 1·52518, d_4^{25} 1·0419 (shogaol, n_D^{25} 1·52467, d_4^{25} 1·0448). E. A. LUNT.

Preparation of fisetol. P. KARRER and H. BIEDERMANN (Helv. Chim. Acta, 1927, **10**, 441).—Condensation of hydroxyacetonitrile with resorcinol in presence of zinc chloride gave fisetol, m. p. 189° (phenylhydrazone, m. p. 107—109°), instead of the 5-hydroxycumaran-2-one obtained by Slater and Stephen (J.C.S., 1920, **117**, 314). The formation of one or the other compound may be due to traces of catalytic substances. C. HOLLINS.

Diarylquinones. II. Yellow and red varieties of diarylquinones. R. PUMMERER and H. FIEDLER (Ber., 1927, **60**, [*B*], 1439—1442).—Yellowish-red dimorphism is a comparatively infrequent phenomenon among diarylquinones. 2 : 5-*Di*-p-*xylyl*-p-*benzoquinone*, m. p. 159—160°, prepared by the action of aluminium chloride on *p*-xylene and *p*-benzoquinone followed by oxidation of the quinhydrone by ferric chloride, exists only in golden-yellow needles. 2 : 5-*Di*-p-*phenetyl*-p-*benzoquinone*, prepared in a similar manner, forms a stable yellow variety, m. p. 186—187°, and a labile red form obtained by slow crystallisation from ethyl acetate, acetone, or benzene. Above 150°, the red passes into the yellow variety. Crystallographic investigation proves physical dimorphism. Solutions of the two forms appear identical or become so with immeasurable rapidity. Differences in solubility are not observable; Beer's law is obeyed. The mol. wt. in a series of solvents is normal. Differences appear confined to the solid state. Chemical differences are, however, established, since the finely-powdered, yellow variety is reduced by phenylhydrazine in acetic acid at the ordinary temperature to the quinhydrone and ultimately to diphenetylquinol, whereas the red form remains unchanged. With phenol, the yellow variety yields a red phenoquinone obtained also from the red form, but related to the former, since it is reduced by phenylhydrazine and loses phenol in a high vacuum at 110°, leaving the yellow compound. H. WREN.

Diarylquinones. III. Condensation of quinones with phenols. R. PUMMERER and G. HUPPMANN (Ber., 1927, **60**, [*B*], 1442—1451).—Contrary to the views of Friedländer and Blumenfeld, condensation between phenols and quinones, when irreversible, invariably occurs in such a manner that the nucleus of the phenol becomes attached to the quinone nucleus; entry of the phenoxy-group has not been observed. Resorcinol and *p*-benzoquinone, heated at 250°/vac., afford 2 : 5 : 2′ : 4′-*tetrahydroxydiphenyl*, m. p. 131° (Friedländer's 2 : 5 : 3′-trihydroxydiphenyl ether), the constitution of which is established by the isolation of a *tetra-acetate*, m. p. 120°, and by oxidation through the *quinhydrone* to 2-2′ : 4′-*dihydroxyphenyl*-p-*benzoquinone*, decomp. 280°, which contains two hydroxyl groups. In presence of 10% sulphuric acid, resorcinol and *p*-benzoquinone very readily yield *diresorcylquinhydrone*, oxidised by *p*-benzoquinone in boiling water to *diresorcylquinone* (2 : 5-*di*-2′ : 4′-*dihydroxyphenyl*-p-*benzoquinone*), m. p. 345°. Reduction of the quinone with stannous chloride in glacial acetic acid gives the corresponding *quinol*, m. p. 193—195° (decomp.). *p*-Benzoquinone and pyrogallol, under the influence of aluminium chloride in carbon disulphide, give the expected quinhydrone, converted by reductive acetylation into 2 : 5-*di*-3′ : 4′ : 5′-*trihydroxyphenylquinol octa-acetate*, m. p. 158°. α-Naphthaquinone and resorcinol are converted by dilute sulphuric acid in glacial acetic acid into 2-2′ : 4′-*dihydroxyphenyl*-α-*naphthaquinol*, m. p. 167°, which gives a tetra-acetyl compound and is oxidised by ferric chloride to 2-2′ : 4′-*dihydroxyphenyl*-α-*naphthaquinone*, m. p. 218°, in which the presence of two hydroxyl groups is established. Similarly, 2-3′ : 4′ : 5′-*trihydroxyphenyl*-α-*naphthaquinol*, m. p. 245° (Friedländer's dihydroxyphenyl dihydroxynaphthyl ether), is obtained from pyrogallol and α-naphthaquinone; the constitution follows from the production of a *penta-acetate*, m. p. 167°, and of 2-3′ : 4′ : 5′-*trihydroxyphenyl*-α-*naphthaquinone*, m. p. 270°, yielding a *triacetate*, m. p. 194 (decomp.); α-naphthaquinone and α-naphthol afford

2-4′-*hydroxynaphthyl*-α-*naphthaquinol*, m. p. 243° (decomp.) [*triacetate*, m. p. 336° (decomp.)], oxidised by *p*-benzoquinone to 2-4′-*hydroxynaphthyl*-α-*naphthaquinone*, m. p. 175° (decomp.), in which the presence of one hydroxyl group is established by the isolation of a *monoacetate*, m. p. 221°. H. WREN.

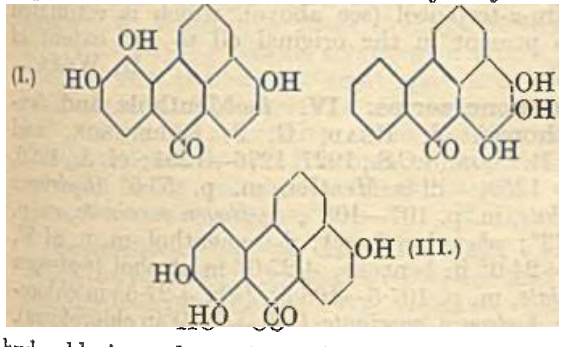
Anthraquinonesulphonic acids. H. E. FIERZ-DAVID (Helv. Chim. Acta, 1927, **10**, 429; cf. this vol., 463).—Priority against Coppens (cf. Wibaut, this vol., 566) is claimed. C. HOLLINS.

Manufacture of anthraquinone derivatives [meso-*pp*′-diaminodiarylanthracenes and 9 : 9-bis-*p*-aminoarylanthrones]. I. G. FARBENIND. A.-G.—See B., 1927, 518.

Reduction products of the hydroxyanthraquinones. VIII. E. J. CROSS and A. G. PERKIN (J.C.S., 1927, 1297—1306).—The positions of the hydroxyl groups in the anthranols derived from anthragallol and anthra- and flavo-purpurins are investigated by the benzanthrone process (Miller and Perkin, A., 1926, 174), and it is shown that they are oriented in the 3 : 4 : 6-, 1 : 2 : 3-, and 1 : 2 : 6-positions, respectively.

Anthrapurpurin-anthranol, when heated with glycerol and sulphuric acid at 125—130° for 1 hr., followed by treatment of the product with acetic anhydride and pyridine, yields *triacetylbenzanthrapurpurin*, m. p. 245—246°. This on treatment with cold sulphuric acid gives *benzanthrapurpurin sulphate*, which in turn yields benzanthrapurpurin (I), unmelted at 340° (*benzanthrapurpurin trimethyl ether*, m. p. 185—185·5°).

Anthragallol-anthranol when heated with potassium hydrogen sulphate and glycerol, followed by acetylation of the product, gives *diacetyl*iso*benzanthragallol*, m. p. 232—233°. The latter when hydrolysed with



hydrochloric and acetic acids yields iso*benzanthragallol*, m. p. 319—321° (II), converted by ethereal diazomethane into iso*benzanthragallol dimethyl ether*, m. p. 152—153°. The methylation cannot be effected by the use of methyl iodide or by methyl sulphate. Attempts to acetylate the dimethyl ether or to prepare the trimethyl ether were unsuccessful.

Diacetylflavopurpurin-anthranol, m. p. 209—212°, obtained by the reduction of flavopurpurin with stannous chloride, yields *tetra-acetylflavopurpurinanthranol*, m. p. 181—182°, on further acetylation, and *flavopurpurin-anthranol*, m. p. 231—233° (heated slowly); on hydrolysis. When heated suddenly at 230°, the latter melts at 243—245° (cf. Graebe and Thole, A., 1906, i, 863). Attempts to prepare the benzanthrone derivative by the methods already indicated were unsuccessful, but on treatment with a solution of acraldehyde in acetic acid containing hydrogen chloride, it yielded finally *diacetyl*iso*benzflavopurpurin*, m. p. 236°. iso*Benzflavopurpurin*, m. p. 293—295°, yields on methylation with methyl iodide the *dimethyl ether*, m. p. 199—200°.

G. A. C. GOUGH.

Reduction products of the hydroxyanthraquinones. IX. A. MACMASTER and A. G. PERKIN (J.C.S., 1927, 1306—1309).—3 : 4 : 6 : 9-*Tetramethoxyanthranol*, m. p. 107°, is obtained by acetylating 3 : 4 : 6-trihydroxyanthranol and methylating the product in absence of air. When oxidised with an acetic acid solution of chromic acid, it yields anthrapurpurin trimethyl ether, m. p. 198° (Graebe and Bernhard, A., 1906, i, 865, give 201°), which on reduction with aluminium–mercury couple in ammonia gives 1 : 2 : 7-*trimethoxyanthracene*, m. p. 95°. 3 : 4 : 6-*Trimethoxyanthranol*, m. p. 149°, is obtained by reduction of anthrapurpurin trimethyl ether with stannous chloride. 9-*Acetyl*-3 : 4 : 6-*trimethoxyanthranol*, m. p. 127°, is obtained in the usual way. 3 : 4 : 6 : 3′ : 4′ : 6′-*Hexamethoxydianthrone*, m. p. 224°, is obtained by oxidation of 3 : 4 : 6-trimethoxyanthranol with an acetic acid solution of ferric chloride. G. A. C. GOUGH.

Phenanthrene series. XXXVI. 2 : 7-Dibromophenanthraquinone and its derivatives. J. SCHMIDT and H. BURKERT (Ber., 1927, **60**, [*B*], 1356—1362; cf. Schmidt and Junghaus, A., 1904, i, 1034).—Phenanthraquinone is converted by phenylhydrazine-*p*-sulphonic acid in boiling, aqueous acid suspension into 9-hydroxyphenanthrene-10-azobenzenesulphonic acid, which, when treated with an excess of bromine in sunlight, affords 2 : 7-dibromophenanthraquinone, m. p. 322—323°, in good yield, a dibromide of the bromo-derivative being probably formed intermediately. When a greater excess of bromine is employed, (?)2 : 4 : 5 : 7-*tetrabromophenanthraquinone*, m. p. 285—287° (characterised by conversion into 2 : 4 : 5 : 7-*tetrabromophenanthraphenazine*, m. p. 262°), appears to be formed. The 2 : 7-dibromo-compound is converted by phenylhydrazine into 2 : 7-*dibromo*-9-*hydroxyphenanthrene*-10-*azobenzene*, m. p. 272—273°, the mother-liquors from which contain 2 : 7-dibromophenanthraquinol, isolated as the *diacetate*, m. p. 242—244°. 2 : 7-*Dibromophenanthraquinonemonosemicarbazone*, m. p. about 300°, is described. Successive treatment of 2 : 7-dibromophenanthraquinone with semicarbazide hydrochloride and hydrochloric acid gives 6 : 11-*dibromo* 3-*hydroxyphenantriazine*, m. p. 295°. Aminoguanidine and 2 : 7-dibromophenanthraquinone yield 6 : 11-*dibromo*-3-*aminophenantriazine hydrochloride*, m. p. 238° (cf. Schmidt, Schairer, and Glatz, A., 1911, i, 239), from which ammonia liberates the *base* which is isolated in the labile, red imino-form, $C_6H_3Br{<}\begin{matrix}C{:}N\\C{:}NH\end{matrix}{>}C_6H_3Br$, and the stable, yellow variety, m. p. 333°, $C_6H_3Br{<}\begin{matrix}C.N{:}C\,NH_2\\C{:}N\end{matrix}{>}C_6H_3Br$. following derivatives are regarded as derived from the amino-form: *perchlorate*, m. p. 258° (decomp.); *picrate*, m. p. 293°;

acetyl derivative, m. p. 309°; *benzoyl* derivative, m. p. 240° (decomp.). Phosphorus pentachloride converts 2 : 7-dibromophenanthraquinone suspended in boiling benzene into 9 : 9-*dichloro*-2 : 7-*dibromophenanthrene*, m. p. 229°, which is reduced by phenylhydrazine to 9-*chloro*-2 : 7-*dibromo*-10-*hydroxyphenanthrene*, m. p. 226° (*benzoyl* derivative, m. p. 193°). H. WREN.

Constitution of the bile acids. XI. Ciloxanic acid. W. BORSCHE and R. FRANK (Ber., 1927, 60, [*B*], 1216—1220).—*Ciloxanic acid*, m. p. 216—217°, $[\alpha]_D^1$ +142·5° in alcohol, is obtained by the oxidation of cilianic acid by potassium permanganate in acid solution, and is conveniently isolated as the *dioxime*, $C_{22}H_{34}O_6N_2$, m. p. 239—240°; the *methyl* ester, m. p. 105°, and its *dioxime*, m. p. 241—242° (decomp.), and, apparently, *ethyl hydrogen ciloxanate dioxime*, m. p. 221—222° (decomp.), are described. The production of ciloxanic acid by the action of concentrated sulphuric acid on cilianic acid is established (cf. this vol., 459). Oxidation of ciloxanic acid by nitric acid (*d* 1·4) affords biloidanic acid, m. p. 229—230° (decomp.), whereas reduction with amalgamated zinc and hydrochloric acid gives *deoxyciloxanic acid*, m. p. 187—188° (*methyl* ester, m. p. 85—87°). H. WREN.

Paprika dyes. II. L. ZECHMEISTER and L. VON CHOLNOKY (Annalen, 1927, 455, 70—81).—Carotin (0·5—0·6 g.), identical in all respects with that obtained from leaves, is isolated from the light-petroleum extract of the dried fruit rind of *Capsicum annuum* (1 kg.) after removal of the capsanthin (4·0 g.) by means of alkali (this vol., 669). The amounts of the two colouring matters isolated represent, respectively, 50% and 54% of the total quantity determined colorimetrically. In agreement with the results of Kylin (this vol., 669), no lycopin or xanthophyll could be detected. J. W. BAKER.

Lupeol. H. D. NOJD (Arch. Pharm., 1927, 265, 381—389).—Two empirical formulæ, viz., Cohen's $C_{31}H_{50}O$ (A., 1907, i, 211) and Vesterberg's $C_{30}H_{50}O$ (A., 1922, i, 825), have been attributed to lupeol. The following investigation of lupeol, isolated from East Indian "bresk" in the way described by Cohen, and separated from amyrin by fractional precipitation of the benzoates from benzene by addition of acetone, has proved that Vesterberg's formula is correct. The physical properties of the lupeol obtained, and those of its acetate and benzoate, agreed with the description given by Cohen. The formate is not homogeneous, but consists of a mixture of α-*allolupeol formate*, m. p. 229°, $[\alpha]_D^{15}$ +50·01° (in chloroform), insoluble in alcohol and forming about 60% of the whole, and β-*allolupeol formate*, m. p. 180—183°, $[\alpha]_D^{15}$ +48·8°, soluble in alcohol. α-*Allolupeol*, $C_{30}H_{49}\cdot OH$, has m. p. 191°, $[\alpha]^{15}$ +28·79°; the *acetate*, m. p. 199°, $[\alpha]^{15}$ +45·46°, and *benzoate*, m. p. 256°, $[\alpha]_D^{15}$ +42·82°, are also described. β-*Allolupeol*, m. p. 151°, $[\alpha]_D^{15}$ +48·08°, similarly yields an *acetate*, m. p. 196°, $[\alpha]_D$ +28·57°, and a *benzoate*, m. p. 228°. Lupeol, having the composition $C_{30}H_{50}O$, is thus isomeric with amyrin. It does not suffer dehydration when heated at 220°, but when it is treated with phosphorus pentachloride in light petroleum it is converted into a *hydrocarbon*, $C_{30}H_{48}$, m. p. 173—174°, b. p. 287°/10 mm., $[\alpha]_D^{15}$ +27·5°, to which the name *lupeylene*, already given by Jungfleisch and Leroux (A., 1906, i, 525, 783) to a similar compound, has been applied. In suffering dehydration when treated with phosphorus pentachloride, lupeol resembles amyrin (cf. Vesterberg and Nojd, A., 1926, 619). Attempts to dehydrogenate lupeol by heating it with sulphur and to break it down by oxidation gave unsatisfactory results. W. A. SILVESTER.

The two stereoisomeric dihydro-α-terpineols; occurrence of the *trans*-variety in American pine oil. O. ZEITSCHEL and H. SCHMIDT (Ber., 1927, 60, [*B*], 1372—1377).—α-Terpineol, m. p. 35°, d^{15} 0·939, α^{100} +8·90°, is hydrogenated at the atmospheric pressure in presence of a nickel catalyst, and the product, after removal of unsaturated compounds and not inconsiderable amounts of hydrocarbons, is fractionally distilled under diminished pressure, whereby trans-*dihydro-α-terpineol*, m. p. 35°, s. p. 34·7°, b. p. 209—209·5°/750 mm., *d* 0·901, n_D^{20} 1·46310, $[\alpha]_D$ ±0°, is obtained (phenylurethane, m. p. 117—118°). The liquid portions of the distillates are transformed into the corresponding phenylurethanes, m. p. 117—118° and 90—92°, respectively, the latter of which when hydrolysed affords cis-*dihydro-α-terpineol*, b. p. 210—210·5°/750 mm., d_{15}^{15} 0·9164, d_4^{20} 0·9124, n_D^{20} 1·46550, $[\alpha]_D$ ±0°.

The fraction of b. p. 205—220° obtained as by-product of the preparation of terpineol from American pine oil, is treated with boric acid, and the difficultly volatile borates are separated from the indifferent components by distillation. Hydrolysis of the esters followed by fractional treatment of the recovered alcohols by boric acid permits the separation of borneol and fenchyl alcohol, leaving terpineol and dihydroterpineol. Oxidation of the mixed tertiary alcohols with permanganate destroys the terpineol, thus permitting the isolation of homogeneous *trans*-dihydro-α-terpineol (see above), which is estimated to be present in the original oil to the extent of 3—5%. H. WREN.

Menthone series. IV. *iso*Menthols and *iso*menthones. J. READ, G. J. ROBERTSON, and A. M. R. COOK (J.C.S., 1927, 1276—1284; cf. A., 1926, 1147, 1250).—dl-iso*Menthol*, m. p. 53·5° (*hydrogen phthalate*, m. p. 107—108°; *hydrogen succinate*, m. p. 72—73°; *phenylurethane*); d-*iso*menthol, m. p. 81·5°, $[\alpha]_D$ +24·0° in benzene, +27·0° in alcohol (*hydrogen phthalate*, m. p. 107·5—108·5°, $[\alpha]_D^{15}$ +27·5° in chloroform; *hydrogen succinate*, $[\alpha]^{15}$ +22·5° in chloroform), and *l-iso*menthol, m. p. 80·5°, $[\alpha]^{15}$ −24·1° in alcohol, have been prepared by the action of nitrous acid on *dl*-, *d*-, and *l-iso*menthylamine, respectively. An equimolecular mixture of *d*- and *l-iso*menthol forms a conglomerate. Both *dl*-menthol and *dl-iso*menthol are produced in the reduction of *dl*-piperitone with sodium and alcohol. Pure *d-iso*menthone, prepared by chromic acid oxidation of *d-iso*menthol, has $[\alpha]_D^{15}$ +91·7°, n_D^{16} 1·4545 [*oxime*, viscid oil, n_D^{14} 1·4865, $[\alpha]_D$ +46·0° in alcohol (p-*nitrobenzoyl* derivative)], and is best characterised by conversion into the *oxime hydrochloride*, m. p. 132°, $[\alpha]^{15}$ +38·6° in chloroform. The following are described: dl-iso*menthone-oxime hydrochloride*, m. p. 127—128° (decomp.), dl-*menthoneoxime hydrochloride*, m. p. 94°; l-*menthone-*

oxime hydrochloride, m. p. 118—119°, $[\alpha]_D^{15}$ −89·1° in chloroform; p-*nitrobenzoyl*-l-*menthoneoxime*, m. p. 102·5°; *salicylidene*-derivative of the hitherto unknown l-neoiso*menthylamine*, m. p. 99—100°, $[\alpha]_D$ −17·9° in chloroform. The claim of Bedos (A., 1926, 729) to have demonstrated the existence of the four racemic menthols and the two corresponding racemic menthones through a study of the interaction of magnesium *iso*propyl bromide and the two isomeric 2-chloro-5-methyl*cyclo*hexanols is criticised adversely. M. CLARK.

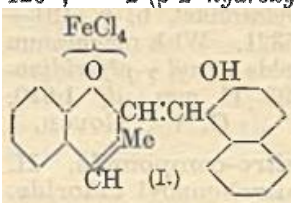
Recovery of pinene from its nitrosochloride. J. C. EARL and J. KENNER (J.C.S., 1927, 1269—1276).—Regeneration of a hydrocarbon from its nitrosochloride by treatment with aniline, hitherto observed only in the case of pinene, is shown to occur under similar conditions, although less readily, with the derivatives of tetramethylethylene and γ-terpinyl acetate. The reaction in the case of pinene nitrosochloride is due to the hydrogen chloride which this compound liberates with remarkable ease. Suppression of hydrogen chloride by the presence of sodium acetate or pyridine leads to the formation of *pinene nitrolanilide*, m. p. 122°, provided that these reagents are employed in a homogeneous solution. Reaction in chloroform solution in presence of either anhydrous sodium acetate or crystalline lead acetate leads to the formation of diazoaminobenzene. In explanation of these results, it is suggested that pinene nitrosochloride may undergo isomeric change under the influence of hydrogen chloride, yielding a product formally analogous with the nitrosochlorides of tetramethylethylene and γ-terpinyl acetate. M. CLARK.

Camphor series. XI. Synthesis of camphor. II. Preparation of liquid and solid camphenes from pinene hydrochloride by the catalytic elimination of hydrogen chloride with copper oxide. B. MASUMOTO (Mem. Coll. Sci. Kyoto, 1927, 10, 175—181).—Alcoholic solutions of pinene hydrochloride were passed over eight specimens of copper oxide (details of preparations and densities given) at 220°, with uniform velocity. The resulting products were fractionated, and fractions of b. p. 150—165° assumed to be camphene. These fractions do not possess the same physical data. H. BURTON.

Stereochemistry of dicyclic ring systems. III. [Correction.] Strain in camphor and *trans*-hexahydrohydrindene. W. HUCKEL (Annalen, 1927, 455, 123—126).—The comparison made by Hückel and Friedrich (this vol., 238) between *trans*-hexahydrohydrindene and camphor is invalid, since the angle subtended by the bridge in the camphor model was erroneously given as 43° instead of 71° 12′. A redetermination of the heat of combustion of *trans*-β-hexahydrohydrindone by Roth gives a value only ~ kg.-cal./mol. less than that of the *cis*-form, a difference comparable with that between *trans*- and *cis*-decalone. These facts are therefore in agreement with Baeyer's strain theory. J. W. BAKER.

Isomerisation of hydrocarbons by phenols. S. KONDAKOV.—See B., 1927, 504.

Pyrylium salts and *spiro*dipyrans. I. Condensation products from *o*-hydroxyaldehydes and α-alkylated β-ketonic esters. S. C. DE (J. Indian Chem. Soc., 1927, **4**, 23—28).—When dry hydrogen chloride was passed into an ethereal solution of salicylaldehyde and ethyl α-methylacetoacetate, 2-(o-*hydroxystyryl*)-3-*methylbenzopyrylium chloride*, m. p. 200°, was formed, and from this the corresponding *ferrichloride*, m. p. 180°, and *perchlorate*, m. p. 240°, were obtained. Decomposition of the above ferric salt by ammonia solution in presence of sodium acetate yielded 3-*methyl*spiro*dibenzopyran*, m. p. 80°. Similarly were obtained: 3-*benzyl*-2-(o-*hydroxystyryl*)*benzopyrylium chloride*, m. p. 129° (corresponding *ferrichloride*, m. p. 194°, and *perchlorate*, m. p. 234°); 3-*benzyl*spiro*dibenzopyran*, m. p. 120°; 2-(β-2′-*hydroxy*-1′-*naphthylethenyl*)-3-*methyl*-



β-*naphthapyrylium ferrichloride* (I) (corresponding *perchlorate*, m. p. >308°); 3-*methyl*spiro-2:2′-*di*-(o:6-β-*naphthyl*-1:2-*pyran*), m. p. 200°; 3-*benzyl*-2-(β-2′-*hydroxy*-1′-*naphthylethenyl*)-β-*naphthapyrylium ferrichloride* (corresponding *perchlorate*, m. p. 204°); 3-*benzyl*spiro-2:2′-*di*-(o:6-β-*naphtha*-1:2-*pyran*), m. p. 205°, and 2-*phenyl*-3-*methylbenzopyrylium perchlorate*, m. p. 179°. The colourless *spiro*dipyrans were converted by strong acids into the deeply-coloured benzopyrylium salts. B. W. ANDERSON.

Constitution of erythrosin and related dyes. W. C. HOLMES and J. T. SCANLAN (J. Amer. Chem. Soc., 1927, **49**, 1594—1598).—The *monosodium* salt of erythrosin contains 1 mol. of water of constitution, similarly to the disodium salt (cf. Wales and Nelson, A., 1923, i, 936). Spectrophotometric investigation of the salt formation of erythrosin, together with the above result, are regarded as supporting the hemiquinonoid structure of the dye suggested by Gomberg and Tabern (A., 1923, i, 112), and an analogous structure is indicated generally for the halogen derivatives of fluorescein. F. G. WILLSON.

Absorption spectra of *o*-cresolbenzein. W. R. ORNDORFF and (MISS) S. A. MCNULTY (J. Amer. Chem. Soc., 1927, **49**, 1588—1593).—A study of absorption spectra indicates that *o*-cresolbenzein exists in absolute alcoholic solution as an equilibrium mixture of the quinonoid hydrate and carbinol forms. Addition of hydrogen chloride completely changes the absorption spectrum, probably owing to the formation of the hydrochloride (this vol., 557). Addition of alkali produces a similar change, the similarity being due to the formation, in both cases, of the quinonoid hydrate, which then combines with the acid or the base. In aqueous 33% potassium hydroxide, *o*-cresolbenzein is present as the dipotassium salt of the carbinol form, the resemblance of the absorption curve for this solution to that of the absolute alcoholic solution supporting the view that some carbinol is present in the latter solution. In 93% sulphuric acid solution, *o*-cresolbenzein is present as the sulphate. F. G. WILLSON.

Action of organo-magnesium compounds on nitriles. γ-Aminonitriles. F. PETIT (Bull. Acad. roy. Belg., 1926, [v], **12**, 775—784; cf. A., 1926,

826, 1044).—γ-Piperidinobutyronitrile, b. p. 110—112°/11 mm., d_4^{20} 0·931, n_D^{20} 1·4672, reacts abnormally with magnesium methyl and ethyl bromides to give, in each case, a dimeride of the nitrile as the principal product, *αη-dipiperidino-δ-imino-ε-cyanoheptane*, m. p. 75—76°, b. p. 265°/12 mm. On hydrolysis with alcoholic picric acid, the latter yields *αη-dipiperidino-ε-cyanoheptan-δ-one dipicrate*, m. p. 205—206°, and with concentrated hydrochloric acid, *αη-dipiperidinoheptan-δ-one*, b. p. 203—204°/13 mm., d_4^{20} 0·9555, n_D^{20} 1·4904.

The nitrile reacts normally with magnesium phenyl bromide (2 mols.) to yield *phenyl γ-piperidinopropyl ketone*, b. p. 185—187°/12 mm., d_4^{20} 1·0238, n_D^{20} 1·5345 (*semicarbazone*, m. p. 164°), which, on reduction, gives *phenyl-γ-piperidinopropylcarbinol*, b. p. 194—195°/12 mm., d_4^{20} 1·017, n_D^{20} 1·5321. With magnesium benzyl chloride, the nitrile yields *benzyl γ-piperidinopropyl ketone*, b. p. 191—193°/11 mm., d_4^{20} 1·010, n_D^{20} 1·5247. G. A. C. Gough.

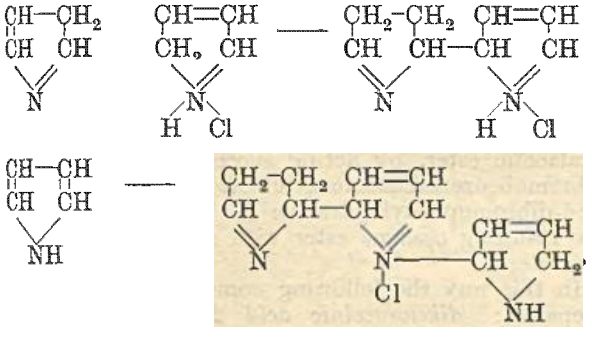
Diazomethane and *o*-nitro-compounds. II. *N*-Hydroxyisatin from *o*-nitrobenzoyl chloride. F. Arndt, B. Eistert, and W. Partale (Ber., 1927, **60**, [*B*], 1364—1370; cf. this vol., 360).—*o*-Nitrobenzoyl chloride is converted by diazomethane in ethereal solution in absence of light into *o-nitro-ω-diazoacetophenone*, $NO_2 \cdot C_6H_4 \cdot CO \cdot CH{:}N{:}N$, m. p. 105—106°, with small amounts of *ω-chloro-o-nitroacetophenone* (*o-nitrophenacyl chloride*), m. p. 66—67°. The diazo-compound is very sensitive towards acids and is converted by concentrated formic acid in presence of glacial acetic acid into *N-hydroxyisatin*, m. p. 200—201° (decomp.) (cf. Alessandri, this vol., 572), characterised by its conversion into *N*-acetoxyisatin, m. p. 151—152°, and *N*-hydroxyisatinphenylhydrazone, m. p. 219—220°; with ethereal diazomethane, it does not appear to yield the corresponding methyl ether. It dissolves in sodium carbonate solution, is converted ultimately by sodium hydroxide into anthroxanic acid and by ammonia into anthroxanamide, m. p. 213°. *o*-Nitro-ω-diazoacetophenone is converted by concentrated hydrochloric acid in presence of glacial acetic acid into ω-chloro-*o*-nitroacetophenone, also prepared by chlorination of *o*-nitroacetophenone; it does not give the customary ketonic reactions with semicarbazide or *p*-nitrophenylhydrazine, although these are shown by *o*-nitro- and ω-chloro-acetophenone. *ω-Bromo-o-nitroacetophenone* (*o-nitrophenacyl bromide*), m. p. 55—56°, is similarly prepared. Treatment of *o*-nitro-ω-diazoacetophenone with iodine in boiling chloroform affords *ωω-di-iodo-o-nitroacetophenone*, m. p. 136—138° (decomp.), reduced by ammonium sulphide to indigotin. Hydrogen cyanide is evolved when *o*-nitro-ω-diazoacetophenone is boiled with 2*N*-sodium hydroxide. H. Wren.

Formation of heterocyclic compounds. II. H. K. Sen and U. Bose (J. Indian Chem. Soc., 1927, **4**, 51–63; cf. Sen-Gupta, J.C.S., 1915, **107**, 1347).—Moir (J.C.S., 1902, **81**, 100) gave an explanation of the mechanism of the reaction between cyanoacetamide and acetylacetone which, in the authors' opinion, is incorrect, as there is evidence that in β-diketones the ketonic group reacts through first setting up an ethylenic linking by enolisation, the ethylenic linking being more reactive than the carbonyl. Thus a negative result was obtained in attempting to condense 2-acetyl-2-methyl*cyclo*hexanone with cyanoacetamide in presence of piperidine, whereas condensation of cyanoacetamide with 2-acetyl*cyclo*hexanone proceeds readily, with formation of crystals (decomp. about 290°)—presumably a mixture of quinoline and *iso*quinoline derivatives, as from the condensation product two isomeric *methyl ethers*, m. p. 179—180° and 158°, were obtained. 2-Acetyl*cyclo*hexanone and methylcyanoacetamide condensed to give the same mixture. By using ethyl *cyclo*hexanonecarboxylate for condensation with cyanoacetamide, the enolising carbon atom was fixed, and the product was not a mixture, but 1 : 3 : 10-*trihydroxy-4-cyanohexahydro*isoquinoline (?), m. p. 278—280° (decomp.). Cyanoacetamide was also condensed with 2-acetyl-6-methyl*cyclo*hexanone, giving a *substance*, $C_{12}H_{14}ON_2$, m. p. 275° (decomp.) (hydrolysed *product*, $C_{11}H_{15}ON$, from this, m. p. 242—243°), with 2-acetyl-5-methyl*cyclo*hexanone, giving a *substance*, $C_{12}H_{14}ON_2$, m. p. >280° (hydrolysed *product*, $C_{11}H_{15}ON$, m. p. 200—201°), and with 2-acetyl-4-methyl*cyclo*hexanone to form a *substance*, $C_{12}H_{14}ON_2$, darkens above 270° (hydrolysed *product*, m. p. 230—232°). B. W. Anderson.

Substitution in hexahydrocarbazole derivatives. J. Gurney and S. G. P. Plant (J.C.S., 1927, 1314—1322).—Hexahydrocarbazole and 9-methylhexahydrocarbazole, m. p. 50° (cf. A., 1923, i, 142), on nitration in concentrated sulphuric acid, give *5-nitrohexahydrocarbazole*, m. p. 69°, and *5-nitro-9-methylhexahydrocarbazole*, m. p. 52°, respectively. 9-Acetylhexahydrocarbazole, when acted on by nitric acid in glacial acetic acid solution, is partly nitrated to give *6-nitro-9-acetylhexahydrocarbazole*, m. p. 150°, and partly oxidised to give 9-acetyltetrahydrocarbazole, which is then converted into a mixture of 5-nitro-9-acetyltetrahydrocarbazole and 9-acetyl-10 : 11-dihydroxyhexahydrocarbazole. 9-Benzoylhexahydrocarbazole also undergoes oxidation to 9-benzoyltetrahydrocarbazole, which then gives 11-nitro-9-benzoyl-10-hydroxyhexahydrocarbazole. In concentrated sulphuric acid, both 9-acetyl- and 9-benzoyl-hexahydrocarbazole can be nitrated to give the 6-nitro-derivative. *6-Nitro-9-benzoylhexahydrocarbazole* has m. p. 106—107°. The structures of these derivatives have been established with reference to the structures assigned to the four isomeric mononitrotetrahydrocarbazoles (J.C.S., 1921, **119**, 1825; 1923, **123**, 676). Bromination of hexahydrocarbazole and its 9-acetyl and 9-benzoyl derivatives leads in every case to the 6-bromo-compound. The following are described: *6-nitro-9-acetylhexahydrocarbazole*, m. p. 142°; *5-aminohexahydrocarbazole*, m. p. 111°; *5-acetamido-9-acetylhexahydrocarbazole*, m. p. 163°; *6-nitrohexahydrocarbazole*, m. p. 84° (*hydrochloride*, m. p. 199°); *6-aminohexahydrocarbazole*; *6-acetamido-9-acetylhexahydrocarbazole*, m. p. 213°; *7-aminohexahydrocarbazole*; *7-acetamido-9-acetylhexahydrocarbazole*, m. p. 233°; *6-bromohexahydrocarbazole*, m. p. 75°; *6-bromo-9-acetylhexahydrocarbazole*, m. p. 104°; *6-bromo-9-benzoylhexahydrocarbazole*, m. p. 125°.

The compound described by von Braun and Ritter (A., 1923, i, 142) as 7-nitro-9-ethylhexahydrocarbazole is shown to be 5-nitro-9-ethylhexahydrocarbazole. M. CLARK.

Polymerisation of pyrrole. B. V. TRONOV and P. P. POPOV (J. Russ. Phys. Chem. Soc., 1926, **58**, 745—758).—The action of acids on pyrrole and its derivatives and the properties and possible structures of the resulting polymerides are discussed, with the conclusion that all earlier hypotheses are unsatisfactory. Analysis of the product of reaction of tripyrrole hydrochloride and aqueous alkali shows it to contain oxygen and so to be probably not the free amine, but the ammonium hydroxide, *i.e.*, the halogen atom is joined to a quaternary nitrogen. The various dynamic tautomeric forms of pyrrole are discussed, and possible intermolecular reactions suggested, resulting in the formation of tripyrrole.

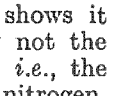


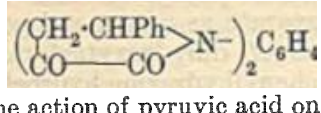
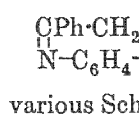
This and similar formulæ explain why only 2 mols. of pyrrole can be obtained on decomposing tripyrrole and why oxidation gives succinic acid.

The mechanism of the breaking down of the pyrrole ring and the formation of pyrrole-red and ammonia by the hydrolysis in neutral or faintly alkaline solutions of tripyrrole, is assumed to be the same as the breaking of the ring in quaternary cyclic ammonium hydroxides, by the migration of the hydroxyl to the α-carbon atom with the formation of an aldehyde and the ultimate elimination of a molecule of ammonia. The free tripyrrole, on long keeping, undergoes some transformation, as it did not give pyrrole-red so readily as before, probably due to the transformation of the quaternary ammonium hydroxide into an amine-oxide-like structure. M. ZVEGINTZOV.

Iodising pyridine derivatives. DEUTSCHE GOLD- U SILBERSCHEIDEANSTALT VORM. ROESSLER.—See B., 1927, 507.

Production of 5-iodo-2-aminopyridine. C. RATH.—See B., 1927, 507.

Dobner's quinoline synthesis and its by-products. S. BODFORSS (Annalen, 1927, **455**, 41—69).—The condensation of benzaldehyde, amines, and pyruvic acid and of cinnamoylformic acid with various aromatic amino-compounds has been studied in order to elucidate the mechanism of formation of quinoline derivatives, pyrrolidine, and other products obtained in the Dobner synthesis. Pyruvanilide condenses with benzaldehyde in alcohol, in presence of aniline, to yield *benzylidenepyruvanilide*, CHPh:CH·CO·CO·NHPh, m. p. 153°. Cinnamoylformic acid reacts with aniline in cold alcohol to yield only 4 : 5-diketo-1 : 2-diphenylpyrrolidine (I) (Schiff and Bertini, A., 1897, 293), but in presence of pyridine it yields a mixture of (I) and the *anil* of cinnamoylformic acid, CHPh:CH·C(:NPh)·CO_2H (II), the latter being readily converted into the former by heating in alcohol. Pyruvic acid and benzaldehyde in ether in presence of aniline give (I), together with its anil, 5-keto-1 : 2-diphenylpyrrolidine-4-anil (III) (*nitro*-derivative, m. p. 143°). The mechanism of formation of these compounds is represented in accordance with the scheme: (II) ⟶ CHPh  C·CO_2H (I) or  (III), fission of the 1 : 2 linking preceding intramolecular change. The formation of (II) is assumed to occur by the interaction of benzylideneaniline with the enol form of pyruvic acid, a four-membered heterocyclic ring being formed intermediately, in accordance with the scheme: CHPh:NPh + CH_2:C(OH)·CO_2H ⟶ CHPh<$^{CH_2}_{NPh}$>C(OH)·CO_2H $\xrightarrow{-H_2O}$ (II). Similarly, by the interaction of cinnamoylformic acid with the appropriate amino-compound are obtained the β-*naphthylimide*, m. p. 138° (decomp.), p-*hydroxyanil*, m. p. 188° (decomp.) (which when heated with aniline yields I); p-*methoxyanil*, m. p. 114° (decomp.), and the p-*tolylimide*, m. p. 139° (decomp.) (which when heated with *p*-aminophenol yields the *p*-hydroxyanil) of cinnamoylformic acid. With *p*-phenylenediamine, it yields a mixture of the *substances* [CHPh:CH·C(CO_2H):N]$_2C_6H_4$ and CHPh:CH·C(CO_2H):N·C_6H_4·NH_2, m. p. 173° (decomp.), the latter being separated from the mixture by means of its slight solubility in acetone. Similarly, with *m*-phenylenediamine is obtained an isomeride of the first compound, and this is identical with the compound, $C_{26}H_{16}O_4N_2$, obtained by Dobner and Ferber (A., 1895, i, 72) by the action of benzaldehyde and pyruvic acid on *m*-phenylenediamine, to which a cyclic structure was erroneously ascribed. When warmed with an alcoholic solution of phenylhydrazine, it is converted into cinnamoylformic acid phenylhydrazone, m. p. 167° (Erlenmeyer, A., 1903, i, 698, gives 158°), which is oxidised by mercuric oxide to a *compound*, decomp. 190°, which is probably a tetrazone. With anthranilic and *p*-aminobenzoic acids, cinnamoylformic acid yields, respectively, 4 : 5-*diketo*-2-*phenyl*-1-*o*-*carboxyphenyl*-, m. p. 192° (decomp.), and -1-*p*-*carboxyphenyl*-*pyrrolidine*, m. p. 205°. When heated with alcohol or acetic acid, the various substituted cinnamoylformic acid anils are converted into pyrrolidine derivatives, and thus are obtained the following 4 : 5-diketo-1-aryl-2-phenylpyrrolidines: β-*naphthyl*-, m. p. 150°; p-*tolyl*-, m. p. 143°; p-*methoxyphenyl*-, m. p. 118° (decomp.), and 1 : 1′-*p*-*phenylene*-*bis*-4 : 5-*diketo*-2-*phenylpyrrolidine* (IV), m. p. 193°.

(IV.)  (V 

The action of pyruvic acid on various Schiff's bases has been investigated. With benzylideneaniline, (I)

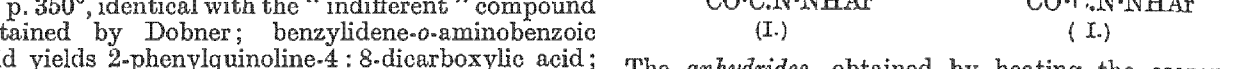
is obtained; benzylidene-β-naphthylamine yields 2-phenyl-β-naphthaquinolinecarboxylic acid; benzylidene-*p*-aminobenzoic acid yields *p*-[5-keto-2-phenyl-4-(carboxyanil)tetrahydropyrrole]-2-benzoic acid, m. p. 350°, identical with the "indifferent" compound obtained by Dobner; benzylidene-*o*-aminobenzoic acid yields 2-phenylquinoline-4 : 8-dicarboxylic acid; benzylidene-*p*-aminophenol yields the *p*-hydroxyanil of cinnamoylformic acid, whilst benzylidene-*p*-anisidine yields this compound together with α-phenylquininic acid and *5-keto-2-phenyl-1-p-anisylpyrrolidine-4-p-methoxyanil*, m. p. 196°; benzylidene-*p*-toluidine yields 4 : 5-diketo-1-*p*-tolyl-2-phenylpyrrolidine (above), 2-phenyl-6-methylquinoline-4-carboxylic acid, and the "indifferent" compound $C_{24}H_{22}ON_2$, m. p. 205°, obtained by Dobner; cinnamylidene-β-naphthylamine yields 2-cinnamyl-β-naphthacinchonic acid. The compound (II) when fused with *p*-nitroaniline at 160—167° for 20 min. yields *5-keto-1 : 2-diphenylpyrrolidine-4-p-nitroanil*, m. p. 258° (decomp.), and with phenylhydrazine it yields *γ-anilino-α-keto-γ-phenylbutyric acid phenylhydrazide*, m. p. 132° (decomp.). The compound (I) with phenylhydrazine yields *1-anilino-5-keto-2-phenylpyrrolidine-4-phenylhydrazone*, m. p. 229° (also obtained by the action of phenylhydrazine on cinnamoylformic acid); with hydroxylamine, it yields the corresponding *monoxime*, and with *o*-phenylenediamine it yields a *compound*, m. p. 250° (decomp.), probably (V), which is also obtained by the action of *o*-phenylenediamine on cinnamoylformic acid. J. W. BAKER.

Nitro- and amino-acridines. K. LEHMSTEDT (Ber., 1927, 60, [*B*], 1370—1372; cf. Jenson and Friedrich, this vol., 575).—Graebe's α-nitroacridine is shown to contain the substituent in position 3, since it is oxidised by chromic acid in glacial acetic acid to 3-nitroacridone (cf. Ullmann and Bader, A., 1907, i, 843); 3-nitro-9-*p*-dimethylaminophenylacridine has m. p. 225°. Similarly, Graebe's 3-nitroacridine, m. p. 172° (corr.), is oxidised to 1-nitroacridone, m. p. 259° (cf. Mayer and Stein, A., 1918, i, 36), and is thus 1-nitroacridine. Reduction of 1-nitroacridine with stannous chloride in glacial acetic acid affords *1-aminoacridine*, m. p. 125° (*picrate*). H. WREN.

Unsaturated dipeptide-anhydrides and dehydration of amino-acid derivatives. E. ABDERHALDEN (Z. physiol. Chem., 1927, 167, 177—178).—A reply to Bergmann's claim for priority (this vol., 474). A. WORMALL.

Action of halogen-substituted phenylhydrazines on dihydroxytartaric acid. F. D. CHATTAWAY and W. G. HUMPHREY (J.C.S., 1927, 1323—1328).—Improved methods for the preparation of dihydroxytartaric acid and the halogen-substituted phenylhydrazines are described; the latter are best prepared by the reduction of the corresponding diazonium salts by means of sodium sulphite.

The halogen-substituted phenylosazones of dihydroxytartaric acid separate as orange-red powders when aqueous solutions of dihydroxytartaric acid and the corresponding phenylhydrazine hydrochloride are mixed. On crystallisation from any solvent, these osazones lose a molecule of water to give *anhydrides* of the general formula (I), together with *pyrazolone* derivatives of the general formula (II)



(I.) (II.)

The *anhydrides*, obtained by heating the osazones with acetic anhydride or benzoyl chloride, are deep red, crystalline solids which are unaffected by boiling with water. When heated with alcohols containing hydrogen chloride they give esters of the isomeric pyrazolone acids. The pyrazolones are obtained from the osazones by crystallisation from acetic acid or by acidification of solutions of their sodium salts. In the last reaction, a varying amount of the isomeric anhydride is simultaneously produced. The free pyrazolonecarboxylic acids are yellow and are esterified only with difficulty. The esters are more readily prepared by boiling the osazones or the anhydrides with alcohols containing hydrogen chloride.

The structure of the pyrazolone derived from di-2 : 4-dibromophenylosazone has been confirmed by synthesis from the potassium derivative of oxalacetic ester, by acting successively with 2 : 4-dibromobenzenediazonium chloride (1 mol.) and 2 : 4-dibromophenylhydrazine (1 mol.) and boiling the resulting osazone ester with alcoholic hydrogen chloride.

In this way the following compounds have been prepared: *diketosuccinic acid* 2 : 4-*dibromophenylosazone*, m. p. 205° (decomp.) [*anhydride*, m. p. 267° (decomp.)]; 1-2 : 4-*dibromophenyl*-4 : 5-*diketo*-3-*pyrazolinecarboxylic acid* 4-2″ : 4″-*dibromophenylhydrazone*, m. p. 248° (decomp.) (*methyl* ester, m. p. 233°; *ethyl* ester, m. p. 229°; n-*butyl* ester, m. p. 175°); *ethyl diketosuccinate* 2 : 4-*dibromophenylhydrazone*, m. p. 95°; *ethyl diketosuccinate* 2 : 4-*dibromophenylosazone*, m. p. 197°; *diketosuccinic acid* p-*bromophenylosazone*, m. p. 201° (decomp.) [*anhydride*, m. p. 262° (decomp.)]; 1-p-*bromophenyl*-4 : 5-*diketopyrazoline*-3-*carboxylic acid* 4-p-*bromophenylhydrazone*, m. p. 260° (decomp.) (*methyl* ester, m. p. 213°; *ethyl* ester, m. p. 191°); *diketosuccinic acid* 2 : 4-*dichlorophenylosazone*, m. p. 198 (decomp.) [*anhydride*, m. p. 242° (decomp.)]; 1-2′ : 4′-*dichlorophenyl*-4 : 5-*diketopyrazoline*-3-*carboxylic acid* 4-2″ : 4″-*dichlorophenylhydrazone*, m. p. 252° (decomp.) (*ethyl* ester, m. p. 212°); *diketosuccinic acid* p-*chlorophenylosazone*, m. p. 195° (decomp.) [*anhydride*, m. p. 257° (decomp.)]; 1-p-*chlorophenyl*-4 : 5-*diketopyrazoline*-3-*carboxylic acid* 4-p-*chlorophenylhydrazone*, m. p. 254° (*ethyl* ester, m. p. 190°). G. A. C. GOUGH.

Dicarbazyls. III. Oxidation of carbazole and *N*-alkylcarbazoles in acid solution. P. MAITLAND and S. H. TUCKER (J.C.S., 1927, 1388—1392).—Acetic acid solutions of carbazole, 9-methylcarbazole, and 9-ethylcarbazole are oxidised by sodium dichromate and sulphuric acid, yielding, respectively, 3 : 3-dicarbazyl, 9 : 9′-*dimethyl*-3 : 3′-*dicarbazyl*, m. p. 200—202°, and 9 : 9′-*diethyl*-3 : 3′-*dicarbazyl*, m. p. 188—190°. The two last-named compounds are alternatively prepared by direct alkylation of 3 : 3′-dicarbazyl (this vol., 162). The mechanism of the acid oxidation of carbazole is considered to be closely

allied to that of the corresponding oxidation of diphenylamine to diphenylbenzidine (Wieland, A., 1913, i, 1386). The production of NN'-*dimethyldiphenylbenzidine*, m. p. 170°, by acid oxidation of *N*-methyldiphenylamine lends support to Wieland's theory that the benzene nuclei unite directly without formation of an intermediate product. Repetition of the experiments of Marqueyrol and Muraour (A., 1914, i, 577) fails to confirm the data on which they base their theory of intermediate compound formation.

M. CLARK.

Triazoles and their derivatives. VII. R. GRUNER, Z. BENES, E. SCHUBERT, and M. ARMAN (Monatsh., 1927, 48, 37—46).—The formation of triazole derivatives by the action of diacylamides on monosubstituted hydrazines in presence of the sodium salts of the corresponding acids (Brunner, A., 1915, i, 1007) is of general application, and the method has been applied to the preparation of the following triazoles: 3 : 5-*diethyl*-1 : 2 : 4-*triazole*, m. p. 61—62° (*hydrochloride*, m. p. 173—174°; *silver* compound; *mercurichloride*, $C_6H_{11}N_3,2HgCl_2$, m. p. 158°); 1-*phenyl*-3 : 5-*diethyl*-1 : 2 : 4-*triazole*, m. p. 37—38° (*mercurichloride*, $C_{12}H_{15}N_3,HgCl_2$, m. p. 117—118°; *picrate*, m. p. 154°); 3 : 5-di*iso*propyl-1 : 2 : 4-triazole (Stollé and Gutmann, A., 1904, i, 696) in the pure state has m. p. 146°; 1-α-*naphthyl*-3 : 5-*dimethyl*-1 : 2 : 4-*triazole*, m. p. 69° [*picrate*, m. p. 198°; *additive* compound, $C_{14}H_{13}N_3,AgNO_3$, m. p. 274° (decomp.); *mercurichloride*, $C_{14}H_{13}N_3,HgCl_2$, m. p. 82°]: 1-β-naphthyl-3 : 5-dimethyl-1 : 2 : 4-triazole (cf. Gastaldi, A., 1924, i, 717) (*picrate*, m. p. 158°; *mercurichloride*, $C_{14}H_{13}N_3,HgCl_2$, m. p. 155°). J. W. BAKER.

Action of aromatic amines on thiosemicarbazide, hydrazodithiodicarbonamide, and their derivatives. I. MACUREVITSCH (Bull. Soc. chim., 1927, [iv], 41, 637—663, and J. Russ. Phys. Chem. Soc., 1927, 59, 27—68).—The action of aromatic amines on thiosemicarbazide affords in the first place hydrazodithiodicarbonamide, $2NH_2{\cdot}CS{\cdot}NH{\cdot}NH_2 \longrightarrow (NH_2)_2+NH_2{\cdot}CS{\cdot}NH{\cdot}NH{\cdot}CS{\cdot}NH_2$, which subsequently yields heterocyclic compounds which are not in general either diazole or triazole derivatives, but disubstituted tetrazines.

These products are crystalline substances which decolorise solutions of bromine in acetic acid or methyl alcohol, but with excess of bromine give resinous products. They also decolorise iodine–potassium iodide solution and react instantly with potassium permanganate in cold sodium carbonate solution. When heated with either sodium peroxide and sodium carbonate or with dry sodium hydroxide they afford (phenyl)carbylamine. They possess acidic properties, two of the hydrogen atoms, probably those in the thiocarbamide groups, being replaceable by metals. The same products are obtained by the action of amines on monosubstituted hydrazodithiodicarbonamides. In addition to these crystalline products, resinous products of similar character are formed. These resinous products afford characteristic colour reactions with alcoholic alkalis, and, like the crystalline products, yield insoluble complex silver salts. Derivatives of diazole and triazole are also produced together with basic by-products, the constitution of which has not been determined. In addition to ammonia and hydrogen sulphide, the gaseous products contain sulphur dioxide. With an aralkylamine, such as benzylamine, the main product is the corresponding *s*-thiocarbamide, *e.g.*, *s*-dibenzylthiocarbamide, together with a small quantity of a *substance*, m. p. 161—162°, probably a triazole derivative.

Aniline and thiosemicarbazide at 180—185° afford a *substance*, $C_{16}H_{16}N_8S_2(+1H_2O$ or $2H_2O)$, m. p. 260—261° (*silver* salt, $C_{16}H_{14}N_8S_2Ag_2,2AgNO_3$), together with 3 : 5-dianilino-4 : 1 : 2-thiodiazole (Fromm and Nerz, A., 1923, i, 1239); hydrazodithiodicarbonamide affords the same substance, m. p. 260—261°, together with a *substance*, m. p. 297—298°, and a volatile *product*, m. p. 137—139°. Aniline and phenylhydrazodithiodicarbonamide, m. p. 169—170° (cf. Arndt, Milde, and Tschenscher, A., 1922, i, 375), yield similarly the product m. p. 260—261°, a volatile substance, m. p. 137—139°, and a little of a substance, m. p. 201—202·5°, probably 2-phenylimino-5-thio-1-phenylurazole (Arndt and Milde, A., 1921, i, 813), whilst hydrazothiophenyldicarbonamide affords a volatile product, m. p. 140—142°, a brown, resinous substance, and 2-anilino-5-thiol-1-phenyl-1 : 3 : 4-triazole, m. p. 206° (Busch and Ulmer, A., 1902, i, 575).

o-Toluidine and thiosemicarbazide or hydrazodithiodicarbonamide afford a *substance*, $C_{18}H_{20}N_8S_2,2H_2O$, m. p. 228—229°, together with a volatile product, m. p. 142—143°, a *substance*, $C_4H_8N_8S_2$, m. p. 297—300° (decomp.) (*silver*, *lead*, and *mercury* salts); an isomeric *substance*, $C_4H_8N_8S_2$, m. p. above 370° (*silver*, *lead*, and *mercury* salts), a resinous product, and traces of a *substance*, m. p. 269—270° (decomp.), which contains carbon, hydrogen, nitrogen, and sulphur. *o*-Toluidine and phenylhydrazodithiodicarbonamide afford a volatile *substance*, m. p. 149—150°, which appears to contain an amino- but no mercaptan group, a *substance*, $C_{17}H_{18}N_8S_2,2H_2O$, m. p. 219—220°, and a white *substance*, decomp. 300°, giving silver, mercury, and lead salts, analogous to that obtained with hydrazodithiodicarbonamide. It is possible that in this case a phenyl group is replaced by a tolyl group. *m*-Toluidine and thiosemicarbazide afford a *substance*, $C_{18}H_{20}N_8S_2,2H_2O$, m. p. 259—260°, and a resinous product; the substance, m. p. 234—236°, previously described (A., 1925, i, 984) could not be obtained. Hydrazodithiodicarbonamide yields the same substance, m. p. 259—260°, a substance, decomp. 300°, probably identical with the product, m. p. 297—300°, (decomp.), described above, and a substance, $C_4H_8N_8S_2$, decomp. 297—298°. *p*-Toluidine and hydrazodithiodicarbonamide afford a volatile *substance*, m. p. 170—172°, containing nitrogen and sulphur, the substance, m. p. 272—273° (Macurevitsch, *loc. cit.*), a crystalline product, decomp. 297—298°, and a product, m. p. above 370° (silver salt, $C_4H_6N_8S_2Ag_2,8AgNO_3$). There is some evidence that the product, m. p. 297—300°, is readily converted into its isomeride, m. p. above 370°.

R. BRIGHTMAN.

Preparation of 1 : 3 : 5-triazine-2 : 4 : 6-tricarboxyl chloride [and vat dyes therefrom]. E. OTT.—See B., 1927, 470.

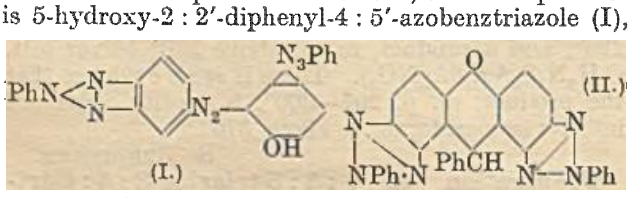
Dicyclic compounds and their analogy with naphthalene. III. K. FRIES (Annalen, 1927, 454, 121—324; cf. A., 1912, i, 656; 1914, i, 569).—The behaviour of a variety of dicyclic compounds in certain critical reactions is examined in order to determine their "benzoid" or "naphthoid" character, those compounds being designated naphthoid in which two types of *ortho*-positions exist (corresponding with αβ and ββ in the naphthalene series). The reactions chosen are: (i) coupling of primary amino-derivatives to give diazoamino-compounds (benzoid) or aminoazo-compounds (naphthoid); (ii) Skraup reaction, in which naphthoid amines give no linear (ββ) ring systems; (iii) nitration and halogenation of "β" derivatives, both *ortho*-positions being attacked in benzoid compounds; (iv) formation of dihalogeno-derivatives (benzoid) or of keto-chlorides and *o*-quinones (naphthoid) by further halogenation and oxidation; (v) conversion of benzylidene-"β"-amino-compounds into acridine derivatives easily (naphthoid) or with difficulty (benzoid).

Benztriazoles are definitely naphthoid in character, benzthiodiazoles less certainly so. Tetralene (tetrahydronaphthalene) and coumarone are completely benzoid. Benziminazoles, benzthiazoles, and benz-*iso*thiazoles are mainly benzoid, but show certain analogies with naphthalene which are more clearly exhibited by indazoles. The naphthoid or benzoid character probably depends on whether the compound exists in one or both of the isomeric forms (*a*) and (*b*),



and this again is related to the ease of formation and the stability of the simple heterocyclic dihydro-derivatives. Thus in contrast with the unstable dihydrobenzenes, dihydroiminazoles and dihydrothiazoles are readily formed and are very stable. *CC*-Dihydro-1 : 2 : 3-triazoles are, on the other hand, unknown. If the dicyclic compound be supposed to exist as an equilibrium of the forms (*a*) and (*b*), then naphthoid characters will be present when the equilibrium amount of (*b*) is very small; this will be the case when the dihydro-derivative of the simple heterocyclic parent compound shows a strong tendency to dehydrogenation. A development of this hypothesis accounts for the results of bromination of "β" hydroxy-compounds, the absence of any tendency in β-naphthylamine to give a linear benzoquinoline by Skraup's reaction, and other similar observations.

Benztriazoles. [With E. SUDHOFF and A. BRETT-SCHNEIDER.]—If in the preparation of 5-hydroxy-2-phenylbenztriazole from the diazotised 5-amino-compound (Fries and Roth, A., 1912, i, 657) a less concentrated sulphuric acid is used, the main product is 5-hydroxy-2 : 2′-diphenyl-4 : 5′-azobenztriazole (I),

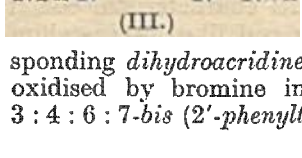


m. p. 258°, which is also obtained by coupling the components in the usual manner. 5-Hydroxy-2-phenylbenztriazole condenses in the 4 : 4′-positions with formaldehyde in presence of 2*N*-sodium hydroxide, giving 5 : 5′-*dihydroxy*-2 : 2′-*diphenyl*-4 : 4′-*bis-benztriazolylmethane*, m. p. 263° (*diacetate*, m. p. 229°), which could not be anhydrised to a xanthen derivative. The corresponding *phenylmethane*, $C_{31}H_{22}O_2N_6$, m. p. 263° (*diacetate*, m. p. 195°), obtained from benzaldehyde, is readily converted by phosphoryl chloride in toluene at 100° into 5-*phenyl*-3 : 4 : 6 : 7-*bis*(*phenyltriazolo*)*xanthen* (5-phenyl-3 : 4 : 6 : 7-bisphenyl-ψ-aziminoxanthen) (II), m. p. 277°. Nitration of 5-acetamido-2-phenylbenztriazole gives the 4-*nitro*-derivative, m. p. 254°, which is hydrolysed by warm concentrated sulphuric acid to 4-*nitro*-5-*amino*-2-*phenylbenztriazole*, m. p. 310°. The 4 : 5-*diamino*-compound, m. p. 126° (*diacetyl* derivative, m. p. 258°), obtained by reduction of the nitroamine, condenses with benzil to give a *quinoxaline*, $C_{26}H_{17}N_5$, m. p. 262°. 5-Hydroxy-2-phenylbenztriazole, like β-naphthol, reacts easily with oxalyl chloride to form a *phenyltriazolocoumarandione*, $C_{14}H_7O_3N_3$, m. p. 203°.

For the preparation of 5-*amino*-6-*methoxy*-2-*phenylbenztriazole*, m. p. 185° (*acetyl* derivative, m. p. 146°), 2 : 4-diaminoanisole, m. p. 67°, is coupled with diazobenzene, and the resulting 2 : 4-diamino-5-methoxyazobenzene, m. p. 134°, is boiled with aqueous alcoholic ammoniacal copper sulphate.

4 : 4 : 5 : 7 : 7-Pentachloro-6-keto-2-phenyl-4 : 5 : 6 : 7-tetrahydrobenztriazole (Zincke and Scharff, A., 1910, i, 140) is converted by fuming nitric acid into the 2-p-*nitrophenyl* compound, decomp. 172°. This, with sodium hydrogen sulphite at 100°, yields 4 : 5 : 7-*trichloro*-6-*hydroxy*-2-p-*nitrophenylbenztriazole*, m. p. 215° (*acetate*, m. p. 194°; red, sparingly soluble *sodium* salt), which by oxidation with nitric acid in acetic acid at 100° is converted into 4 : 5-*dichloro*-6 : 7-*diketo*-2-p-*nitrophenyl*-6 : 7-*dihydrobenztriazole*, m. p. 193°. The *o*-quinone, heated at 100° with aniline and acetic acid, gives the hydroxyquinone-anil, 5-*chloro*-4-*phenylimino*-6-*hydroxy*-7-*keto*-2-p-*nitrophenyl*-4 : 7-*dihydrobenztriazole*, m. p. 236°.

5-Amino-2-*p*-tolylbenztriazole (Willgerodt and Klein, A., 1899, i, 882; Schmidt and Hagenbocker, A., 1921, i, 897) is converted by Zincke's method (*loc. cit.*) into 4 : 4 : 5 : 7 : 7-*pentachloro*-6-*keto*-2-p-*tolyl*-4 : 5 : 6 : 7-*tetrahydrobenztriazole*, m. p. 197° (decomp.), from which are prepared, by a similar series of reactions, 4 : 5 : 7-*trichloro*-6-*hydroxy*-2-p-*tolylbenztriazole*, m. p. 188°, 4 : 5-*dichloro*-6 : 7-*diketo*-2-p-*tolyl*-6 : 7-*dihydrobenztriazole*, m. p. 223°, and 5-*chloro*-4-*phenylimino*-6-*hydroxy*-7-*keto*-2-p-*tolyl*-4 : 7-*dihydrobenztriazole*, m. p. 236°; reduction of the *o*-quinone with stannous chloride gives 4 : 5-*dichloro*-6 : 7-*dihydroxy*-2-p-*tolylbenztriazole*, m. p. 203° (*diacetate*, m. p. 197°).



5-*Benzylideneamino*-2-*phenylbenztriazole*, m. p. 156°, when boiled in glacial acetic acid for a few minutes, is converted into the corresponding *dihydroacridine* (III), m. p. 315°, which is oxidised by bromine in nitrobenzene to 5-*phenyl*-3 : 4 : 6 : 7-*bis* (2′-*phenyltriazolo*)*acridine*, m. p. 294°.

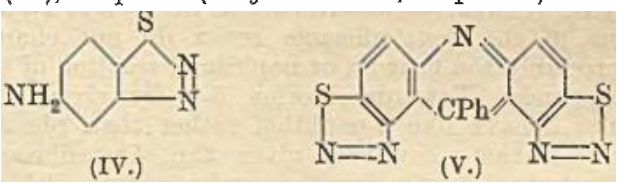
o-*Benzylideneamino*-2-p-*tolylbenztriazole*, m. p. 150°, gives in similar manner a *dihydroacridine*, m. p. 321°. 5-*Benzylideneamino*-1-*phenylbenztriazole*, m. p. 137°, when heated with 5-amino-1-phenylbenztriazole hydrochloride in a little alcohol, yields (like the corresponding β-naphthylamine derivative) an acridine, 5-*phenyl*-3 : 4 : 6 : 7-*bis*-(1′-*phenyltriazolo*)*acridine*, m. p. 336°. 5-*Benzylideneamino*-1-*methylbenztriazole*, m. p. 165°, is yellow and gives a yellow *acridine*, m. p. 364° (the 1-phenyltriazole compounds are colourless).

[With A. MADJID.]—5 : 6-(2′-*Phenyltriazolo*)*quinoline*, m. p. 160°, prepared by Skraup's reaction from 5-amino-2-phenylbenztriazole, is converted by way of the *methiodide*, m. p. 266° (decomp.), into N-*methyl*-5 : 6-(2′-*phenyltriazolo*)-2-*quinoline*, m. p. 218°. 5 : 6-(1′-*Phenyltriazolo*)*quinoline*, m. p. 122° (*methiodide*, m. p. 258°), and the *methylquinoline*, m. p. 215°, are similarly obtained. 5-Amino-1-methylbenztriazole gives 5 : 6-(1′-*methyltriazolo*)*quinoline*, m. p. 167° (*methiodide*, m. p. 244°). By chlorinating 5-acetamido-1-methylbenztriazole in boiling acetic acid there is obtained the 4-*chloro*-derivative, m. p. 214°, hydrolysed by aqueous alcoholic hydrogen chloride to 4-*chloro*-5-*amino*-1-*methylbenztriazole*, m. p. 178°. No triazoloquinolines are obtainable from the 4-chloro-5-amino-derivatives of 1-methyl-, 1-phenyl-, and 2-phenyl-benztriazoles by Skraup's reaction under a variety of conditions.

[With A. ARNEMANN.]—2-Bromo-3 : 5-dinitro-*p*-xylene, m. p. 115°, fails to react with phenylhydrazine alone or in presence of cuprous iodide, and with alcoholic ammonia in presence of cuprous iodide or copper-bronze. By boiling together equal parts of 2-bromo-3 : 5-dinitro-*p*-xylene and aniline for 2 hrs., a 61% yield of 2 : 4-*dinitro*-3 : 6-*dimethyldiphenylamine*, m. p. 132°, is obtained. Reduction of this with sodium sulphide gives the 4-*nitro*-2-*amino*-compound, m. p. 171° (*acetyl* derivative, m. p. 203°, cannot be converted into a benziminazole), from which by the action of nitrous acid 5-*nitro*-1-*phenyl*-4 : 7-*dimethylbenztriazole*, m. p. 208°, results. The 5-*amino*-compound, m. p. 179° (*acetyl* derivatives, m. p. 206°), obtained by reduction, couples with diazobenzene to give a *diazoamino*-compound, m. p. 161°, whereas 5-amino-1-phenylbenztriazole yields an azo *dye*, $C_{18}H_{14}N_6$, m. p. 231° (*acetyl* derivative, m. p. 207°). The aminodimethylbenztriazole is chlorinated in concentrated hydrochloric acid to give 4 : 6 : 6 : 7-*tetrachloro*-5-*keto*-1-*phenyl*-4 : 7-*dimethyl*-4 : 5 : 6 : 7-*tetrahydrobenztriazole*, m. p. 170°, which on reduction with stannous chloride in acetic acid yields 6-*chloro*-5-*hydroxy*-1-*phenyl*-4 : 7-*dimethylbenztriazole*, m. p. 168° (*acetate*, m. p. 174°). Treatment of the chlorohydroxy-compound with fuming nitric acid gives 6-*chloro*-4-*nitro*-5-*keto*-1-*phenyl*-4 : 7-*dimethyl*-4 : 5-*dihydrobenztriazole*, m. p. 124° (decomp.), from which by boiling the acetic acid solution, 6-*chloro*-4-*hydroxy*-5-*keto*-1- : 7-*dimethyl*-4 : 5-*dihydrobenztriazole*, m. p. 201°, is obtained. As in the naphthalene series, there is here no tendency to form a ββ(5 : 6)-quinone.

Oxidation of 5-amino-2-phenylbenztriazole with permanganate gives in 50% yield 2-phenyl-1 : 2 : 3- : 5-dicarboxylic acid (von Pechmann, A., 1901 1110; Beretta, A., 1926, 182), m. p. 255° (decomp.), which, contrary to the statements of von Pechmann and Beretta, when heated forms no anhydride, but is decarboxylated to 2-phenyltriazole-4-carboxylic acid, m. p. 191° (methyl ester, m. p. 54°). The 4 : 5-dicarboxylic acid gives a *chloride*, m. p. 122°, *diamide*, m. p. 274°, and *dianilide*, m. p. 213°. The *methyl* ester, m. p. 91°, is converted by way of the *dihydrazide*, m. p. 232°, *diazide* (detonates by rubbing or shock), and *diurethane*, m. p. 135°, into 4 : 5-diamino-2-phenyl-1 : 2 : 3-triazole dihydrochloride (Thiele, A., 1897, i, 377), which condenses with benzil to form a *quinoxaline*, but gives no benziminazole derivatives. By the action of nitric acid on 5-amino-2-phenylbenztriazole there is obtained 2-p-*nitrophenyl*-1 : 2 : 3-*triazole*-4 : 5-*dicarboxylic acid*, m. p. 253° (decomp.; *methyl* ester, m. p. 163°; *dianilide*, m. p. 258°), which also gives no anhydride. 2-p-*Carboxyphenyl*-1 : 2 : 3-*triazole*-4 : 5-*dicarboxylic acid*, m. p. 232° (decomp.); *methyl* ester, m. p. 128°; *chloride*, m. p. 110°; *triamide*, m. p. 308° (+3AcOH) or 330° (not quite pure); *trianilide*, m. p. 238° (+AcOH), obtained by oxidation of 5-amino-2-*p*-tolylbenztriazole with permanganate, gives no anhydride, but when rapidly sublimed yields 2-p-*carboxyphenyl*-1 : 2 : 3-*triazole*, m. p. 282° (*methyl* ester, m. p. 128°). 5-Amino-1-phenylbenztriazole is oxidised to 1-phenyl-1 : 2 : 3-triazole-4 : 5-dicarboxylic acid (Zincke and Petermann, A., 1901, i, 104; Beretta, *loc. cit.*), m. p. 149° (methyl ester, m. p. 127°; *dihydrazide*, m. p. 168°).

Benzthiodiazoles. [With M. VORBRODT and G. SIEBERT.]—4-*Nitro*-2-*aminothiophenol*, m. p. 183° (*methyl thioether*, m. p. 105°; *disulphide*, m. p. 211°), prepared from 2-bromo-5-nitroaniline and sodium polysulphide, gives with acetic anhydride 4-*nitro*-1-*methylbenzthiazole*, m. p. 139°, and with nitrous acid 5-*nitrobenzthiodiazole*, m. p. 144°, which is reduced by tin and hydrochloric acid to 5-*aminobenzthiodiazole* (IV), m. p. 94° (*acetyl* derivative, m. p. 161°). This



(IV.) (V.)

amine behaves like β-naphthylamine. Its *benzylidene*-derivative, m. p. 90°, reacts with the hydrochloride in hot alcohol to give 5-*phenylacridine*-3 : 4 : 6 : 7-*bisdiazosulphide* (V), m. p. 216°. The amine couples in acetic acid with diazobenzene to give directly an aminoazo *dye*, m. p. 222° (decomp.) (*acetyl* derivative, m. p. 231°). On chlorination in hydrochloric acid, the amine forms 4 : 4 : 6 : 6 : 7-*pentachloro*-5-*keto*-4 : 5 : 6 : 7-*tetrahydrobenzthiodiazole*, m. p. 149° (decomp.), reducible by stannous chloride in acetic acid to 4 : 6 : 7-*trichloro*-5-*hydroxybenzthiodiazole*, m. p. 187° (*acetate*, m. p. 122°), from which by chlorination 4 : 4 : 6 : 6 : 7 : 7-*hexachloro*-5-*keto*-4 : 5 : 6 : 7-*tetrahydrobenzthiodiazole*, m. p. 151°, is obtained. The trichloro-compound is oxidised by nitric acid to 6 : 7-*dichlorobenzthiodiazole*-4 : 5-*quinone*, m. p. 164°, which condenses with *o*-phenylenediamine to form a *quinoxaline*, m. p. 287°, and is reduced by stannous chloride to the corresponding *dihydroxy*-compound, m. p. 219° (*diacetate*, m. p. 137°). 5-Aminobenzthio-

diazole is diazotised in concentrated sulphuric acid solution, and by heating the diluted diazo-solution, *5-hydroxybenzthiodiazole*, m. p. 161° (*acetate*, m. p. 122°), is obtained. This yields on halogenation *4-bromo-* (m. p. 196°) and *4-chloro-* (m. p. 197°) derivatives. *4-Nitro-o-hydroxybenzthiodiazole*, m. p. 206°, results from nitration of the 5-hydroxy-compound or of its 4-bromo-derivative.

6-Hydroxybenzthiodiazole, m. p. 211°, prepared by demethylation of the methyl ether (Fries and Engelbertz, A., 1915, i, 155), yields on bromination the *7-bromo-* (m. p. 210°) and, less easily, the 5 : 7-*dibromo*-derivative, m. p. 228° (decomp.). Nitration of 6-hydroxybenzthiodiazole or of its 7-bromo-derivatives gives *7-nitrobenzthiodiazole*, m. p. 180° (*sodium* salt described). 6-Hydroxybenzthiodiazole is converted by chlorine into the *7-chloro*-derivative, m. p. 200°, which is also obtained by demethylation of *7-chloro-6-methoxybenzthiodiazole*, m. p. 114°, synthesised from 6-chloro-5-methoxy-1-phenylbenzthiazole (Fries and Buchler, below) by hydrolysis with alcoholic alkali to *6-chloro-2-amino-5-methoxythiophenol*, followed by diazotisation. Further chlorination of 6-hydroxybenzthiodiazole yields first an *o*-quinone dichloride, probably 7 : 7-*dichloro-6-keto*-6 : 7-*dihydrobenzthiodiazole*, then a sulphur-free diazo-salt, probably 2 : 3 : 3-*trichloro-4-keto*-3 : 4-*dihydrobenzenediazonium chloride*, m. p. 155—160° (decomp.), which gives with 2-naphthol-3 : 6-disulphonic acid a red *dye*, and by reduction with stannous chloride 2 : 3-*dichloro-4-hydroxyphenylhydrazine*, m. p. 158° (decomp.); the final chlorination product is 2 : 3 : 4 : 6-tetrachlorophenol, m. p. 67° (lit., 70°; benzoate, m. p. 166°). 6-Methoxybenzthiodiazole is similarly converted by way of a diazonium salt into 2 : 3-*dichloro-4-methoxyphenylhydrazine*, m. p. 200° [p-*nitrobenzylidene*-compound, m. p. 210° (decomp.)].

Benziminazoles. [With E. Modrow, B. Raeke, and K. Weber.]—Substituents in the 1- and 2-positions in the benziminazole series do not change appreciably the benzoid or naphthoid reaction of the compounds. Towards chlorine, 5-hydroxybenziminazoles behave like β-naphthol rather than phenol; dibromination, however, gives the 4 : 6-dibromo-derivatives; 5-aminobenziminazoles couple with diazobenzene to form diazoamino-compounds as in the benzene series, and the Skraup reaction gives both linear and angular tricyclic quinolines. Moreover, a 5 : 6(*i.e.*, ββ)-quinone is obtainable.

Chlorination of 5-acetamido-1-phenyl-2-methylbenziminazole (von Walther and Kessler, A., 1904, i, 348), m. p. 233°, gives after hydrolysis with aqueous-alcoholic hydrochloric acid *4-chloro-5-amino-1-phenyl-2-methylbenziminazole*, m. p. 257° (*acetyl* derivative, m. p. 228°), and the *6-chloro*-isomeride, m. p. 208° (*acetyl* derivative, m. p. 199°). The latter base is synthesised from 5-chloro-2 : 4-diaminodiphenylamine and acetic anhydride. *o-Hydroxy-1-phenyl-2-methylbenziminazole*, m. p. 243° (*acetate*, m. p. 141°), prepared by decomposition of the diazotised 5-amino-compound, is brominated in water to the *4-bromo*-derivative, m. p. 266°, and in acetic acid with 2 mols. of bromine to the 4 : 6-*dibromo*-derivative, m. p. 190°. *4-Chloro-5-hydroxy-1-phenyl-2-methylbenziminazole*, m. p. 287° (*acetate*, m. p. 161°), obtained by chlorination, is converted with great difficulty into a dichloro-derivative, m. p. 215° (impure), the main product, even when only one further molecule of chlorine is used, being a *keto-chloride*, which is reducible by stannous chloride to the pure 4 : 6-*dichloro-5-hydroxy-1-phenyl-2-methylbenziminazole*, m. p. 216° [*hydrochloride*, m. p. 283° (decomp.); *O-acetate*, m. p. 183°]. Nitration of the 4-chloro-5-hydroxy-compound gives no chloronitro-ketone (a naphthoid reaction), but *4-chloro-6-nitro-o-hydroxy-1-phenyl-2-methylbenziminazole*, m. p. 211°.

5-Nitro-1-p-chlorophenyl-2-methylbenziminazole, m. p. 210°, is prepared from *4'-chloro-4-nitro-2-aminodiphenylamine*, m. p. 176° (*monoacetyl* derivative, m. p. 210°), the sodium sulphide partial reduction product of 4'-chloro-2 : 4-dinitrodiphenylamine, and gives on reduction *5-amino-1-p-chlorophenyl-2-methylbenziminazole*, m. p. 170°. This amine couples with diazobenzene to form a *diazoamino*-compound, m. p. 194° (decomp.), and is converted by way of its diazo-salt into the *5-hydroxy*-compound, m. p. 228°. Chlorination of the latter gives *4-chloro-5-hydroxy-1-p-chlorophenyl-2-methylbenziminazole*, m. p. 270° (*acetate*, m. p. 186°), and eventually a *keto-chloride*, reducible to the 4 : 6-*dichloro-o-hydroxy*-compound.

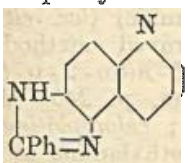
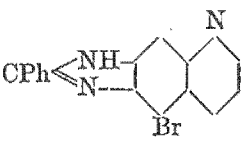
From 2'-chloro-2 : 4-dinitrodiphenylamine a similar series of reactions gives *2'-chloro-4-nitro-2-aminodiphenylamine*, m. p. 117°, *5-nitro-1-o-chlorophenyl-2-methylbenziminazole*, m. p. 140°, the *5-amino-* (m. p. 130°) and *5-hydroxy-* (m. p. 245°) compounds, and *4-chloro-5-hydroxy-1-o-chlorophenyl-2-methylbenziminazoles*, m. p. 250°. *5-Hydroxy-1-phenylbenziminazole*, m. p. 244° (*acetate*, m. p. 88°), obtained from 5-amino-1-phenylbenziminazole (Reissert and Goll, A., 1905, i, 248), behaves like the other 5-hydroxybenziminazoles on chlorination; the *4-chloro*-derivative has m. p. 220°.

Similar relations are found in the 1-*p*-tolylbenziminazole series. *5-Amino-1-p-tolylbenziminazole*, m. p. 128° (*acetyl* derivative, m. p. 210°; *benzylidene*-derivative, m. p. 142°, gives no acridine), yields with *p*-nitrodiazobenzene a *diazoamino*-compound, m. p. 214° (decomp.). *4-Chloro-5-amino-1-p-tolylbenziminazole*, m. p. 128° (*acetyl* derivative, m. p. 209°; *formyl* derivative, m. p. 178°), is prepared by chlorination and hydrolysis of the acetyl derivative.

o-Chloro-2 : 4-dinitro-4'-methyldiphenylamine, m. p. 154°, is converted by sodium sulphide into 2 : 2' : 4 : 4'-*tetranitro-5 : 5'-di-p-toluidinodiphenyl sulphide*, m. p. 252°, or by tin and hydrochloric acid into the 2 : 4-*diamino*-compound, which condenses with formic acid to give *6-chloro-5-formamido-1-p-tolylbenziminazole*, m. p. 195°. *5-Hydroxy-1-p-tolylbenziminazole*, m. p. 239° (*acetate*, m. p. 133°), yields by chlorination the *4-chloro*-derivative, m. p. 217°, and a *keto-chloride*.

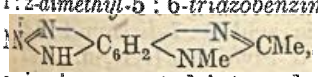
4-Chloro-5-aminobenziminazole, m. p. 102° (+EtOH; *hydrochloride*; *formyl* derivative, m. p. 222°), is obtained by the action of tin and hydrochloric acid on 5-nitrobenziminazole. *6-Chloro-5-formamidobenziminazole*, m. p. 205°, and 4 : 6-*dichloro-5-formamidobenziminazole*, m. p. 225°, are prepared from 3-chloro-4 : 6-dinitroaniline by reduction with stannous chloride, or with tin and hydrochloric acid, respectively, followed by condensation with formic acid.

[With A. ABDURRACHMAN.]—5-Amino-2-phenylbenziminazole gives by Skraup's reaction the *ang.*-quinoline, 2′-*phenyl*-5′ : 4′-*benziminazolo*-2 : 3-*pyridine* (VII), m. p. 90—95° (+H_2O), or 270° (anhyd.; *methiodide*, m. p. 295°). 4-*Bromo*-5-*amino*-2-*phenylbenziminazole*, m. p. 238—239° (obtained by hydrolysis of the *acetyl* derivative, m. p. 160°), gives with equal ease the *lin.*-quinoline, -*bromo*-2′-*phenyl*-6′ : 5′-*benziminazolo*-2 : 3-*pyridine* (VIII). Similarly, 5-amino-1-phenylbenziminazole is converted into an

(VII.)   (VIII.)

ang.-*quinoline*, m. p. 165° [*methiodide*, m. p. 280° (decomp.)], and its 4-*chloro*-derivative, m. p. 143° (*acetyl* derivative, m. p. 205°), into a *lin.*-*quinoline*, m. p. 199—201° (*methiodide* described). The corresponding 1-*p*-tolyl compounds melt, respectively, at 180° (*ang.*) and 235° (*lin.*; chloro-compound).

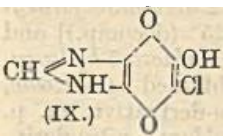
5 : 6-Diamino-2-methylbenziminazole (Kym and Ratner, A., 1913, i, 102) is converted by chlorine in hydrochloric–acetic acid into 4 : 4 : 7 : 7-*tetrachloro*-5 : 6-*diketo*-2-*methyl*-4 : 5 : 6 : 7-*tetrahydrobenziminazole* (*hydrochloride*, decomp. 300° without melting), which is more easily obtained by chlorination of its reduction product, 4 : 7-*dichloro*-5 : 6-*dihydroxy*-2-*methylbenziminazole* (base and *hydrochloride* decomp. 300° without melting; *diacetate*, m. p. 267°). This dihydroxy-compound, unlike the 6 : 7-dichloro-4 : 5-dihydroxy-isomeride, is not convertible into a quinone by oxidation. 5-*Nitro*-1 : 2-*dimethylbenziminazole*, m. p. 226°, prepared from *p*-nitro-*o*-aminomethylaniline and acetic anhydride, gives on nitration a mixture of the 5 : 6- and 4 : 5-*dinitro*-compounds, m. p. 232° and 170°, respectively. The former is reduced by sodium sulphide to the 5-nitro-6-amino-compound, m. p. 309°, and by tin and hydrochloric acid to the 5 : 6-*diamine*, m. p. 279°, which gives with benzil a *quinoxaline*, m. p. 232°, and with nitrous acid 1 : 2-*dimethyl*-5 : 6-*triazobenziminazole*,



m. p. 311°. The diamine is converted into a *keto-chloride*, $C_9H_6O_2N_2Cl_4$ (decomp. about 200°), and thence by reduction into 4 : 7-*dichloro*-5 : 6-*dihydroxy*-1 : 2-*dimethyl*-5 : 6-*triazobenziminazole* (base and *hydrochloride* blacken at about 300°; *diacetate*, m. p. 200°). 5-*Amino*-1 : 2-*dimethylbenziminazole*, m. p. 167° (*acetyl* derivative, m. p. 209°), gives by chlorination and reduction a mixture of *di*- and *tri*-*chloro*-compounds, which are oxidised by nitric–acetic acid to the quinone, 6 : 7-*dichloro*-4 : 5-*diketo*-1 : 2-*dimethyl*-4 : 5-*dihydrobenziminazole*, m. p. above 300°, reducible to a *dihydroxy*-compound.

On nitration of 5-nitro-1-*p*-chlorophenyl-2-methylbenziminazole, the new nitro-group enters the phenyl residue *ortho* to chlorine, giving a *product*, m. p. 220°, which condenses with aniline to form 5-*nitro*-*o*-p-*anilinophenyl*)-2-*methylbenziminazole*, m. p. 199

[With O. DIECKMANN and A. FINGERLING.]—Ketochlorides, quinones, and dihydroxy-compounds are obtainable by the methods above described from benziminazole and its 2-methyl, 2-phenyl, and 1-phenyl-2-methyl derivatives. The following are new: 4 : 6-*Dichloro*-5-*hydroxybenziminazole*, m. p. above 250° (*acetate*, m. p. 212°); 6 : 7-*dichloro*-4 : 5-*diketo*-4 : 5-*dihydrobenziminazole*, decomp. 280° [*nitrate*, m. p. 162° (decomp.); corresponding *dihydroxy*-compound, m. p. 196° (*diacetate*, m. p. 213°)]; 6-*chloro*-7-*phenylimino*-5-*hydroxy*-4 : 7-*diketo*-4 : 7-*dihydrobenziminazole*, decomp. 280°, obtained from the quinone and aniline, hydrolysable to the 4 : 7-*quinone* (IX), m. p. above 250°; 4 : 6-*dichloro*-5-*hydroxy*-2-*methylbenziminazole* [*hydrochloride*, m. p. above 250° (decomp.)]; 6 : 7-*dichloro*-4 : 5-*diketo*-2-*methyl*-4 : 5-*dihydrobenziminazole*, decomp. above 280° [corresponding *dihydroxy*-compound, m. p. above 250° (decomp.; *diacetate*, m. p. 148°); 7-*anil*, decomp. above 250°]; [with K. FINK] 4 : 4 : 6 : 7-*tetrachloro*-5-*keto*-2-*phenyl*-4 : 5-*dihydrobenziminazole*, m. p. 199° (decomp.); 4 : 6-*dichloro*-5-*hydroxy*-2-*phenylbenziminazole*, m. p. 240°; 6 : 7-*dichloro*-4 : 5-*diketo*-2-*phenyl*-4 : 5-*dihydrobenziminazole*, m. p. 305° (decomp.); 6 : 7-*dichloro*-4 : 5-*diketo*-1-*phenyl*-2-*methyl*-4 : 5-*dihydrobenziminazole*, m. p. 229° [corresponding *dihydroxy*-compound, m. p. indefinite above 160° (decomp.)]. 5-Nitro-2-phenylbenziminazole is best prepared by the action of alcoholic potassium hydroxide on 4-*nitrodibenzoyl*-*o*-*phenylenediamine*, m. p. 234°.


(IX.)

Benzthiazoles. [With W. BUCHLER.]—Benzthiazoles, like benziminazoles, yield "α" derivatives when nitrated. The β-amines couple with diazobenzene to form diazoamino-compounds, and their benzylidene-derivatives are not convertible into acridines. The more purely benzoid character of benzthiazoles as compared with benziminazoles is further shown by the formation of 4 : 6-dichloro- and 4-bromo-derivatives from the 5-hydroxy-compounds.

Thiobenz-p-*anisidide*, m. p. 135°, oxidised with alkaline ferricyanide, yields 5-*methoxy*-1-*phenylbenzthiazole*, m. p. 117°, which is converted by alcoholic alkali into 2 : 2′-diamino-5 : 5′-dimethoxydiphenyl disulphide, m. p. 81°, and by hydrobromic–acetic acid into 5-*hydroxy*-1-*phenylbenzthiazole*, m. p. 227° (*acetate*, m. p. 140°). 5-*Hydroxy*-1-*methylbenzthiazole*, m. p. 162°, is prepared from the 5-methoxy-compound (Fries and Engelbertz, A., 1915, i, 155).

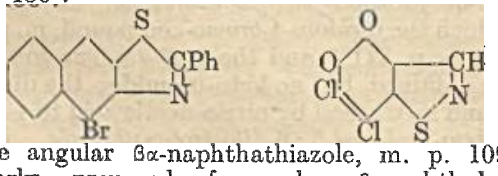
5-Hydroxy-1-phenylbenzthiazole gives on chlorination the 6-*chloro*-compound, m. p. 165° (*methyl ether*, m. p. 138°), and by further chlorination the 4 : 6-*dichloro*-derivative, m. p. 199°, but no keto-chloride. The dichloro-compound is oxidised by nitric acid to an *o*-*quinone*. Bromination, on the other hand, gives 4-*bromo*-5-*hydroxy*-1-*phenylbenzthiazole*, m. p. 169°, from which the 6-*chloro*-4-*bromo*-compound, m. p. 205° (*acetate*, m. p. 211°), and the 4 : 6-*dibromo*-compound may be obtained, but no keto-bromide; the dibromo-compound is oxidised by nitric–acetic acid to 4-*bromo*-5 : 6-*diketo*-1-*phenyl*-5 : 6-*dihydrobenzthiazole*, m. p. 163° (impure). 6-*Nitro*-5-*hydroxy*-1-*phenylbenzthiazole*, m. p. 171°, obtained with a little 4-*nitro*-compound by direct nitration, is reduced to the 6-*amino*-compound, m. p. 178° (decomp.). 4-*Bromo*-6-*nitro*- and 6-*chloro*-4-*nitro*-5-*hydroxy*-1-*phenylbenzthiazoles*,

m. p. 189° (decomp.) and 203°, respectively, are similarly prepared by nitration.

2 : 5-*Dichloro*-4-*nitrophenol*, m. p. 117° (*acetate*, m. p. 89°; 2 : 5-*dichloro*-4 : 6-*dinitrophenol*, m. p. 146°), prepared from 2 : 5-dichlorophenol by nitration in chloroform, reacts with sodium disulphide to give 4 : 4′-*dichloro*-2 : 2′-*dinitro*-5 : ɔ′-*dihydroxydiphenyl disulphide*, m. p. 277° (decomp.; *diacetate*, m. p. 194°), which is converted, by reduction to 4-*chloro*-2-*amino*-5-*hydroxythiophenol* [*hydrochloride*, m. p. 225° (decomp.)] and subsequent benzoylation, into 4-*chloro*-ɔ-*hydroxy*-1-*phenylbenzthiazole*, m. p. 219°, obtained as *benzoate*, m. p. 152°. The 4-*chloro*-6-*bromo*-derivative, m. p. 196° (*acetate*, m. p. 225°), the 4-*chloro*-6-*nitro*-derivative, m. p. 189°, and the 4-*chloro*-6-*amino*-derivative are prepared from the 4-*chloro*-compound; the amine gives on chlorination the tetrachloroketo-chloride, m. p. 177° (see below).

Chlorination of 5-hydroxy-1-phenylbenzthiazole gives successively 4 : 6-*dichloro*-ɔ-*hydroxy*-1-*phenylbenzthiazole*, m. p. 198°, 3 : 3 : 4 : 4 : 6 : 6-*hexachloro*-5-*keto*-1-*phenyl*-3 : 4 : 5 : 6-*tetrahydrobenzthiazole*, m. p. 204°, and finally a *hepta*- and an *octa*-*chloroketochloride*. The hexachloro-compound is reduced by stannous chloride in acetic acid to 3 : 4 : 6-*trichloro*-ɔ-*hydroxy*-1-*phenylbenzthiazole*, m. p. 173°, obtained also by hydrolysis of its *methyl ether*, m. p. 201° (prepared by chlorination of 5-methoxy-1-phenylbenzthiazole). 3 : 3 : 4 : 4-*Tetrachloro*-ɔ : 6-*diketo*-1-*phenyl*-3 : 4 : 5 : 6-*tetrahydrobenzthiazole*, m. p. 177°, the chlorination product of 6-amino- or of 4-chloro-6-amino-5-hydroxy-1-phenylbenzthiazole, is reduced to 3 : 4-*dichloro*-5 : 6-*dihydroxy*-1-*phenylbenzthiazole*, m. p. 247°, which is oxidised to the *quinone*, m. p. 231°, obtainable also from the above trichloro-compound of m. p. 173°.

Thiobenz-p-*nitroanilide*, m. p. 147°, gives on oxidation with alkaline ferricyanide at 90—100° 5-nitro-1-phenylbenzthiazole, m. p. 193°, prepared also by direct nitration; cold oxidation yields *bis*-p-*nitrophenyliminobenzoyl disulphide*, m. p. 145°. 5-Benzylideneamino-1-phenylbenzthiazole shows no tendency to form an acridine derivative when heated with its hydrochloride. The free 5-amino-compound couples with *p*-nitrodiazobenzene to form a *diazoamino*-compound, m. p. 209° (decomp.). 2 : 4-Dinitrophenyl thiobenzoate is converted quantitatively by chlorination into 2 : 4-*dinitrophenyl chloromercaptan*, $(NO_2)_2C_6H_3$·SCl, m. p. 99°. *Benz*-1-*bromo*-2-*naphthylamide*, m. p. 159°, prepared by benzoylation of 1-bromo-2-naphthylamine or by bromination of benz-β-naphthylamide, gives with phosphorus pentasulphide the *thioamide*, m. p. 161°, which is oxidised to the linear 3-*bromo*-1-*phenyl*-ββ-*naphthathiazole* (X), m. p. 156°.

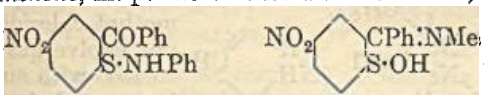
(X.)  (XI.)

The angular βα-naphthathiazole, m. p. 109°, is similarly prepared from benz-β-naphthylamide. Attempts to obtain 5-methoxy-1-phenylbenzthiazole from benz-*p*-anisidide or benzylidene-*p*-anisidine were unsuccessful. By the action of hydrogen sulphide on benzylidene-aniline or -*p*-anisidine, polymeric thiobenzaldehyde results in quantitative yield.

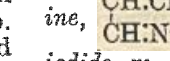
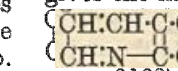
Benz*iso*thiazoles. [With K. Eishold and B. Vahlberg.]—The reactions of benz-4′ : ɔ′-*iso*thiazoles show a purely benzoid character, except in the formation of a keto-chloride and a dichloro-*o*-quinone from 5-hydroxybenz*iso*thiazole. Several new benz*iso*thiazolium salts are described (cf. Fries and Brothuhn, A., 1923, i, 842). 4-Nitro-2-aldehydophenyl bromomercaptan (5-nitro-2-bromothiolbenzaldehyde, 4-nitro-2-aldehydophenylsulphur bromide) (*loc. cit.*), m. p. 171°, prepared by an improved method, reacts with *p*-toluidine to form 5-*nitro*-2-*p*-*tolylbenz*-4′ : 5′-iso*thiazolium bromide*, m. p. 240° [decomp.; *chloride*, m. p. 240° (decomp.); *chloroplatinate*, m. p. 265° (decomp.)], and with methylamine to give the corresponding 2-*methyl* compound, m. p. 212° (decomp.; *chloroplatinate*). These, like the 2-phenyl compound (*loc. cit.*), are converted by alcoholic ammonia into 5-nitrobenz-4′ : 5′-*iso*thiazole, m. p. 151°; the action of sodium hydroxide, carbonate, or acetate is different in the case of the aryl compounds, the products being the *di*(*phenylimine*), m. p. 183°, and *di*-(p-*tolylimine*), m. p. 202°, of 4 : 4′-dinitro-2 : 2′-dialdehydodiphenyl disulphide, [ArN:CH·$C_6H_3(NO_2)$·S·$_2$]. The *di*(*methylimine*), m. p. 165° (decomp.), is obtained only by prolonged action of sodium carbonate solution. The di(arylimines) on chlorination in warm chloroform regenerate ɔ-nitro-2-arylbenz-4′ : 5′-*iso*thiazolium chlorides.

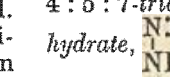
5-*Aminobenz*-4′ : 5′-iso*thiazole*, m. p. 130° [*hydrochloride*, m. p. 225° (decomp.); *acetyl* derivative, m. p. 172°], obtained by reduction of the ɔ-nitro-compound, is converted by decomposition of its *diazo*-compound in concentrated sulphuric acid into 5-*hydroxybenz*-4′ : 5′-iso*thiazole*, m. p. 156° [*benzoate*, m. p. 125°; *hydrobromide*, m. p. 240° (decomp.)]. Chlorination of the hydroxy-compound yields successively the 4-*chloro*-derivative, m. p. 195°, the 4 : 6-*dichloro*-derivative, m. p. 176°, and finally 4 : 4 : 6 : 6 : 7-*pentachloro*-ɔ-*hydroxy*-4 : 5 : 6 : 7-*tetrahydrobenz*-4′ : 5′-iso*thiazole*, m. p. 183°, reducible to 4 : 6 : 7-*trichloro*-5-*hydroxybenz*-4′ : ɔ′-iso*thiazole*, m. p. 234°, from which by oxidation with nitric acid 6 : 7-*dichloro*-4 : ɔ-*diketo*-4 : ɔ-*dihydrobenz*-4′ : 5′-iso*thiazole* (XI), m. p. 145°, is obtained. 4-*Bromo*- [m. p. 247° (decomp.)] and 4 : 6-*dibromo*- (m. p. 171°) derivatives are prepared by bromination of 5-hydroxybenz-4′ : 5′-*iso*thiazole. 4-*Nitro*-2-*hydroxybenz*-4′ : 5′-iso*thiazole*, m. p. 145°, and its 6-*bromo*-derivative, m. p. 185°, are obtained by direct nitration of the 4-bromo- and 4 : 6-dibromo-compounds, respectively, the former also from 5-hydroxybenz-4′ : ɔ′-*iso*thiazole. Oxidation of the 4 : 6-dibromo-compound with nitric acid in acetic acid yields 6-*bromo*-4 : 5-*diketo*-4 : 5-*dihydrobenz*-4′ : 5′-iso*thiazole*, m. p. 131° (decomp.; *anilino*-derivative described), also obtainable from 4-*chloro*-6-*bromo*-5-*hydroxybenz*-4′ : ɔ′-iso*thiazole*, m. p. 186°, the product of bromination of the 4-chloro-compound. 5-Aminobenz-4′ : 5′-*iso*thiazole (*benzylidene*-derivative, m. p. 101°, is not convertible into an acridine) couples with diazobenzene to form a *diazoamino*-compound, but with *p*-nitrodiazobenzene to give an *aminoazo*-compound, m. p. 225° [decomp.; *acetyl* derivative, m. p. 270° (decomp.)].

3-*Nitro*-6-*thiolbenzophenone*, m. p. 125° (*methyl ether*, m. p. 89°; *disulphide*, m. p. 177°), is prepared from 6-chloro-3-nitrobenzophenone, m. p. 86° (Ullmann and Ernst, A., 1906, i, 205), by the action of sodium sulphide and sulphur. By using less sulphide, there is obtained 4 : 4′-*dinitro*-2 : 2′-*dibenzoyldiphenyl sulphide*, m. p. 205°, and, by subsequent bromination in boiling carbon tetrachloride, 3-*nitro*-6-*bromothiolbenzophenone*, m. p. 146° (decomp.), which is converted by ammonia into 5-*nitro*-3-*phenylbenz*-4′ : 5′-*isothiazole*, m. p. 124°. The bromo-mercaptan reacts as usual with aniline, *p*-toluidine, and methylamine to give *benzisothiazolium bromides*, $NO_2{\cdot}C_6H_3{<}\begin{matrix}CPh\\S\end{matrix}{>}NRBr$, melting and decomposing at 303—306°, 319—320°, and 201°, respectively. By the action of aqueous ammonia or sodium hydroxide on a cold alcoholic solution of the phenobromide, there is formed 5-*nitro*-2-*anilinothiolbenzophenone* (XII), m. p. 147°, which is stable to alkali, but is converted by hydrogen bromide in cold benzene into aniline hydrobromide and the bromo-mercaptan. The *p*-tolyl compound similarly gives 5-*nitro*-2-*p*-*toluidinothiolbenzophenone*, m. p. 148°. The methobromide, on the

(XII.)  (XIII.)

other hand, gives with ammonia 5-nitro-2-phenylbenz-4′ : 5′-*iso*thiazole, and with sodium hydroxide a *compound*, $C_{14}H_{12}O_3N_2S$ (probably XIII), m. p. 110°, which regenerates the methobromide when ground with dilute hydrobromic acid. A similar, but much less stable, *compound* is obtained by the action of sodium hydroxide on 5-nitro-2-methylbenz-4′ : 5′-*iso*thiazolium bromide. 5-*Amino*-3-*phenylbenz*-4′ : 5′-*isothiazole*, m. p. 131° (*hydrochloride*, m. p. 266°; *acetyl* derivative, m. p. 109—110°), prepared by reduction of the 5-nitro-compound, is diazotised in 50% sulphuric acid, forming a *diazonium sulphate*, m. p. 166° (decomp.; couples normally with R-salt and dimethylaniline), which when heated in acetic acid gives 5-*hydroxy*-3-*phenylbenz*-4′ : 5′-*isothiazole*, m. p. 226° (decomp.; *acetate*, m. p. 100°; *methyl ether*, m. p. 80°), or in alcohol with copper powder gives 3-*phenylbenz*-4′ : ɔ′-*isothiazole*, m. p. 71°. From the 5-hydroxy-compound are prepared the 4-*chloro*- (m. p. 206°; *acetate*, m. p. 81°), 4 : 6-*dichloro*- (m. p. 216°; *acetate*, m. p. 170°), 4-*bromo*- (m. p. 216°; *acetate*, m. p. 89°), 4 : 6-*dibromo*- (m. p. 201°; *acetate*, m. p. 162°), and 4-*nitro*- [m. p. 220° (decomp.); *acetate*, m. p. 159°] derivatives; no keto-halide is formed. Nitration of 5-acetamido-3-phenylbenz-4′ : 5′-*iso*thiazole gives the 4-*nitro*-derivative, m. p. 222°, and on hydrolysis the 4-*nitro*-5-*amino*-compound, m. p. 208°, which gives with diazobenzene a *diazoamino*-compound, m. p. 140—143°.

Indazoles. [With H. TAMPKE.]—In the indazole series, linear quinolines, keto-chlorides, and *o*-quinones are obtainable, but the naphthoid character is not we marked. 5-Aminoindazole, m. p. 181° (von Auwers and Lange, A., 1922, i, 684; *acetyl* derivative, m. p. is best obtained as *sulphate* from the *zinc chloride* double salt, prepared by reduction of e nitro-compound in alcohol with zinc and hydrochloric acid. Methylation of 5-nitroindazole with methyl sulphate gives a mixture of 5-nitro-1-methylindazole, m. p. 129° (Noelting, A., 1904, i, 690), and 5-*nitro*-2-*methylindazole*, m. p. 163°, separable by extraction of the former with 20 parts of water at 90°. Both give the same *methiodide*, m. p. 203° (decomp.), and are reduced by ferrous sulphate and ammonia to the corresponding *amines*, m. p. 105° and 127°, respectively. Attempts to prepare 5-hydroxyindazoles by decomposition of diazotised 5-aminoindazole and -2-methylindazole give only azo-compounds, 5-*hydroxy*-4 : 5′-*azoindazole*, decomp. 290° (*triacetyl* derivative, m. p. 245°), and ɔ-*hydroxy*-2 : 2′-*dimethyl*-4 : 5′-*azoindazole*, m. p. 215° (decomp.; *acetyl* derivative, m. p. 206°). Isomeric 2-*chloro*-5-*nitrobenzophenonephenylhydrazones*, red crystals, m. p. 171°, and yellow crystals, m. p. 134°, separable by means of alcohol, are both converted by warm aqueous-alcoholic sodium hydroxide into 5-*nitro*-1 : 3-*diphenylindazole*, m. p. 181°, reducible by stannous chloride to the *amine*, m. p. 60—65° [*hydrochloride*, m. p. 312° (decomp.); *acetyl* derivative, m. p. 163°; stable *diazonium sulphate*, m. p. 165° (decomp.), coupling normally with R-salt, but giving no hydroxydiphenylindazole on decomposition]. Reduction with tin and hydrochloric acid gives 4-*chloro*-ɔ-*amino*-1 : 3-*diphenylindazole*, m. p. 149° (*acetyl* derivative, m. p. 233—234°). 5-Amino-1 : 3-diphenylindazole is converted by chlorination into a keto-chloride, 4 : 4 : 6 : 7 : 7-*pentachloro*-5-*keto*-1 : 3-*diphenyl*-4 : 5 : 6 : 7-*tetrahydroindazole*, m. p. 159° (decomp.), which on reduction yields difficultly separable *di*- and *tri*-*chloro*-5-*hydroxy*-1 : 3-*diphenylindazoles*. 6-Aminoindazole (Witt, Noelting, and Grandmougin, A., 1893, i, 46) forms a triacetyl derivative, 6-*diacetylamino*-2-*acetylindazole*, m. p. 133° (*monoacetyl* derivative, m. p. 248°; *diacetyl*, m. p. 184—185°), and is converted by Skraup's reaction into 5 : 6-*pyrazoloquinoline*,  , m. p. 278° (*methiodide*, m. p. 220°). 7-*Chloro*-6-*aminoindazole*, m. p. 179°, obtained in the form of its *acetyl* derivative, m. p. 215°, by chlorination of 6-acetamidoindazole, gives the linear 8-*chloro*-7 : 6-*pyrazoloquinoline*,  m. p. 228° (*hydrochloride*, m. p. 212°).

[With R. WELDERT.]—6-Aminoindazole is converted by chlorination into a *keto-chloride*, not obtained pure, which when heated with dilute acetic acid yields 4 : 5 : 7-*trichloro*-7-*hydroxy*-6-*keto*-6 : 7-*dihydroindazole hydrate*,  , m. p. 155—160° (decomp.), hydrolysable to an *o*-quinone. Reduction of the keto-chloride gives 4 : 5 : 7-*trichloro*-6-*hydroxyindazole*, m. p. 220° [decomp.; *diacetyl* derivative, m. p. 172° (decomp.)], which is readily converted into the same *o*-quinone, 4 : 5-*dichloro*-6 : 7-*diketo*-6 : 7-*dihydroindazole*, exploding above 350°, and the corresponding *dihydroxy*-compound (*diacetate*, m. p. 243°). The *o*-quinone condenses with aniline to form 5-*chloro*-4-*phenylimino*-6-*hydroxy*-7-*keto*-4 : 7-*dihydroindazole*, m. p. above 500° (decomp.), which is hydrolysed by hydrochloric acid to give the ɔ-*chloro*-6-*hydroxy*-4 : 7-

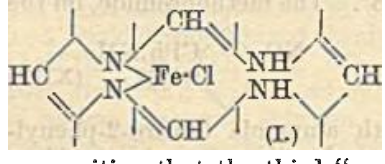
quinone (*acetate*, m. p. 174°). This is oxidised by chlorine to 5 : ɔ-*dichloro*-4 : 6 : 7-*triketo*-4 : 5 : 6 : 7-*tetrahydroindazole*, m. p. 183° (decomp.), and further by nitric acid to the 4 : 5 : 6 : 7-*tetraketone*, m. p. above 300° (decomp.). The dichlorotriketone and the tetraketone condense with *o*-phenylenediamine, giving, respectively, the *compounds*, $C_{13}H_6ON_4Cl_2$ and $C_{19}H_{10}N_6$, both melting and decomposing above 300°. Treatment of the tetraketone with sodium carbonate solutions converts it into the 5 : 6-*dihydroxy*-4 : 7-*quinone*, m. p. 290° (decomp.), similar in properties to *iso*naphthazarin. Pyrazolone-4 : 5-dicarboxylic acid, m. p. 244°, results from the oxidation of 4 : 5-*dichloro*-6 : 7-*diketo*-6 : 7-*dihydroindazole* with bleaching-powder solution. C. HOLLINS.

Thiazole series. I. Action of hydrochloric acid on allylthiosemicarbazide. S. C. DE (J. Indian Chem. Soc., 1927, **4**, 6—10).—δ-Allylthiosemicarbazide (I), when heated with hydrochloric acid in a sealed tube, yielded 2-*hydroxy*-5-*methylthiazole*, m. p. 200° (*acetyl* derivative, m. p. 242°; *benzoyl* derivative, m. p. 243°; *nitroso*-derivative, m. p. 138°). An unsuccessful attempt was made to prepare a thiazolehydrazine by hydrolysis of thiazoles similarly derived from α-substituted δ-allylthiosemicarbazides. The action of benzaldehyde on (I) gave α-*benzylidene*-δ-*allylthiosemicarbazide*, m. p. 125°, which, when treated as above, yielded 2-*benzylidenehydrazido*-5-*methylthiazole*, m. p. 141° (*acetyl* derivative, m. p. 119°; *benzoyl* derivative, m. p. 150°; *nitroso*-derivative, m. p. 120°), and this, on hydrolysis, gave the same hydroxymethylthiazole. From α-phenyl-δ-allylthiosemicarbazide was obtained 2-*phenylhydrazido*-5-*methylthiazole*, m. p. 94° (*acetyl* derivative, m. p. 190°; *benzoyl* derivative). Treatment of (I) with boiling phenylthiocarbimide yielded α-thiocarbanilido-δ-allylthiosemicarbazide, and this, when heated with hydrochloric acid, formed 2-*allylimino*-5-*thion*-1 : 3 : 4-*thiodiazole*, m. p. 136°. B. W. ANDERSON.

Action of carbamide on thiosemicarbazides: simultaneous formation of thiourazoles, aminoketothiodiazoles, endoxytriazole, and aminothioltriazoles. P. C. GUHA and P. C. SEN (J. Indian Chem. Soc., 1927, **4**, 43—50; cf. A., 1922, i, 875).—Carbamide was heated at 130—140° with various δ-arylthiosemicarbazides for 5—6 hrs. Four types of compound were simultaneously formed in each case, the formation of which can be explained by assuming that both *syn*- and *anti*-forms of the δ-arylthiosemicarbazides take part in the reaction. Thus from δ-phenylthiosemicarbazide 4-phenylthiourazole (*dimethyl* derivative, m. p. 110°); 2-*anilino*-5-*thiol*-1-*phenyl*-1 : 3 : 4-*triazole*, m. p. 210° (*methyl* derivative, m. p. 209°); 2 : ɔ-*endoxy*-1 : 3 : 4-*triazole*, m. p. 250° (*acetyl* derivative, m. p. 242°), and 5-*anilino*-2-*keto*-2 : 3-*dihydroxy*-1 : 3 : 4-*thiodiazole*, m. p. 246°, were obtained. Similarly, δ-(*p*-tolyl)thiosemicarbazide yielded 4-p-*tolylthiourazole*, m. p. 175° (*dimethyl* derivative, m. p. 142°); 2-p-*toluidino*-ɔ-*thiol*-1-p-*tolyl*-1 : 3 : 4-*triazole*, m. p. 187° (*benzoyl* derivative, m. p. 100°; *methyl* derivative, m. p. 178°); endoxytriazole, and 5-p-*toluidino*-2-*keto*-2 : 3-*dihydro*-1 : 3 : 4-*thiodiazole*, m. p. 227°, and δ-xylylthiosemicarbazide yielded 4-*xylylthiourazole*, m. p. 195° (*disulphide*, m. p. 240°); 2-*xylylamino*-5-*thiol*-1-*xylyl*-1 : 3 : 4-*triazole*, m. p. 200°; endoxytriazole, and 5-*xylylamino*-2-*keto*-2 : 3-*dihydro*-1 : 3 : 4-*thiodiazole*, m. p. 218—219°. The endoxytriazole was also formed when carbamide reacted with thiosemicarbazide or semicarbazide.

B. W. ANDERSON.

Catalytic hydrogenation of hæmin. R. KUHN, L. BRAUN, C. SEYFFERT, and M. FURTER (Ber., 1927, **60**, [*B*], 1151—1159).—Contrary to the observations of Fischer and Hahn (A., 1914, i, 887), hæmin adds only 1 mol. of hydrogen in sodium hydroxide solution in presence of palladised charcoal or platinum oxide; from this solution the product cannot be isolated, but if the operation is performed in a mixture of pyridine and chloroform, *dihydrohæmin*, $C_{34}H_{32}O_4N_4FeCl$, is obtained. The absorption spectra of hæmin and dihydrohæmin are very closely similar, but the substances are distinguished from one another by their catalytic activity and by the possession of 3 and 5 "active hydrogen atoms," respectively. The formation and properties of the new compound lend support to Küster's hæmin formula, and indicate the probable presence of the grouping (I). The observation that triphenylmethyl chloride does not evolve gas when treated with magnesium methyl halide deprives Fischer's supposition that the third "active hydrogen atom" of hæmin is actually the chlorine atom attached to iron of some of its support. The presence of 5, 3, 3, and 3 "active hydrogen atoms" in *meso*porphyrin dihydrochloride, *meso*porphyrin, the complex copper salt of *meso*porphyrin, and *meso*hæmin, respectively, appears to strengthen the view of Kunz and Kress that a FeCl group with univalent iron is present in hæmin.



(I.)

In aqueous-alkaline solution, the hydrogenation of hæmin at a platinum oxide or other contact cannot be caused to proceed beyond the dihydro-stage; in piperidine–chloroform, the strongly basic *perhydrohæmin* is formed, which gives the characteristic hæmin spectrum.

Ability of hæmin and its derivatives to effect the catalytic decomposition of hydrogen peroxide appears to be intimately connected with the chemical constitution of the molecule. The sequences of activity vary greatly with the experimental conditions.

H. WREN.

Hæmochromogen and hæmoglobin. W. KUSTER (Ber., 1927, **60**, [*B*], 1139—1141).—Repetition of Clement's work has shown that the action of sodium hydroxide on hæmin in absence of air and reducing agents yields a sodium salt of hydroxyhæmin which does not give the hæmochromogen spectrum unless, as in Clement's experiments, hydrazine hydrate is added to its solution. It is therefore unnecessary to abandon the hypothesis (cf. A., 1920, 315) that hæmin has its radical nature masked because the unsaturated position is not localised.

Hæmatin is converted by hydrogen bromide in acetic acid into two *porphyrins*, $C_{34}H_{34}O_5N_4$ and $C_{34}H_{35}O_3N_4Br$; the latter substance is a monobasic acid containing one methoxyl group. H. WREN.

β-Pyridyl-α-pyrrolidine (nornicotine). M. POLONOVSKI and M. POLONOVSKI (Compt. rend., 1927, 184, 1333—1335; cf. A., 1926, 367).—*N-Acetylnornicotine*, $[\alpha]_D$ −13·6°, and *N-benzoylnornicotine*, prepared from the *N*-oxide of nicotine, give on hydrolysis, *nornicotine*, $[\alpha]_D$ −20° [*picrate*, m. p. 135° (*mono-* and *di-hydrochloride*), *chloroaurate*, m. p. 210—212° (decomp.), *nitroso*-derivative]. E. H. SHARPLES.

Vasicine—an alkaloid present in *Adhatoda vasica*. II. T. P. GHOSE (J. Indian Chem. Soc., 1927, 4, 1—5).—Vasicine, when treated with phosphorus oxychloride and pentachloride, yields *chlorovasicine*, $C_{11}H_{11}N_2Cl$, m. p. 136—137°, which on reduction gives a *base*, $C_{11}H_{12}N_2,0{\cdot}5H_2O$, m. p. 87—88° (*hydrochloride*, m. p. 255—256°; *chloroplatinate*). Vasicine is oxidised by potassium permanganate to 4-hydroxyquinazoline, and yields *o*-aminobenzoic and acetic acids when fused with potassium hydroxide. Thus vasicine is probably either 2-propyl- or 2-*iso*propyl-4-hydroxyquinazoline. B. W. ANDERSON.

Microchemical reactions of codeine. M. WAGENAAR (Pharm. Weekblad, 1927, 64, 671—676).—A summary of the optical properties of the alkaloid, and of its commoner reactions. S. I. LEVY.

Microchemical detection of alkaloids. II. A. HEIDUSCHKA and N. I. MEISNER (Arch. Pharm., 1927, 265, 455—461).—Tables are given showing the smallest quantities of caffeine, theobromine, strychnine, brucine, quinine, morphine, and codeine that can be detected by various reagents in simple aqueous solution and in a 2% aqueous solution of lactic acid. W. A. SILVESTER.

Identification of alkaloids. W. M. CUMMING (Proc. Roy. Phil. Soc. Glasgow, 1927, 54, 26—31).—See A., 1925, i, 572.

Phosphino-magnesium compounds. A. JOB and G. DUSOLLIER (Compt. rend., 1927, 184, 1454—1456).—Phenylphosphine and magnesium ethyl bromide react in benzene–ethereal solution to give ethane in amount corresponding with the equation $PH_2Ph+2PhMgBr=PPh(MgBr)_2+2C_2H_6$. The greenish-brown solution probably contains dimagnesium phenylphosphine dibromide. Since it is decomposed by water, yielding phenylphosphine, and affords a white precipitate with carbon dioxide, probably of $PPh(CO_2MgBr)_2$, whilst with ethyl chloroformate in benzene it gives *ethyl phenylphosphinodicarboxylate*, $PPh(CO_2Et)_2$, b. p. 150—153°/4—5 mm. Similarly, diphenylphosphine affords *magnesium diphenylphosphine bromide*, $PPh_2{\cdot}MgBr$, yielding *ethyl diphenylphosphinocarboxylate*, b. p. 185—188°/5—6 mm. Phosphine and magnesium ethyl bromide afford a white powder in which two phosphine hydrogen atoms have apparently been replaced by magnesium bromide. Only one hydrogen atom in phenylphosphine could be replaced by zinc iodide when treated with zinc ethyl iodide (cf. Gal, A., 1883,). R. BRIGHTMAN.

Organic compounds of arsenic. V. Electrolytic reduction of 3-nitro-4-hydroxyphenylarsinic acid. K. MATSUMIYA and H. NAKATA (M Coll. Sci. Kyoto, 1927, 10, 199—210).—Electrolytic reduction (in an atmosphere of carbon dioxide) of 3-nitro-4-hydroxyphenylarsinic acid with a mercury cathode in presence of hydrochloric acid gives 3-amino-4-hydroxyphenylarsine hydrochloride or 3 : 3′-diamino-4 : 4′-dihydroxyarsenobenzene hydrochloride (salvarsan), according as the hydrochloric acid is below or above 4·7*N*. The arsine is the sole product if the hydrochloric acid is replaced by sulphuric acid of varying concentration. The effects of different cathodes, current density, and temperature were studied; the results are tabulated. H. BURTON.

Manufacture of asymmetrically acylated amino-derivatives of arylarseno-compounds. G. NEWBERY, and MAY & BAKER, LTD.—See B., 1927, 507.

Manufacture of asymmetrical aryl-arseno-compounds. G. NEWBERY, F. J. PAXON, and MAY & BAKER, LTD.—See B., 1927, 507.

Porphyrins. E. MERTENS (Z. physiol. Chem., 1927, 167, 179—187).—The spectrochemical reaction with bromine (Schumm, A., 1926, 538) and the grating-spectrometer of Schumm (this vol., 437) are used to differentiate between the different porphyrins, spectra of the bromine compounds showing marked differences. Aqueous and alcoholic solutions of bromine give similar results, except in the case of mesoporphyrin, and this compound can be distinguished from all the other porphyrins investigated by this alcoholic bromine test. Eight preparations of Nencki's hæmatoporphyrin gave absorption bands practically identical with those previously recorded by Schumm (A., 1914, ii, 401). A. WORMALL.

Isolation of some hitherto undescribed products of hydrolysis of proteins. IV. S. B. SCHRYVER and H. W. BUSTON (Proc. Roy. Soc., 1927, B, 101, 519—527).—The diamino-nitrogen fraction of the amino-acids formed from gelatin by hydrolysis is increased if the gelatin is first treated with cold hydrochloric acid. This is entirely accounted for by an increase in the arginine and lysine and by the presence of *dl*-lysine. It is improbable that the *dl*-lysine arises from racemisation of the active lysine normally present (cf. A., 1926, 749, 1049). W. O. KERMACK.

Mol.-wt. determinations of proteins in phenol. N. TROENSEGAARD and J. SCHMIDT (Z. physiol. Chem., 1927, 167, 312—313).—A reply to the criticism by Cohn and Conant (A., 1926, 891) of a previous paper (A., 1924, i, 581). A. WORMALL.

Analysis of proteins and the products of their degradation by adsorption. E. WALDSCHMIDT-LEITZ and A. SCHAFFNER (Ber., 1927, 60, [*B*], 1147—1151).—The product is submitted to fractional adsorption, and comparative determinations of some analytical characteristic of it are made in the residual solutions. The constancy or inconstancy of the quotients from the data thus supplied (*e.g.*, nitrogen content, free amino-group content, or specific rotation) is a criterion of the homogeneous or heterogeneous nature of the product. The behaviour of clupeine, salmine, scombrine, and histone towards ferric hydroxide causes them to be regarded as homogeneous.

Tryptoclupeon in neutral or acid media is separated by ferric hydroxide into a more complex, readily adsorbed portion, the individuality of which is not established at a less complex, difficultly adsorbed portion which appears homogeneous as judged by the constancy of the specific rotation or the ratio N/NH_2 in the residual solutions. In alkaline solution tryptoclupeon behaves as an individual towards ferric hydroxide, since the basic properties of the components are too pronounced and too similar to permit separation under these conditions. H. WREN.

Volumetric determination of hexamethylenetetramine. (MRS.) C. KOLLO and B. N. ANGELESCU (Bul. Soc. Chim. Romania, 1926, **8**, 17—20).—Hexamethylenetetramine (0·15—0·2 g.) is treated with an excess of 0·5*N*-picric acid solution, and after separation of the precipitated hexamethylenetetramine picrate, m. p. 157°, the excess of picric acid is determined by titration with standard sodium hydroxide solution. The method is accurate to ±0·3%, and can be used for the determination of small amounts of hexamethylenetetramine in wine. H. BURTON.

Biochemistry.

Determination of respiratory quotient of small animals. L. G. WESSON (J. Biol. Chem., 1927, **73**, 499—506).—An apparatus of the closed-circuit type is described, in which the air is circulated by a pump; the carbon dioxide is determined by absorption in standard sodium hydroxide solution, with subsequent titration; the oxygen used up is replaced from a graduated container, so as to maintain a constant pressure, and is thus determined volumetrically.
C. R. HARINGTON.

Blood as a physicochemical system. V. Composition and respiratory exchanges of normal human blood during work. A. V. BOCK, D. B. DILL, L. M. HURXTHAL, J. S. LAWRENCE, T. C. COOLIDGE, M. E. DAILEY, and L. J. HENDERSON (J. Biol. Chem., 1927, **73**, 749—766; cf. A., 1924, i, 780).—Tables, and a nomographic representation, are given of the changes occurring in normal human blood as the result of work sufficient to raise the oxygen consumption to seven times the basal value. By such work, the oxygen capacity was raised about 10%; there was a 10% increase in the concentration of serum-proteins and a slight increase in that of base; the lactic acid is increased, and the hydrogen carbonate, to a much less extent, decreased.
C. R. HARINGTON.

Colorimetric determination of oxygen saturation of blood. J. HOLLÓ and S. WEISS (Biochem. Z., 1927, **185**, 373—378).—A colorimeter of the Duboscq type is so modified that a layer of hæmolysed blood 1 mm. thick can be matched against a 20 mm. layer of the same blood 20 times diluted and fully oxygenated or fully reduced plus a layer of similarly diluted blood fully reduced or fully oxygenated. The thickness of the last-mentioned layer, determined by experiment, indicates the proportion of hæmoglobin to oxyhæmoglobin, or *vice versa*, in the undiluted blood. The error of the method is about 5%.
C. R. HARINGTON.

Total carbon dioxide content of the blood of marine and of fresh-water invertebrates. M. DUVAL and P. PORTIER (Compt. rend., 1927, **184**, 1594—1596).—The total carbon dioxide content of the blood of marine invertebrates ranges from 5 to 17 c.c. (at 0° and 760 mm.) per 100 c.c. of blood, that of fresh-water invertebrates from 21·5 to 62 c.c. These values do not, apparently, bear any relationship to the amount of carbon dioxide in the particular water in question. The corresponding value for the blood of terrestrial gastropods is from 45 to 60 c.c. Figures are given for typical crustaceans, gastropods, and cephalopods. G. A. C. GOUGH.

Regulation of [H·] of the blood. I. Course of the potential of blood measured with the quinhydrone electrode. II. Influence of process of dissolution of quinhydrone on course of the potential. III. Potentials of serum, plasma, red blood-corpuscles, and hæmoglobin solutions. S. K. LIU (Biochem. Z., 1927, **185**, 242—254, 255—262, 263—274).—I. The quinhydrone electrode indicates a slightly higher p_H for blood than does the hydrogen electrode. The potential of blood *diluted* with 3 vols. of water as observed by the quinhydrone method, using a platinum electrode, shows a sharp rise in the first minute, a constant level for 1—2 min., and thereafter a steady fall of about 1 millivolt per min.; the effect is exaggerated by insufficient mixing of the solution. A less marked variation is obtained by the use of a gold electrode.

II. The variation in potential observed with quinhydrone, owing to the slow process of dissolution of the substance, is largely suppressed by the presence of buffers; the more acid the solution the less the variation and the more easily it is suppressed; whole blood is a much more efficient buffer, in this respect, than a simple phosphate mixture or than urine.

III. Potential variations, of the type described above for diluted whole blood, are observed in an exaggerated form with diluted serum and plasma and, to a much less extent, with solutions of hæmoglobin and suspensions of red blood-corpuscles which are rich in buffer substances. In view of these results, the quinhydrone electrode is not adapted to the investigation of poorly-buffered tissue fluids.
C. R. HARINGTON.

Permeability of human red blood-corpuscles. A. M. WAKEMAN, A. J. EISENMAN, and J. P. PETERS (J. Biol. Chem., 1927, **73**, 567—580).—After addition to human blood *in vitro* of various sodium and potassium salts in amounts of 29·1—100·4 milliequiv. of base per 1000 c.c. of blood-serum, the changes observed, as between red blood-corpuscles and serum, consisted entirely in a transfer of water, carbon dioxide, and chlorine across the cell membrane; no evidence could be obtained that the latter was permeable to the cations. C. R. HARINGTON.

Determination of chlorine in organs and in blood. M. DELAVILLE and D. BROUN (Bull. Soc. Chim. biol., 1927, 9, 621—623).—The dried material is destroyed by fuming nitric acid in presence of silver nitrate at 100°. Small additions of potassium permanganate accelerate the decomposition, and the excess may be removed by means of oxalic acid. The silver chloride so obtained is purified by reprecipitation, dried, and weighed. E. A. LUNT.

Distribution of non-protein sulphur of the blood between serum and corpuscles. L. REED and W. DENIS (J. Biol. Chem., 1927, 73, 623—626).—In human blood, inorganic sulphates are present almost exclusively in the plasma, whilst in the dog, the ox, and the goat they are distributed more or less equally between plasma and corpuscles. Neutral sulphur, in all species investigated, is present for the most part in the corpuscles. C. R. HARINGTON.

Proteolytic enzymes in blood-serum. VIII. Possibility of fundamental unity of blood enzymes. M. VON FALKENHAUSEN (Biochem. Z., 1927, 185, 334—343).—Galvialo's preparation (*ibid.*, 177, 266) shows diastatic, lipolytic, and proteolytic activity in a non-specific alkaline medium; in the first two cases, the activity is somewhat enhanced by the presence of the electrolytes of saliva and of duodenal juice, respectively, but the proteolytic activity is greater in the alkaline medium than in presence of the electrolytes of gastric juice; moreover, by fractional heating the various enzymic activities are destroyed at different temperatures, so that it is improbable that they pertain to a single substance. C. R. HARINGTON.

Sugar content of capillary and venous blood after muscular activity. M. DORLE and W. LIEHR (Biochem. Z., 1927, 185, 365—372).—Moderate localised muscular activity raises the concentration of sugar in the capillary blood of the limb immediately concerned; activity carried to the point of fatigue reverses the effect, the venous blood-sugar in both cases being little affected. General moderate muscular activity raises the sugar content of both capillary and venous blood of relatively inactive parts; extreme general activity has the reverse effect on capillary blood-sugar and leaves venous blood-sugar unchanged. Variations in blood-sugar could not, in these experiments, be related to changes in lactic acid. C. R. HARINGTON.

Determination of blood-sugar by the method of Hagedorn and Jensen. L. CSIK and A. JUHASZ (Biochem. Z., 1927, 185, 420—422; cf. A., 1923, ii, 265, 440).—The blood is weighed in a special vessel on a torsion balance. C. R. HARINGTON.

Micro-determination of sugar in blood. E. MARTINSON (Biochem. Z., 1927, 185, 400—404).—The accuracy of the method of Hagedorn and Jensen (A., 1923, ii, 265, 440) depends on exactness of measurement of the potassium ferricyanide; by allowing 5 min. for drainage of the latter from the pipette before proceeding to the titration, the error of the method is reduced to 2%. C. R. HARINGTON.

Ovomucoid. J. NEEDHAM (Biochem. J., 1927, 21, 733—738).—The carbohydrate content of the ovomucoid molecule increases as the egg develops, only 7·4% calculated as dextrose being present on the 5th day, against 15·4% on the 18th day. The average figure is about 11·5%. An enzyme which hydrolyses ovomucoid appears to exist in the yolk and the yolk-sac of the hen's egg at the 5th day of development, possibly also in the white and the blastoderm, but not in the embryo. S. S. ZILVA.

Application of the Copaux method for the determination of small amounts of phosphorus in tissues. (MME.) H. HINGLAIS (Bull. Soc. Chim. biol., 1927, 9, 540—553).—The Copaux method of determining phosphorus by measuring the volume of a water–ether–phosphomolybdic acid complex can be adapted to give accurate results and has been applied successfully to plant-tissues. E. A. LUNT.

Determination of iron in muscle by means of titanium chloride. V. HENRIQUES and (MME.) A. ROCHE (Bull. Soc. Chim. biol., 1927, 9, 527—539).—Experiments on the non-pigment iron content of muscle from the cat, dog, rabbit, rat, codfish, eel, lobster, frog, and mussel have failed to establish a constant value for any given species. The mean value for the lobster and mussel is sensibly the same as that of the rabbit. E. A. LUNT.

Adenylic acid and muscle function. I. Presence of adenylic acid in skeletal muscle. G. EMBDEN and M. ZIMMERMANN (Z. physiol. Chem., 1927, 167, 137—140).—Appreciable quantities of this acid have been isolated from rabbit muscle. After recrystallisation from hot water, the dried substance had m. p. 195° (uncorr.). The physiological significance of this acid and its relationship with inosic acid are briefly discussed. A. WORMALL.

Cystine content of hair and other epidermal tissues. R. H. WILSON and H. B. LEWIS (J. Biol. Chem., 1927, 73, 543—553).—The following values were obtained for the cystine content of various keratin-containing tissues, as determined by the colorimetric method of Folin and Looney (A., 1922, ii, 539); human hair 15·6—21·2%, sheep wool 8·0—10·9%, feathers 7·05—12·2%, rabbit hair 11·9—14·0%, tortoise shell 6·4—8·1%, rat hair 14·1%, cat hair 13·1%, dog hair 18·0%; human skin and connective tissue 1·82—2·34%. For the keratin of any given species the nitrogen : sulphur ratio is more constant than the actual content of nitrogen and sulphur. The figures given above are higher than those obtainable by the gravimetric method of determination, owing to the losses inherent in this method due to the solubility of cystine. No considerable amounts of non-cystine sulphur were detected, nor could any correlation be found between the cystine content of the hair and the age, sex, or colouring of the individual. C. R. HARINGTON.

Presence of arginine in the spleen. W. S. GULEVITSCH and S. J. KAPLANSKI (J. Russ. Phys. Chem. Soc., 1926, 58, 620—622; cf. Gulevitsch and Jochelson, A., 1901, ii, 29).—Fresh ox-spleen was rapidly extracted with water at 60°, to avoid autolysis of the proteins, and the extract treated in turn with phosphotungstic acid, silver nitrate, copper nitrate, bismuth iodide, and absolute alcohol, the solid in

each case being removed and examined. No trace of arginine could be found, its detection by Gulevitsch and Jochelson (*loc. cit.*) being due to autolysis. The autolysis of spleen at the ordinary temperature is more rapid than that of tendon, liver, and spleen, being detectable after 3 hrs., as compared with 9 and 6 hrs. for the other organs. The chemical analysis of the spleen, consequently, should be carried out not later than 2 hrs. after the death of the animal.

M. Zvegintzov.

Compounds extracted from tendon. XXIV. Carnosine and carnitine as specific constituents. W. S. Gulevitsch (J. Russ. Phys. Chem. Soc., 1926, **58**, 610—619).—A review of the work of the author and others, and a description and discussion of the chemistry and physiology of carnosine and carnitine.

M. Zvegintzov.

Detection of iron in ashed sections of spinal cord. W. Keuscher (Mikrokosmos, 1927, **20**, 126—127). Chemical Abstracts.

Shell-depositions in oysters. J. H. Orton and C. Amirthalingam. **Composition of chalky deposits on the shells of *Ostrea edulis*.** H. O. Bull (J. Marine Biol. Assoc., 1927, **14**, 935—954).—The function of the chalky deposit is to fill in rapidly grooves and hollows which are inimical to efficient functioning in the changing needs of the individual.

The chalky deposits consist of a powder mainly crystalline in appearance under the microscope, and of the composition, $CaCO_3$, 78·5%; water and organic matter 19·2%; undetermined, 2·3%.

W. Robson.

Tubular sheath of *Spirographis Spallanzani*. S. Frankel and C. Jellinek (Biochem. Z., 1927, **185**, 379—383).—After exhaustive digestion of the sheath secreted by *Spirographis Spallanzani*, first with pepsin and then with trypsin, there was obtained an insoluble residue which gave no protein reactions, except Millon's reaction. After purification by dissolving in ammonia and precipitation with acetic acid, the substance had the formula $C_{38}H_{68}O_{17}N_8S$; it had two acidic groups, one of which was a sulphonic acid group. Hydrolysis with hydrochloric acid and analysis of the products indicated the presence of two tyrosine groups and one arginine group in the molecule. C. R. Harington.

***Limulus polyphemus*.** S. Frankel and C. Jellinek (Biochem. Z., 1927, **185**, 384—388).—The carapace of *Limulus polyphemus* differs from that of typical crustaceans in containing no calcium carbonate, and in containing 70% of protein; the chitin obtained after removal of the protein has a higher content of carbon and hydrogen and a lower content of nitrogen than chitins which have been previously investigated. C. R. Harington.

Edible Holothuria. S. Frankel and C. Jellinek (Biochem. Z., 1927, **185**, 389—391).—Certain edible Holothuria were exhaustively digested first with pepsin and then with trypsin. More than 90% of the substance of the animals passed into solution under the action of the pepsin. Figures are given for the nitrogen distribution in the substance of the animals, determined by the method of Van Slyke.

C. R. Harington.

Reaction changes of human saliva. G. W. Clark and K. L. Carter (J. Biol. Chem., 1927, **73**, 391—404).—Whilst saliva obtained directly from the glands is only very slightly more acid than saliva freshly expectorated, resting saliva is markedly more acid than activated saliva obtained by chewing paraffin wax. The carbon dioxide content of saliva kept in an open vessel alters scarcely at all, owing, probably, to equilibrium between loss and production of carbon dioxide. Chloroform is without effect on the formation of carbon dioxide, and slightly inhibits that of ammonia; mercuric chloride strongly inhibits both processes; these processes are therefore regarded as being enzymic rather than bacterial in character.

C. R. Harington.

Constituents of sweat, urine, and blood. I. Chlorides. G. A. Talbert and C. O. Haugen. **II. Total nitrogen of sweat and urine; total non-protein nitrogen of blood.** G. A. Talbert, S. Silvers, and W. Johnson (Amer. J. Physiol., 1927, **81**, 74—80, 81—85).—I. There is some correlation of the concentration of chlorides in the sweat with that in the blood, but none with the chlorides in the urine.

II. The total nitrogen of the sweat is, in general, more than double the non-protein nitrogen of the blood, but there is no definite correlation between these quantities or between them and the total nitrogen of the urine. R. K. Cannan.

Determination of bismuth in urine. H. Baggesgaard-Rasmussen, K. A. Jackerott, and S. A. Schou (Dansk Tidsskr. Farm., 1927, **1**, 391—403).—Small amounts of bismuth present in urine (0·05—0·4 mg.) can be determined as follows: 100 c.c. of urine are mixed with 50 c.c. of 68% nitric acid and cautiously heated until the mass is almost dry. After cooling, 3 c.c. of sulphuric acid are added, and the mixture is evaporated until fumes are evolved; 1—2 c.c. of nitric acid are added, drop by drop, and the evaporation is continued: more nitric acid must be added if necessary, until the liquid is quite colourless after cooling. Finally, 10 c.c. of a saturated solution of oxalic acid are added, and the solution is evaporated until copious fumes appear, to ensure complete removal of nitric acid. The cooled liquid is diluted with hot water to 20 c.c., filtered, and 1 c.c. each of 10% potassium iodide, 15% sodium citrate, and 10% sodium sulphite solutions are added. The resultant yellow liquid is diluted to 25—50 c.c., and the tint matched in a colorimeter against a standard solution of bismuth; the solution must not be exposed to direct sunlight, nor kept for very long before comparison, or incorrect results will be obtained owing to liberation of iodine. Chlorides render the result low, but mercuric salts and the salts usually present in urine have no effect on the reaction; the presence of ferric salts leads to high results, but their effect can be counteracted by the addition of citric acid. Instead of employing a colorimeter, the light absorption of the solution for the blue line 4359 Å. may measured, the absorption being compared with that produced by a similar solution of known bismuth content. The results are accurate to about 5%.

H. F. Harwood.

Chemistry of cancerous tissue. ENSELME and (MME.) ENSELME (Compt. rend., 1927, **184**, 1353—1354).—From a study of the amounts of lipoid and nucleic phosphorus in cancerous and normal tissue both before and after irradiation with ultra-violet light, the following conclusions are reached. In cancerous tissue there is a notable increase of nucleic phosphorus compared with that in the healthy organ; *e.g.*, in tumours of the breast, uterus, and thyroid the nucleic phosphorus (mg./100 g. of fresh tissue) varies from 28 to 30 and in the normal tissues of the same organs the amounts are 18, 13, and 21, respectively. Irradiation causes this excess to disappear, and the nucleic phosphorus content of the irradiated cancer is no larger than that of the normal tissue. On the other hand, lipoid phosphorus increases in the irradiated tumour at the same time as the proportion of fat, and thus under the influence of irradiation the tendency is for the nucleic constituents to be decreased and for the cancerous tissue to be transformed into fat. E. H. SHARPLES.

Nitroprusside reaction in normal tissues and tumours. E. L. KENNAWAY and I. HIEGER (Biochem. J., 1927, **21**, 751—759).—Analyses of normal tissues and of tumours in man and in the fowl show that tumours are not distinguished by any deficiency in glutathione. S. S. ZILVA.

Chemical constitution of gallstones and bile in relation to cholelithiasis. A. A. F. PEEL (Z. physiol. Chem., 1927, **167**, 250—284).—A chemical analysis has been made of the whole stone, kernel, and cortex of the various types of gallstones and an analysis of the bladder bile, in an attempt to determine the chemical differences between the different groups of stones and between the different parts of these stones, and the extent to which these differences may be attributed to changes in the bile. The precipitation of cholesterol crystals cannot be explained simply by a rise in the cholesterol content of bladder bile. The three main groups of stone kernels—pure cholesterol stones, pure pigment stones, and cholesterol–pigment–chalk stones—are quite different chemically, whilst the stones of each group give more or less constant values. These differences in the different groups are attributed to different changes in the bile, and a transformation of any stone into one of a different type is regarded as improbable. That condition of bile, mainly a metabolic change such as an increase in the cholesterol content, which leads to the formation of a pure cholesterol stone is entirely different from that producing a cholesterol–pigment–chalk kernel. For the formation of a pure pigment stone, the presence of copper is necessary. Three other types of stones are mentioned, and single stones of two of these groups have been examined. The chemical analysis of the different stones supports the morphological classification of Aschoff.

A. WORMALL.

Does diabetic blood-serum influence the permeability of cells to dextrose? E. BISSINGER (Biochem. Z., 1927, **185**, 229—237).—The uptake of dextrose by the surviving liver of the frog is largely suppressed by addition of diabetic (frog or human) blood-serum to the perfusion fluid; at the same time the amount of free dextrose in the liver is greater than can be accounted for by that taken up during the perfusion; it appears therefore that the effect of the diabetic serum is to slow down the process of diffusion of dextrose by increasing the concentration of the latter in the liver cells, rather than that it alters the permeability of the cell-wall (cf. Geiger and Loewi, Pflüger's Arch., 1923, **198**, 633).

C. R. HARINGTON.

Blood-sugar. II. Magnitude of non-dextrose fraction under various conditions. B. SJOLLEMA (Biochem. Z., 1927, **185**, 355—364; cf. this vol., 476).—Cows suffering from *post partum* paralysis, and excreting lactose in the urine, show an increase in the non-dextrose fraction of the blood-sugar; in ketosis a similar increase is observed, but is accompanied by a decrease in the dextrose. In glycolysis of ox-blood, the non-dextrose fraction is very little decreased, and in starvation in rabbits it is somewhat increased. In diabetic blood, it is of normal magnitude and it is not markedly affected by administration of insulin. Hexosemonophosphates are partly adsorbed by charcoal in presence of acetic acid, but not in presence of ether; compounds of this type may therefore form part of the non-dextrose fraction of the blood-sugar. The latter fraction is contained for the most part in the red blood-corpuscles.

C. R. HARINGTON.

Inorganic salt content of blood and the acid–alkali equilibrium of blood in fever. I and II. M. AKIYA (Proc. Imp. Acad. Tokyo, 1927, **3**, 187—190).—Clinical data on the variation of the calcium, sodium, potassium, chlorine, and protein content of serum, the hæmoglobin and solid content of blood in typhus fever are compared with the corresponding data relating to the pyrexia following piqure in dogs.

E. A. LUNT.

Chemical composition of the liver in experimental spirochætosis. J. INADA (Proc. Imp. Acad. Tokyo, 1927, **3**, 175—176).—The influence of icterohæmorrhagic spirochætosis and of yellow fever on the water, solid matter, total and non-protein nitrogen, coagulable protein, glycogen, fat, and sodium chloride content of the liver of guinea-pigs has been investigated. E. A. LUNT.

Cerebrospinal fluid in nephritis. J. D. LYTTLE and L. ROSENBERG (Arch. Int. Med., 1927, **39**, 808—816).—In chronic nephritis, the cerebrospinal fluid is usually clear, has a cell-count varying from 2 to 16 per mm.^{3} (the cells are all lymphocytes), has an increased non-protein nitrogen content (the ratio of the cerebrospinal non-protein nitrogen to the blood non-protein nitrogen, normally 46%, rises to 80% in presence of nitrogen retention), shows an unaltered chloride content, an increase in albumin and globulin, and an increased value for the ratio of the blood-sugar to the cerebrospinal sugar. In acute nephritis, the cerebrospinal fluid in absence of uræmic manifestations is normal; in their presence it shows a rise in protein content. E. A. LUNT.

Total sugar content of cerebrospinal fluid and the influence of syphilis. B. GLASSMANN, L. ZWILLING, and M. ISRAILSOHN (Z. physiol. Chem., 1927, **167**, 245—249).—The total sugar values for

47 cases, obtained by the colorimetric method of Glassmann (A., 1926, 192), varied from 0·083 to 0·183%, with a mean value of 0·135%. In three cases of syphilis only were definitely high sugar values obtained. No relationship was found between the total sugar content and the results of the Wassermann and the mastic reactions or the lymphocyte count. The polysaccharide content of the fluid is 0·085% (as dextrose), but the protein-sugar of the normal fluid is very small. A. WORMALL.

Rickets in rats. I. Metabolism on diets high in calcium and low in phosphorus. II. Effect of adding phosphate to diet of rachitic rats. S. KARELITZ and A. T. SHOHL (J. Biol. Chem., 1927, **73**, 655—664, 665—677).—I. In young rats suffering from rickets as the result of a diet lacking vitamin-*D*, rich in calcium, but poor in phosphorus, the retention of calcium is 50% and that of phosphorus 20% of the normal.

II. Addition of phosphate to the diet of such rats, to bring the Ca : P ratio of the diet to 1 : 1, no other factors being altered, much improves the retention of calcium and phosphorus and causes healing of the rickets. C. R. HARINGTON.

Variation in relative weight and composition of the dog's heart in certain pathological conditions. P. JUNKERSDORF and S. HANISCH (Arch. exp. Path. Pharm., 1927, **123**, 231—251).—A *resumé* is given of published and hitherto unpublished results on the variation in relative weight, dry weight, glycogen and fat content of the dog's heart induced by various diets, total starvation, pancreatic and phloridzin diabetes, and administration of adrenaline, insulin, or choline. E. A. LUNT.

Influence of menstruation on the concentration of calcium in blood-plasma. H. SHARLIT, J. A. CORSCADEN, and W. G. LYLE (Arch. Int. Med., 1927, **39**, 780—786).—Observations made on three subjects over a period of 2½ months indicate a rise in the calcium content of the blood-plasma at the approach and onset of menstruation. E. A. LUNT.

Modifications of the urinary deposit after muscular exercise. M. G. CARPENTIER and M. M. BRIGAUDET (Bull. Soc. Chim. biol., 1927, **9**, 580—587).—Microscopical examination of the urinary deposit of four subjects before and after muscular exercise suggests that incipient albuminuria and hæmaturia may be detected by such a procedure. E. A. LUNT.

Intermediate carbohydrate metabolism. II. Ketosis in phloridzin diabetes. III. Vital action of dextrose in phloridzin diabetes. M. WIERZUCHOWSKI (J. Biol. Chem., 1927, **73**, 417—444, 445—458).—II. After administration of 1—4 g. of dextrose per kg. body-weight to completely phloridzinised dogs, 81·5% was recovered as extra dextrose in the urine; a constant sparing effect on the nitrogen metabolism was observed, and, parallel with this, a decreased excretion of ketones, 1 g. of dextrose ingested accounting for 0·1 g. of acetone. The view is therefore supported that small amounts of ingested dextrose are oxidised in the phloridzinised animal. Administration of olive oil to a phloridzinised dog causes increased excretion of ketones, and injection of adrenaline produces coma.

III. In phloridzin diabetes, ingestion of dextrose has a twofold physiological action. By raising the blood-sugar it prevents or relieves the hypoglycæmic convulsions which otherwise ensue, and by its ketolytic action it relieves the symptoms of ketosis. C. R. HARINGTON.

Lactic acid formation in muscle extract. H. A. DAVENPORT and M. COTONIO (J. Biol. Chem., 1927, **73**, 463—475).—Fresh extracts of muscle were incubated at 25° under various conditions and the changes observed in lactic acid, phosphate, free sugar, and total sugar, the latter being determined by acid hydrolysis. No marked changes were observed in untreated extracts or in extracts to which were added phosphate alone or phosphate with fluoride. When, however, glycogen was added, lactic acid formation increased (except in presence of fluoride), whilst phosphate and total sugar decreased; increases in the free sugar owing to the action of muscle amylase on the glycogen were observed. In all cases, the difference between the decrease of total sugar and the increase of lactic acid was approximately equivalent to the decrease of phosphate; the hypothesis of the intermediate participation of a hexosephosphate in the process of lactic acid formation is therefore supported. C. R. HARINGTON.

Succinic acid in muscle. II. Metabolic relationships of succinic, malic, and fumaric acids. D. M. NEEDHAM (Biochem. J., 1927, **21**, 739—750).—In minced muscle suspended in buffer solution and placed alternately under anaerobic and aerobic conditions, there is a rise in succinic acid when in nitrogen and a fall when in oxygen. The total amount of succinic, fumaric, and malic acids also rises in anaerobiosis and fall on oxygenation. The succinic acid produced in nitrogen is formed from some other source than reversibly from fumaric and malic acids, and it is oxidised in oxygen further than to the latter acids. The malic acid content is highest in the fresh muscle. It falls to practically zero in nitrogen, and on admission of oxygen it may rise very slightly. The total amount of the acids was determined by precipitating the silver salts and titrating the latter with potassium thiocyanate. After filtering off the silver thiocyanate, malic acid was determined polarimetrically in the filtrate as the molybdenum compound. S. S. ZILVA.

Fate of sugar in the animal body. VI. Sugar oxidation and glycogen formation in normal and insulin-treated rats during absorption of lævulose. G. T. CORI and C. F. CORI (J. Biol. Chem., 1927, **73**, 555—566).—Rats which have been starved for 24 hrs. absorb and oxidise more lævulose than those which have been starved 48 hrs. After 24 hrs. starvation, 81·2%, in normal rats, and 89·7%, in insulin-treated rats, of administered lævulose was accounted for by oxidation and glycogen storage, but the ratio of glycogen stored to lævulose oxidised was 1·16 in the normal and 0·3 in the insulin-treated animals. Insulin therefore increases the oxidation of lævulose.

In the case of the rats starved for 48 hrs., it was necessary to continue the observations for 6 hrs. instead of 4 hrs. in the normal animals, in order to account for all of the ingested lævulose; this was due to a lag in oxidation, since, under the influence of insulin, recovery of the ingested lævulose was complete in 4 hrs. C. R. HARINGTON.

Renal threshold for dextrose. R. L. MACKAY (Biochem. J., 1927, 21, 760—764).—A number of cases have been examined for blood-sugar at intervals before, during, and after anæsthesia. The first urine passed after recovery from the anæsthetic was also examined for sugar. The explanation of the results obtained in terms of the doctrine of the renal threshold (the concentration in the blood which has to be reached before a recognisable quantity of sugar appears in the urine) for sugar at about 0·180% is unsatisfactory. S. S. ZILVA.

Influence of certain bile acids on fat metabolism. S. IKOMA (J. Biochem. [Japan], 1926, 6, 383—393).—Cholic acid, in a concentration of 0·5%, causes an acceleration of the hydrolysis of fat in the liver; the same concentration inhibits the hydrolysis of fat in other organs. Deoxycholic acid, however, which stimulates the hydrolysis of fat even in a concentration of 0·3%, causes inhibition in the liver. CHEMICAL ABSTRACTS.

Physiological significance of the ethylenic linkings in fatty acids. E. F. TERROINE, R. BONNET, G. KOPP, and J. VECHOT (Bull. Soc. Chim. biol., 1927, 9, 605—620).—Determinations of the iodine value of the natural fats in various poikilothermous animals and in moulds grown at various temperatures have shown that when growth takes place at a comparatively low temperature the naturally synthesised fat is less saturated than that formed during growth at a comparatively high temperature. *Aspergillus niger* grows more rapidly on an unsaturated than on a saturated fat, and the formation of saturated fatty acids by bacilli and moulds entails a greater expenditure of energy than the formation of unsaturated fatty acids. E. A. LUNT.

Protein test for urea-formation function of the liver. P. COHEN and S. J. LEVIN (Arch. Int. Med., 1927, 39, 787—798).—A new test for liver function, based on the normal conversion by the liver of amino-acids into urea, is described. After a protein meal of 1 g. per kg. body-weight, the blood-urea increases normally from 50% to 70% above the fasting level in 4 hrs. In cases of liver injury this increase is much diminished. E. A. LUNT.

Indole derivatives in connexion with a diet deficient in tryptophan. R. W. JACKSON (J. Biol. Chem., 1927, 73, 523—533).—Dietary deficiency of tryptophan could not be made good by administration of β-indolealdehyde or of *r*- or *l*-3-β-indolelactic acid; nor could tryptophan, absent from the diet, be replaced by tryptophan injected subcutaneously. C. R. HARINGTON.

Nucleic phosphorus balance and relation to the course of growth. M. JAVILLIER, H. ALLAIRE, and (MLLE.) S. ROUSSEAU (Compt. rend., 1927, 184, 1351—1353; cf. A., 1926, 969, 1268).—The relationships and significance of the lipoid and nucleic phosphorus during the early growth of white mice have been examined. Determinations have been carried out at intervals from birth to 40 days after. At birth, the animal is richer in nucleic phosphorus than in lipoid phosphorus. The nucleic phosphorus of the young animal (*i.e.*, the amount of phosphorus of nucleoproteins per 100 g. of living tissue) decreases very considerably during the period between birth and the end of lactation, and then after the 21st day it rises to a level which, however, is much below that of the lipoid phosphorus. The percentage of lipoid phosphorus rises quickly during the first week, then regularly during the period of lactation and even up to the 40th day (cf. Mayer and Schaeffer, Compt. rend., 1914, 159, 102). The proportion of "transitional phosphorus" (soluble inorganic phosphorus and organic phosphorus of the intermediate synthetic and degradation products) rises quickly after birth and then oscillates within narrow limits. The relationship nucleic phosphorus/lipoid phosphorus varies largely; from 1·14 at the beginning, it falls to 0·46. Nucleic phosphorus/total phosphorus falls from 0·14 to 0·07; lipoid phosphorus/total phosphorus rises from 0·12 to 0·19. Nucleic phosphorus/active phosphorus (nucleic+lipoid+transitional phosphorus) falls in 3 weeks from 0·40 to 0·20, whilst lipoid phosphorus/active phosphorus increases from 0·35 to 0·47. E. H. SHARPLES.

Fate of cholesterol in the animal organism. I. LIFSCHUTZ (Arch. Pharm., 1927, 265, 450—455).—A review of the literature, with particular reference to the author's own work. W. A. SILVESTER.

Cholesterol metabolism and the reticulo-endothelial system. F. GOEBEL and H. GNOINSKI (Biochem. Z., 1927, 185, 414—419).—Blocking of the reticulo-endothelial system, or removal of a considerable part of it by splenectomy, causes a reduction in the cholesterol content of the blood; this system appears therefore to be actively concerned in the metabolism of cholesterol. C. R. HARINGTON.

Decomposition of bile acids in the organism. F. ROSENTHAL, L. WISLICKI, and H. POMMERNELLE (Arch. exp. Path. Pharm., 1927, 122, 159—183).—Decomposition of bile acids may take place on either side of the intestinal wall, that occurring in the alimentary tract being bacterial in nature and attacking the cholic acid complex of the coupled bile-acid, whilst the parenteral mechanism involves enzymes which split the bile acid at the linking with glycine or taurine. The patho-physiological significance of these conclusions is discussed. W. ROBSON.

Influence of heat and hydrogen-ion concentration on biological transportation systems containing sulphur. F. F. NORD (J. Physical Chem., 1927, 31, 867—876).—The oxygen-additive product which brings the reduced and oxidised forms of sulphur compounds into equilibrium can be prepared at p_H 7·4—3·8, but the solutions are much less active at the lower p_H values. After destruction of the additive product by heat, re-activation by oxygen is possible. Muscle, liver, and yeast suspensions

probably form no reversible systems with oxidised glutathione after they have been boiled.

L. S. THEOBALD.

Sulphur metabolism. C. P. SHERWIN, G. J. SHIPLE, and A. R. ROSE (J. Biol. Chem., 1927, **73**, 607—615).—Substitution of the hydrogen of the sulphydryl group of cysteine by the benzyl group, or conversion of cysteine (or cystine) into the phenylcarbamido-derivative or the phenylhydantoin, suppresses the normal physiological oxidation of these compounds to about the same extent, viz., 30—50%. The oxidation of cysteine is entirely suppressed when both sulphydryl and amino-groups are blocked in this way; it is concluded that both groups are open to attack in physiological oxidation. Diphenylacetylcystine is efficiently metabolised. The fact that, after administration of some of these compounds, the output of sulphur becomes greater than the intake, indicates a possible disturbing effect on the sulphur metabolism as a whole.

C. R. HARINGTON.

Metabolism of sulphur. XII. Value of cystine peptides and peptide anhydrides for nutrition of the rat. G. T. LEWIS and H. B. LEWIS (J. Biol. Chem., 1927, **73**, 535—542).—A diet deficient in cystine could be made good for the requirements of growing rats by addition of diglycylcystine or of dialanylcystine, but not of dialanylcystine dianhydride; the failure with the last-named compound was, however, not due to failure of absorption, since traces only could be detected in the fæces.

C. R. HARINGTON.

Effect of diminished atmospheric pressure on the liver. A. LOEWY (Biochem. Z., 1927, **185**, 287—319).—The livers of animals (especially guinea-pigs) which have been exposed to low atmospheric pressures show a general chemical and histological similarity to those of animals poisoned with phosphorus. C. R. HARINGTON.

Effect of turnips and turnip-juice on the blood-sugar, phosphorus, and cholesterol of rabbits. A. A. HORVATH (Amer. J. Physiol., 1927, **81**, 215—221).—Subcutaneous injection of turnip-juice into rabbits produced hyperglycæmia and a fall in inorganic phosphorus and cholesterol of the blood. The boiled juice produced hyperglycæmia and a rise in inorganic phosphates. R. K. CANNAN.

Chemical activity of the spleen. I. Relation to methæmoglobin in the blood. G. B. RAY and B. B. STIMSON (Amer. J. Physiol., 1927, **81**, 62—73).—Small doses of nitrobenzene caused the appearance of methæmoglobin in the blood of dogs. By comparative studies on normal and splenectomised dogs it is concluded that the spleen plays some part in hindering the formation and hastening the removal of methæmoglobin, possibly by an active reducing action. R. K. CANNAN.

Relation of connective tissue content of meat to its nutritional value. H. H. MITCHELL, J. R. BEADLES, and J. H. KRUGER (J. Biol. Chem., 1927, **73**, 767—774).—The biological value of the nitrogen of a sample of pork containing little connective tissue was 79, that of "crackling" was 25, and that of a 3 : 1 mixture of the two was 72; the last figure indicates that there must have been a supplementary action between the constituents of the two tissues. Pork tends to have a higher and more constant biological value than beef, since in the latter the content of connective tissue is both higher and more variable. C. R. HARINGTON.

Pentamethylenetetrazole ("cardiazole"). VI. Elimination of cardiazole by the kidneys. H. LEPPERT (Arch. exp. Path. Pharm., 1927, **122**, 362—365).—A method is described by which "cardiazole," added to urine, may be approximately quantitatively measured. Only a small proportion of the cardiazole injected subcutaneously appeared in the urine.

W. ROBSON.

Error of determination of toxicity. J. W. TREVAN (Proc. Roy. Soc., 1927, **B**, **101**, 483—514).—The principles which govern the determination of toxicity and of physiological activity in general by means of animal experiments are discussed, and fresh experimental data are presented.

W. O. KERMACK.

Influence of plankton on the phosphate content of stored sea-water. R. GILL.—See this vol., 747.

Relation of plankton to chemical and physical factors in the Clyde sea area. S. M. MARSHALL and A. P. ORR.—See this vol., 747.

Arginase. IV. Optimum p_H and purification of arginase by adsorption. S. EDLBACHER and E. SIMONS (Z. physiol. Chem., 1927, **167**, 76—87; cf. Edlbacher and Rothler, A., 1925, *i*, 1505).—The optimum reaction is found to be p_H 9·0, in contrast to the value of p_H 7·34—7·51 given by Hino (this vol., 173). Purification is effected by the removal of impurities from a glycerol extract of calf-liver by alumina, adsorption of the enzyme on kaolin, elution by a solution containing glycine, sodium chloride, and sodium hydroxide at p_H 9·0, and precipitation by acetone. The preparation is at least thirty times as active as the original material, and gives only very feeble biuret and diazo-reactions. Arginase is not identical with either histidase or histozyme.

A. WORMALL.

Influence of arsenic and antimony compounds on enzymic functions of the organism. IV. Cause of inhibitory influence of tartar emetic on salivary amylase. J. A. SMORODINCEV and E. A. ILJIN (Biochem. Z., 1927, **185**, 328—333).—In well-buffered solutions, tartar emetic has no effect on salivary amylase; the previously observed inhibitory action was due solely to its effect in increasing the acidity of the solution. C. R. HARINGTON.

Regeneration of invertase from certain carriers. A. FODOR and C. EPSTEIN (Z. physiol. Chem., 1927, **167**, 1—16; cf. Fodor and Schoenfeld, this vol., 76).—The enzyme is considered as composed of two parts, the "zymohaptic" substance and the non-specific and interchangeable carrier. A macerate of air-dried top yeast loses part of its activity on treatment with dilute sulphuric acid, but if kept at the ordinary temperature for 24 hrs., the neutralised solution regains part of its activity. The activity of the untreated macerate does not alter under these conditions. The addition of

lævulose to the macerate does not affect the results in either case. With an invertase preparation from autolysed yeast the results are in striking contrast. No regeneration of the enzyme occurs with either the untreated or acid-treated solutions, with or without the addition of lævulose; indeed, in the absence of lævulose, the acid-treated invertase preparation, after neutralisation, undergoes a definite weakening on keeping. The invertase present in the macerate is principally bound to its natural carriers (zymostable form), but in the preparation of the enzyme from autolysed yeast these carriers are destroyed and the enzyme is bound to secondary carriers (zymolabile form). In the former case, after inactivation of part of the enzyme by acid, there is a regeneration of active enzyme from the enzymic or zymohaptic component of the zymostable form and secondary carriers; no regeneration can take place with the invertase preparation, since practically all the enzyme is attached to secondary carriers. A. WORMALL.

Catalase. II. H. VON EULER and K. JOSEPHSON (Annalen, 1927, **455**, 1—16).—The effect of varying concentrations of hydrocyanic acid and of substrate (hydrogen peroxide) on the activity of liver catalase has been studied, the highly reactive specimens previously obtained (this vol., 376) being employed. The poisoning action of the hydrogen cyanide is greater the greater its concentration (a concentration of $5\times10^{-5}N$ reduces the catalase activity to 2%), but, whilst in the absence of hydrogen cyanide the unimolecular reaction constant (k) decreases continuously throughout the reaction, in presence of hydrogen cyanide it increases at first and then diminishes, owing to the destruction of the enzyme by the hydrogen peroxide, which is greater than the reactivation due to the destruction of the hydrogen cyanide. In presence of hydrogen cyanide concentrations of 2 and $5\times10^{-6}N$ and with varying concentrations of hydrogen peroxide (below $0{\cdot}02N$), the value of k extrapolated to zero time is lowered by the hydrogen cyanide independently of the substrate concentration, but the increase in k in presence of hydrogen cyanide is more rapid at higher than at lower concentrations of hydrogen peroxide. By means of these extrapolated values of k, activity–substrate curves are plotted for varying concentrations of substrate, and from these the affinity constant of the system catalase–substrate, $k_M=40$, is deduced (cf. Hennichs, A., 1926, 756, who found $k_M=22$). The poisoning action of hydrogen cyanide is independent of the amount of iron in the catalase preparation, the activity of the authors' specimen (C.F. 31,000) being reduced to one half by the presence of 1700 mols. of hydrogen cyanide/1 mol. iron (cf. Kuhn and Braun, A., 1926, 1215, who found the ratio 1500/1 for hæmin). Small concentrations of manganese chloride solution ($10^{-7}N$) have no activating effect on catalase, but higher concentrations have a slight poisoning action. J. W. BAKER.

Possibility of transformation of one enzymic activity into another according to experimental conditions. M. J. GRAMENITZKI (Biochem. Z., 1927, —437).—The guaiacum reaction for the detection of blood fails if the proportion of blood be high in relation to the hydrogen peroxide. The apparent predominance of catalase action under these conditions is explained not on the ground that blood can normally act as catalase and as peroxidase, but that the normal peroxidase action, which is responsible for the guaiacum reaction, is masked in presence of high concentrations of hæmoglobin by the tendency of the active oxygen to be converted into molecular oxygen.

C. R. HARINGTON.

Inhibition of liver esterase by esters of keto-acids. R. WILLSTATTER, R. KUHN, O. LIND, and F. MEMMEN (Z. physiol. Chem., 1927, **167**, 303—309).—In the action of liver esterase (cf. Willstatter and Memmen, A., 1924, i, 1145) on ethyl mandelate there is a distinct latent period, and this period is directly proportional to the concentration of the ester and inversely proportional to the amount of enzyme added. The delay in the hydrolysis is due to the presence in the substrate of ethyl phenylglyoxylate, and when the mandelic ester is recrystallised from light petroleum, the latent period disappears completely. The inhibitory effect is attributed to the great affinity of the enzyme for phenylglyoxylic ester and the very slow rate of decomposition of the product formed. Ethyl oxalacetate and benzoylacetate give marked latent periods, but ethyl pyruvate does not, presumably because it is very readily hydrolysed even in the absence of the enzyme.

A. WORMALL.

Action of oxidoreductase on glyceraldehyde. A. N. LEBEDEV (J. Russ. Phys. Chem. Soc., 1926, **58**, 712—725).—Mixtures of glyceraldehyde, enzyme, water, and methylene-blue were heated at various temperatures, and the time taken for the change of colour of the dye was noted.

In all cases when oxidoreductase was present, the methylene-blue was reduced, and a solution, giving the reactions of a hydroxy-acid, obtained, thus indicating the probable presence of glyceric acid. The oxidoreductase had no action on methylglyoxal or dihydroxyacetone, but readily oxidised crotonaldehyde. M. ZVEGINTZOV.

Liver hexose-redoxase [mutase]. H. VON EULER, R. NILSSON, and D. RUNEHJELM (Z. physiol. Chem., 1927, **167**, 221—235).—Rat liver contains large amounts of the carbohydrate redoxase (mutase) which decolorises methylene-blue, and this reduction is accelerated by co-zymase, especially if hexose-diphosphate is added as well. Preliminary attempts at purification by adsorption, dialysis, and precipitation of the proteins with acetic acid are described.

A. WORMALL.

Isoelectric precipitation of pepsin. F. FENGER and R. H. ANDREW (J. Biol. Chem., 1927, **73**, 371—377).—Pig's gastric mucous membrane is extracted with 50% acetone at p_H 3·5; the filtered extract is treated further with acetone to make 75% concentration of the latter; the resulting precipitate, containing the pepsin, is dissolved in dilute hydrochloric acid and the solution dialysed against water. The first and most active pepsin-containing precipitate separates at p_H 2·4—2·5; slightly less active, but more constant, preparations are obtained at p_H 2·5—

3·0 and 3·0—3·85. The above described process of extraction is carried out at 0°.

C. R. HARINGTON.

Peptidases. V. Specific action of yeast and intestinal peptidases. H. VON EULER and K. JOSEPHSON (Ber., 1927, **60**, [*B*], 1341—1349; cf. this vol., 175).—Characteristic differences are not observed in the action of yeast and intestinal peptidases towards glycylglycine, benzoylglycylglycine, or the biuret base, $NH_2{\cdot}CH_2{\cdot}CO{\cdot}[NH{\cdot}CH_2{\cdot}CO]_2{\cdot}NH{\cdot}CH_2{\cdot}CO_2Et$. Benzoylglycylglycylglycine does not suffer fission under the influence of yeast erepsin, whereas the biuret base is smoothly hydrolysed. Restriction of the action of yeast peptidase by glycine and alanine is of the same order of magnitude and similarly dependent on the acidity of the medium as that of intestinal peptidase. The experiments do not support the views of Waldschmidt-Leitz, Grassmann, and Schaffner (this vol., 345) of the subdivision of peptidases into amino- and carboxy-peptidases. H. WREN.

Proteolytic enzymes of the spleen. E. WALDSCHMIDT-LEITZ and W. DEUTSCH (Z. physiol. Chem., 1927, **167**, 285—302).—The activity curve for the action of spleen extracts on gelatin shows two optima, one at p_H 4·0 and another at p_H 8·0. These optima are not due to the presence of two proteases (α-protease and β-protease), but are those of a protease, which acts on proteins only and not on simple peptides, and a peptidase (erepsin), respectively. The most active enzyme extract is obtained by extracting the spleen with a glycerol solution containing a small amount of acetic acid. Separation of the enzyme by adsorption methods is described, and it is observed that neither isolated enzyme has any measurable action on proteins (gelatin) in an alkaline solution.

A. WORMALL.

Plant proteases. VIII. Adsorption and separation of yeast proteases. W. GRASSMANN and W. HAAG. **IX. Dipeptidase and polypeptidase of yeast.** W. GRASSMANN (Z. physiol. Chem., 1927, **167**, 188—201, 202—220).—VIII. The adsorption of the two proteases of yeast by alumina (Willstatter and Grassmann, A., 1926, 759) has been investigated further to determine the conditions which yield the best separation. Maximum adsorption of the yeast trypsin is effected in slightly acid solution from the diluted yeast autolysate, and the enzyme is obtained in the purest state from the alumina by elution with diammonium hydrogen phosphate, adsorption again on alumina from slightly acid solution, followed by elution with dilute ammonia. By modifying the separation, a yield of from 30% to 70% of the "yeast dipeptidase," free from tryptic activity, can be obtained.

IX. The dipeptidase hydrolyses all the dipeptides tested, but has no action on various natural proteins, three tripeptides, and one tetrapeptide. In this respect, it differs from intestinal and pancreatic erepsins, which hydrolyse tripeptides and even more complex peptides. The hydrolysis of tri- and tetrapeptides by autolysed yeast is due to the presence of "polypeptidase" (yeast trypsin), which hydrolyses all the natural proteins, but has no action on dipeptides, and this enzyme appears to remove dipeptide molecules from the peptide chain. The optimum reaction for the polypeptidase is p_H 6·7—7·0, and that for the dipeptidase p_H 7·8. A. WORMALL.

Phytase of malt. H. LUERS and K. SILBEREISEN (Woch. Brau., 1927, **44**, 263—268).—Phytase possesses a sharp temperature optimum at 48° and an optimum p_H at 5·2—5·3, the activity at p_H 4 and 6 being only one half that at the optimum. The anions used in the buffering mixtures play only a secondary role, whilst the enzyme is just as active in an arsenate buffer as in one containing acetate or citrate. The preparations of phytase and phytin are described.

W. ROBSON.

Synthesis of proteins by *Saccharomyces*. J. EFFRONT (Compt. rend., 1927, **184**, 1302—1304).—From a quantitative examination of the products of fermentation of dextrose by yeast in presence of ammonium sulphate it is shown that, under anaerobic conditions, the course of the synthesis of the protein of yeast closely approaches the formula $2nC_6H_{12}O_6+4nNH_3=(C_{12}H_{20}O_4N_4)_n+8nH_2O$. Probably hydrated pyruvaldehyde is first produced, and this with ammonia forms alanine, which, by condensation, forms substances having the nature of polypeptides. With strong aeration, it is concluded that the sugar is first transformed to acetaldehyde, and that the reaction is (1) $3C_6H_{12}O_6+3O_2=6CH_3{\cdot}CHO+6CO_2+6H_2O$; (2) $6CH_3{\cdot}CHO+3N=C_{12}H_{20}O_4N_3+2H_2O$. The presence of traces of acetaldehyde was established, the amount being greatly increased by changing the p_H value or with insufficient aeration. No alcohol was formed, but a quantity of the dextrose was completely oxidised, and the yield of carbon dioxide was much larger than that formed under anaerobic conditions. E. H. SHARPLES.

Formation and decomposition of hexosediphosphoric acid in alcoholic fermentation. H. VON EULER and K. MYRBACK (Z. physiol. Chem., 1927, **167**, 236—244).—Sodium hexosemonophosphate (Robison, A., 1923, i, 86) is fermented by dried bottom yeast-H and also by top yeast, but the fermentation curves show important differences. With the former, the velocity falls suddenly when half the total carbon dioxide evolution has occurred; this corresponds with the disappearance of all the hexosemonophosphate, half being fermented and the other half converted into the diphosphate. With top yeast, the curve is symmetrical and smooth, and indicates that although top yeast accumulates hexosediphosphoric acid more slowly, this compound is decomposed almost as fast as it is formed. Co-zymase is necessary for the fermentation of hexosediphosphoric acid by yeast, as it is in the case of muscle (Meyerhof, this vol., 75). Purified hexosediphosphate is fermented by yeast only when co-zymase is present, and the earlier contrary results (Euler, Nilsson, and Jansson, this vol., 697) are possibly due to the presence of co-zymase in the impure hexosediphosphoric acid used. A. WORMALL.

Products formed by *Bacterium pruni* in milk. S. L. JODIDI (J. Amer. Chem. Soc., 1927, **49**, 1558).—The crystalline deposit obtained when *pruni* is grown in skimmed milk contains tyrosine,

leucine, and myristic, palmitic, and stearic acids, together with the calcium salts of these acids.

F. G. Willson.

Bactericidal action of *X*-rays. J. J. Trillat (Ann. Inst. Pasteur, 1927, 41, 583—606).—The bactericidal action of *X*-rays on *B. prodigiosus* becomes more marked as the wave-length increases, and is much increased by secondary rays, particularly from metals of high atomic weight. This secondary effect is apparently due to the bombardment of the culture by electrons liberated from the metal.

W. O. Kermack.

p_H of the blood and the response of the vascular system to adrenaline. G. E. Burget and M. B. Visscher (Amer. J. Physiol., 1927, 81, 113—123).—The adrenaline response of the vascular system of the pithed cat can be made to vary at any time by varying the p_H of the blood. From p_H 6·9—8·0 the response progressively increases. The thyroid plays no part in this reaction, which may be due to increased sensitivity of the sympathetic nervous system or to the increased alkalinity causing more rapid and complete oxidation of the adrenaline.

R. K. Cannan.

Adrenaline in water and salt metabolism. S. Ederer (Arch. exp. Path. Pharm., 1927, 122, 211—218).—The hypochloruric oliguria with the transfer of salt and generally also of water from the blood to the tissues illustrates the typical adrenaline reaction. Salt transfer occurs especially in those cases where the chlorine tension between the blood and tissues is high on account of changed physico-chemical ratios, which hinder the normal equalisation of the salt between the blood and tissue.

W. Robson.

Diabetes and action of insulin. IX. Appearance in the blood after pancreatectomy of the substance antagonistic to insulin. H. Hausler and O. Loewi (Arch. exp. Path. Pharm., 1927, 123, 56—62).—The blood of a dog after pancreatectomy contains a substance which inhibits the uptake from the plasma of dextrose by human blood-corpuscles. This substance, which is dialysable and can be extracted by alcohol, is similar to that which appears in the blood of human diabetics and of adrenalinised animals.

W. O. Kermack.

Diabetes and action of insulin. X. Glycæmin, the hormone antagonistic to insulin. Its importance in the mechanism of diabetes. S. Dietrich, H. Hausler, and O. Loewi (Arch. exp. Path. Pharm., 1927, 123, 63—71).—The substance antagonistic to insulin which can be extracted by dialysis and treatment with alcohol from the plasma of dogs after pancreatectomy or treatment with adrenaline causes increased glycogenolysis when added to the liquid perfusing an isolated liver. This substance, which is proposed to call glycæmin, is considered to be of importance in effecting the increase in blood-sugar concentration which occurs in human diabetes.

W. O. Kermack.

Hormone activity after administration of dextrose. I. Secretion of insulin after subcutaneous administration of dextrose. II. Insulin and glycæmin secretion after oral administration of dextrose. III. Fasting animals. H. Häusler and O. Loewi (Arch. exp. Path. Pharm., 1927, 123, 72—87, 88—119, 120—128).—I. A method has been devised for the determination of insulin in blood based on the observation that a larger amount of dextrose is taken up by red blood-corpuscles in presence of insulin than in its absence. The quantity of insulin present in the blood increases after the subcutaneous administration of dextrose. After vagotomy, administration of atropine, or pancreatectomy, subcutaneous injection of dextrose is not followed by an increase of insulin in the blood.

II. After oral administration of dextrose, the largest quantity of insulin is found in the plasma after 3 hrs. In the case of plasma taken from animals after vagotomy or treatment with atropine, administration of dextrose actually results in a decrease in the amount of sugar taken up by red blood-corpuscles. This inhibiting action is due to glycæmin, a substance which can be dialysed and recovered from the dialysate. The dialysed plasma has no inhibiting action. The dialysate when precipitated by alcohol and injected into the animal organism causes hyperglycæmia to develop. Plasma taken from normal animals after administration of dextrose has a greater effect in increasing the uptake of dextrose by the corpuscles after dialysis than it has before dialysis.

III. The methods elaborated in the two preceding papers are applied to elucidate the cause of the abnormal hyperglycæmia which ensues when dextrose is administered to a fasting animal. It appears that this abnormal hyperglycæmia is due not to an excessive glycæmin secretion, but to defective secretion of insulin.

W. O. Kermack.

Effect of insulin on respiratory exchange of fed and fasting rabbits. I. L. Chaikoff and J. J. R. Macleod (J. Biol. Chem., 1927, 73, 725—747).—Rabbits were fed on a diet rich in carbohydrates until their respiratory quotient reached unity; administration of insulin to such animals caused no change in oxygen consumption or in respiratory quotient; insulin administered to the same rabbits after starvation caused a rise in oxygen consumption and in respiratory quotient, indicating that a little less than 10% more of the total energy production was being derived from oxidation of carbohydrate. In the first set of experiments, since the unchanged oxygen consumption and respiratory quotient indicated the absence of increased oxidation of dextrose, or formation of dextrose from other substances, and since, in view of the previous dieting, the glycogen stores of the body were probably full, the results favour the hypothesis of the conversion of dextrose into an unknown intermediate product under the action of insulin. The reasons for the discrepancy between this conclusion and that reached by Burn and Dale (J. Physiol., 1924, 59, 164) and Best and others (A., 1926, 870) are discussed.

C. R. Harington.

Blood- and insulin-sulphur eliminated by hydrogen and its behaviour on treatment with hydrogen cyanide and cyanamide. J. Kühnau (Arch. exp. Path. Pharm., 1927, 123, 24—49).—When

hydrogen is passed through blood, hydrogen sulphide is liberated apparently from some non-protein substance contained in the red blood-corpuscles. The liberation of hydrogen sulphide from blood is increased by hydrogen cyanide and malononitrile, but is inhibited by cyanamide. Hydrogen does not liberate hydrogen sulphide from cysteine, but the quantity of hydrogen sulphide formed from a solution of cystine is increased by potassium cyanide and decreased by cyanamide. Hydrogen sulphide is also liberated from a solution of insulin by a current of hydrogen, but in this case both potassium cyanide and cyanamide are without action. W. O. KERMACK.

Effect on normal calves of administration of parathyroid extract. C. S. ROBINSON, C. F. HUFFMAN, and K. L. BURT (J. Biol. Chem., 1927, **73**, 477—482).—Calves are less sensitive than dogs to the effects of parathyroid extract. Injection of large doses, however, caused an increase of the blood-calcium to 18 mg. per 100 c.c., a decrease in the blood-phosphorus, and an increase in the urinary excretion of calcium and phosphorus; the fæcal excretion of these elements was little affected. Persistent over-dosage caused drowsiness and swelling, with eventual death of the animals.

C. R. HARINGTON.

Effect of pituitrin administration on carbohydrate metabolism. H. M. HINES, C. E. LEESE, and J. D. BOYD (Amer. J. Physiol., 1927, **81**, 27—35).—Continuous intravenous injection of pituitrin along with dextrose led to a greater degree of hyperglycæmia and glycosuria than when dextrose was injected alone. There were no differences in extra-heat production or respiratory quotient. This diminished retention of carbohydrate under the influence of pituitrin is not explained by a direct action on the kidney or by changes in the acid–base equilibrium of the blood, and may be due to altered capillary circulation. R. K. CANNAN.

Vitamin-*A* content of skimmed milk. J. B. PLATON (Biochem. Z., 1927, **185**, 238—241).—The greatest amount that could be consumed (20 g. per diem) of skimmed milk was insufficient to supply the vitamin-*A* requirements of young rats; 1·75—2·0 g. per diem of the whole milk was sufficient for this purpose. C. R. HARINGTON.

Antirachitic and calcifying properties of dried summer and winter milk, irradiated and non-irradiated. G. C. SUPPLEE and O. D. DOW (J. Biol. Chem., 1927, **73**, 617—622).—Dried summer milk had greater antirachitic activity than dried winter milk; on irradiation, both products became more active, but the proportional increase of activity was greater in the case of the winter milk, so that both irradiated products exhibited approximately the same degree of antirachitic activity.

C. R. HARINGTON.

Relationship between antirachitic activity and the dielectric constant of irradiated cholesterol solutions. P. ELLINGER (Arch. exp. Path. Pharm., 1927, **122**, 238—246).—A method and an apparatus are described by which changes in the dielectric constants of liquids during irradiation with ultra-violet light may be followed. Oils and solutions of cholesterol in alcohol and paraffin on such irradiation show a rise in their dielectric constants. This rise does not take place if the irradiation is conducted in the absence of oxygen; the formation of the anti-rachitic factor, on the other hand, takes place in the absence of oxygen. The processes are accordingly independent of one another. The rise of the dielectric constant produced by ultra-violet irradiation may probably be traced to the formation of an oxidation product of cholesterol. W. ROBSON.

Influence of intense *X*-ray and *γ*-ray radiation on cholesterol. M. C. REINHARD and K. W. BUCHWALD (J. Biol. Chem., 1927, **73**, 383—388).—Irradiation of cholesterol, in solution in chloroform or alcohol with *X*-rays or *γ*-rays causes a shift in the ultra-violet absorption curve towards longer wave-lengths. The change in optical rotatory power was slight. Pure cholesterol could not be recovered on evaporation of the irradiated solutions.

C. R. HARINGTON.

Vitamin-*D* content of the stomach oil of the Australasian petrel (*Aestralata lessoni*). J. L. LEIGH-CLARE (Biochem. J., 1927, **21**, 725—727).—The presence of vitamin-*D* in amount equal to about one fifth of that present in a good cod-liver oil has been demonstrated in the oil. S. S. ZILVA.

Synthesis of the antineuritic factor (torulin) by yeast. F. HAWKING (Biochem. J., 1927, **21**, 728—732).—*Saccharomyces cerevisiæ* can synthesise the curative factor (torulin) for pigeons in small amounts. S. S. ZILVA.

Evolution of *B*-avitaminosis in its relation with the constitution of the carbohydrates of the diet. L. RANDOIN and R. LECOQ (Compt. rend., 1927, **184**, 1347—1349; cf. A., 1925, i, 751).—Eleven separate diets (deficient in vitamin-*B*) having the same percentage composition, but each containing a different carbohydrate, were administered to eleven groups of pigeons. From the observations of their behaviour, together with the results of Cori (A., 1926, 429, 1271) and Reinhold and Karr (this vol., 480), the following conclusions are reached. The slower or more feeble the intestinal absorption of a given sugar [potato-starch, lactose (?)] or the greater its ability to be converted into glycogen the slower is the development of avitaminosis-*B*; conversely, the quicker the absorption (galactose, dextrose) and the smaller the ability to be transformed into glycogen (galactose) or the greater the tendency to produce hyperglycæmia (galactose, maltose), the more rapidly it produces death in complete absence of vitamin-*b*.

E. H. SHARPLES.

Existence of two active factors in vitamin-*B* complex. W. D. SALMON (J. Biol. Chem., 1927, **73**, 483—497).—The seeds of the velvet and soya beans have a greater protective action against neuritis or beri-beri but a less marked growth-promoting action than the leaves, for animals on a diet deficient in vitamin-*B*; on treatment of an extract of these materials with fuller's earth, the precipitate obtained was antineuritic, whilst the residue in the filtrate, which, alone, had very little physiological action, acquired growth-promoting properties when added to the precipitate. It there-

fore appears that vitamin-*B* is a complex of at least two active substances. C. R. HARINGTON.

Effect of desiccation on the nutritive properties of egg-white. M. A. BOAS (Biochem. J., 1927, 21, 712—724).—A diet of crude egg-white, boiled and supplemented with wheat-starch, cotton-seed oil, cod-liver oil, lemon juice, marmite, salts, and water, supports young rats in growth and health. If the egg-white is previously dried, the diet is inadequate, unless the carbohydrate is supplied in the form of potato-starch or arrowroot, or unless certain substances are added in small amounts. The condition which is developed by rats fed on this unsatisfactory diet is described in detail. The change which takes place in the dried egg-white is independent of the reaction of the solution during drying, is not due to a thermolabile enzyme, and does not appear to be a process of oxidation. Egg-white previously coagulated by boiling is not damaged by desiccation. The crude proteins of horse-serum and milk do not suffer a similar change during desiccation. The foodstuffs which possess the power of counteracting the ill effects resulting from ingesting the dried egg-white are raw potato, potato-starch, arrowroot, dried yeast, fresh egg-white, egg-yolk, milk, commercial caseinogen, crude lactalbumin, spinach and cabbage leaves, banana, and dried horse-serum. The presence of a protective factor *X* in these substances is postulated. The factor shows a similar distribution in many ways to that of the water-soluble *B*-vitamins, but is not, however, identical with either the antineuritic factor or Goldberger's pellagra-preventive vitamin. Its resistance towards heat and desiccation varies according to the substance in which it is found. There are indications that rats can store reserves of the protective factor *X*.

S. S. ZILVA.

Formation of fat from carbohydrate by the rat under abnormal conditions; relationship to a possible new dietary factor. L. G. WESSON (J. Biol. Chem., 1927, 73, 507—522).—Rats were kept for several weeks on a diet of dextrin, salts, and water, or on such a diet with the addition of small amounts of oatmeal or caseinogen; they were starved for —3 days and then 3 g. of dextrin per 100 g. of body-weight were administered; as a result, respiratory quotients of 1·5—2·0, or higher, were observed, indicating conversion of carbohydrate into fat. Addition of very small amounts of lard or of an ethereal extract of pig's liver to the restricted diet abolished this effect, which was therefore not due to a demand for fat as such, but possibly for some unknown factor contained in the fat. C. R. HARINGTON.

Energy of growth. X. Formation of fats from carbohydrates by micro-organisms. E. F. TERROINE and R. BONNET (Bull. Soc. Chim. biol., 1927, 9, 588—596).—Cultures of *Aspergillus niger* in media containing from 3% to 40% of dextrose show a remarkable increase in the fat content of the cells, and little change in protein, ash, and unsaponifiable a . By means of an energy balance-sheet, it is shown that the change from dextrose to fatty acid is carri.. out by the cell with about 90% efficiency.

E. A. LUNT.

Energy of growth. XI. Formation of carbohydrates from fatty acids by moulds. E. F. TERROINE, R. BONNET, and P. DUQUENOIS (Bull. Soc. Chim. biol., 1927, 9, 597—604).—The rate of growth of cultures of *Aspergillus niger* in media rich in the fatty acids of butter fat, arachis oil, linseed oil, cod-liver oil, oleic acid, and castor oil is retarded, whilst the transformation of fatty acid into carbohydrate is carried out by the cells with 75—80% energy efficiency. The transformation is less efficient for saturated than for unsaturated fatty acids.

E. A. LUNT.

Physiology of fruit trees. I. Seasonal starch content and cambial activity in one- to five-year-old apple branches. T. SWARBRICK (J. Pomology, 1927, 6, 137—156).—The seasonal changes in starch content in one- to five-year-old branches of normal bush type apple trees have been followed, and observations made on the seasonal changes in cambial activity. Special attention was directed to the order of disappearance and reappearance of starch, and to the beginning and cessation of cambial activity. In vegetative shoots, cambial activity was early and starch disappearance tended to lag behind, whereas the reverse was the case in flowering shoots.

C. T. GIMINGHAM.

Plastic substances in stems of grape vines growing in Kakhetin. V. G. ALEKSANDROV and E. A. MAKAREVSKAYA (Naukh-Agron. Zhurnal [Russia], 1926, 3, 324—333).—In winter, there is much starch in the lignin portion of the medullary rays, less in the lignin itself, and little in the bark; there is also sugar in the lignins and bark. The sieve-like tubes of the phloem, which contain proteins, are always free from sugar; the secondary tubes are full of sugar. During the first period of bleeding, starch diminishes and sugar increases. Towards the end of the sap movement in the old wood there is much starch both in the lignins and in the bark. The phloem is filled with proteins which come from the roots. The bast fibres are also filled with protein; some proteins are found in the medullary rays. Whenever the walls of the medullary rays begin to fill with proteins, the starch begins to disappear. During the winter, there is no protein in the medullary rays. During leaf formation, the upper zones of the shoots are free from starch; the sugar content also decreases. Only in some places in the sieve-like tubes some protein still persists. During blooming, there is an abundance of crystals in the young shoots. In the upper zones of such shoots in the lignin-like medullary rays starch is present; in the last parenchyma protein is found. An abundance of crystals is also found in the outer cells of the medullary rays, in the bark. After blooming, the bast fibres of the medullary rays and the entire phloem are free from starch. There is sugar in the thin-walled bast fibres, some in the thick-walled. In the cambium, the quantity of sugar diminishes; in the lignins, some sugar is found in the vessels, but there is more sugar in the bark. At that time the proteins are present in the upper zone of the growing shoot, where most of the sugar may be located. During the ripening of the fruit, starch begins to accumulate in the bark; the phloem also begins to fill with starch. The proteins

are located in the sieve-like tubes. In the lignins, an increase in the starch content is noticeable. Then all the fibres became filled with starch except the sieve-like tubes. The elements close to the cambium are filled less than those which are nearer to the periphery. Calcium oxalate crystals are obscured. The quantities of sugar and protein increase. This is the period during which the plant prepares to go into the so-called rest period. CHEMICAL ABSTRACTS.

Relation of antitoxic power to ionisation. L. MAUME and J. DULAC (Compt. rend., 1927, **184**, 1194—1196).—An amplification of previous work (*ibid.*, 1081). It is concluded that for mixtures of sodium and calcium chlorides, the minimum toxicity of the solutions for germinating wheat is given by that quantity of the salts which, separately dissolved in a quantity of water equal in volume to that of the mixture, would give solutions having the same degree of ionisation. M. CLARK.

Influence of sodium carbonate and calcium chloride on the acidity of maize sap (*Zea mais*, L.). S. KARASIEWICZ (Compt. rend., 1927, **184**, 1192—1194).—When maize is grown in culture media containing sodium carbonate the amount of acid present in the sap is diminished on account of the insoluble calcium salts formed. The use of culture media containing calcium chloride, however, gives a progressive increase of the total acidity. The amount of water-soluble acid present, whether as free acid or as soluble salt, is unaltered by either treatment. M. CLARK.

Distribution of potassium and sodium in plants. G. ANDRE and E. DEMOUSSY (Compt. rend., 1927, **184**, 1501—1503).—The ratio of potassium to sodium shows a preponderance of the former in the older wood of ligneous plants and in the interior of tap-roots during the period of growth, but an almost equal distribution during the resting period. Figures are given for the distribution of these elements in beet, in chestnut, and in *Tamarix gallica*. G. A. C. GOUGH.

Nutrient ions of plants and ion activation of plant enzymes. G. DOBY and R. P. HIBBARD (J. Biol. Chem., 1927, **73**, 405—416).—The leaves of young sugar-beet plants contain more amylase and less sucrose than those of old ones; in plants grown in sand with a synthetic nutrient medium, deficiency of potassium in the latter leads to increase in the amount of both the above enzymes. The amylase is activated by potassium and nitrate ions, and still more so by chloride ions; the sucrose is activated by nitrates and inhibited by chlorides; all effects of salts on the enzymes are exaggerated in the case of the plants grown on the medium deficient in potassium. C. R. HARINGTON.

Iodine as a biogenic element. X. Iodine content of cultivated plants. K. SCHARRER and J. SCHWAIBOLD (Biochem. Z., 1927, **185**, 405—413).—Figures are given for the iodine content of numerous edible plants. Application of iodine-containing manure to plants, whether growing in pots or in the open ground, caused a great increase in their iodine content. In the case of sugar-beet, the increase occurred both in roots and leaves. C. R. HARINGTON.

Phosphorus compounds in plants. I. Solubility and distribution of phosphorus compounds in seeds. S. KOEHLER (Bull. Acad. Polonaise, B, 1926, 707—848).—The discrepancies in the mineral phosphate content of seeds, recorded in the literature, may be accounted for by the fact that the results are dependent on the nature and concentration of the acid used for extraction, and by the fact that many seeds contain phosphatases. The distribution of phosphorus in the seeds of various plants has been examined. In the seeds of the scarlet runner, in castor-oil beans, and in the seeds of dentate maize, the mineral P_2O_5 is 13·2%, 4·82%, and 5·38%, respectively, the phytin P_2O_5 is 60%, 91%, and 1·5%, respectively, whilst the organic P_2O_5 is 27%, 4%, and 13%, respectively. In maize, dentate maize, and the carob tree the embryos contain 86—90% of the total phosphorus; in castor-oil beans, the embryos contain only 3·4%, and the endosperm 95%; in the scarlet runner, the cotyledons contain 98·5%, and the rest of the seed 1·47%. Further results are given for the amounts of mineral, phytin, and organic phosphorus in each part of the seeds of all these plants. E. A. LUNT.

Hitherto unsuspected source of arsenic in human environment. R. E. REMINGTON (J. Amer. Chem. Soc., 1927, **49**, 1410—1416).—Samples of American tobacco, examined by a micro-Marsh method, contained 0·05—0·27 grain of arsenious oxide per pound. Half the arsenic in pipe tobacco is evolved in the smoke, and half of that in "plug" tobacco is soluble in water. S. K. TWEEDY.

α-Hæmatin, the iron-containing porphyratin of plants, and the corresponding porphyrins. O. SCHUMM (Z. physiol. Chem., 1927, **166**, 319; cf. this vol., 685).—The methyl ether of the dimethyl ester of hæmatoporphyrin, described in the original paper as being obtained by boiling α-hæmatin with a solution of hydrochloric acid in methyl alcohol and subsequent removal of the iron with hydrazine in glacial acetic acid solution, appears to be identical with Küster's tetramethylporphyrin. H. D. KAY.

Corn [maize] wax. R. L. SHRINER, F. P. NABENHAUER, and R. J. ANDERSON (J. Amer. Chem. Soc., 1927, **49**, 1290—1294).—The pasty deposit obtained when crude maize oil is cooled contains a wax, which is obtained as feathery crystals, m. p. 81—82·5°, by dilution of the crude material with light petroleum, centrifuging, and recrystallising from amyl alcohol, acetone, and light petroleum. The wax is a mixture of the myricyl esters of tetracosoic acid and an *isobehenic acid*. The *amide* of the latter, m. p. 110—111°, and the *methyl* ester, m. p. 47—52°, are described. F. G. WILLSON.

Non-volatile acids of the pear, quince, apple, loganberry, blueberry, cranberry, lemon, and pomegranate. E. K. NELSON (J. Amer. Chem. Soc., 1927, **49**, 1300—1302; cf. A., 1925, i, 762).—The non-volatile acids of Bartlett pears consist of citric and *l*-malic acids in the proportion 2 : 1. Quinces contain *l*-malic acid. Winesap apples contain *l*-malic acid with a trace of citric acid, whilst York Imperial apples contain *l*-malic acid only (cf. Franzen an

Helwert, A., 1923, i, 637). The non-volatile acids of the loganberry are citric (96%) and *l*-malic (4%); of the blueberry, citric, with a trace of *l*-malic; of the cranberry, citric (80%), *l*-malic (20%), and benzoic (0·069%); of California lemons, citric, with a trace of *l*-malic; and of the pomegranate, citric acid only. F. G. WILLSON.

Oil of *Secale cornutum* and its daturic acid content. H. DIETERLE, H. DIESTER, and T. THIMANN (Arch. Pharm., 1927, **265**, 171—187).—The oil has $d^{16\cdot2}$ 0·9259; n_D^{20} 1·5420; acid value, 13·19; saponification value, 193·3; ester value, 180·11; Hehner value, 96·13; Reichert–Meissl value, 0·47; Polenske value, 0·48; iodine value (Hübl) 69·55, (Hanus) 66—67. The oil is not a drying oil. The above data agree with those of Mjoen (A., 1896, ii, 500).

The fatty acid mixture is composed of palmitic, daturic, and other solid fatty acids (20·48% of the original oil), oleic acid (70·99%), and α-linoleic acid (4·58%). Hydroxy-fatty acids, which Mjoen supposed to be present, were not discovered. The daturic acid isolated was examined in detail, but satisfactory conclusions were not reached. Stearic acid, however, is definitely absent from the oil. No characteristic differences were found between the methyl and ethyl esters of palmitic, stearic, and daturic acids, nor between the sodium salts of the corresponding hydroxamic acids. 1·9% of the oil is unhydrolysable, consisting of hydrocarbons, phytosterols, etc. W. A. SILVESTER.

Kuromoji oil. H. SHINOSAKI and H. MAKINO (Rep. Imp. Ind. Res. Inst. Osaka, 1927, **7**, No. 15, 27—44).—The low b.-p. fraction of kuromoji (*Lindera sericea*, Bl.) oil consists chiefly of *l*-α-phellandrene, with small quantities of dipentene and limonene. The important components of the oil are nerolidol, linalool, and geraniol. α-Pinene, camphene, a dicyclic sesquiterpene, a monocyclic (?) sesquiterpene alcohol, and an ester of an unknown acid (m. p. 126—126·5°) were also isolated. CHEMICAL ABSTRACTS.

Toxicity of flax lolium (*Lolium remotum*, Schrank). A. VON LINGELSHEIM (Arch. Pharm., 1927, **265**, 244—250).—*Lolium remotum*, Schrank, is poisonous, like *L. temulentum*, and is frequently present as an impurity in linseed. Data are given from many mid-European agricultural stations showing that, although the risk of fatal effects to cattle or human beings from this cause is not great, further investigation is desirable. The toxic properties appear to be connected with the presence of a parasitic fungus. W. A. SILVESTER.

Ether-soluble substances of cabbage-leaf cytoplasm. III. Fatty acids. A. C. CHIBNALL and H. J. CHANNON (Biochem. J., 1927, **21**, 479—

e greater part of the fatty acids of the cytoplasm of the cabbage leaf consists of the unsatura- ea acids, linolenic and linoleic acids; palmitic and stearic acids constitute the saturated acids. e presence of oleic acid could not be established. ie e seems a definite difference in the amounts of f ++ acids and of the unsaponifiable matter in e ethereal extracts obtained from spring and summer material. S. S ZILVA.

***Helleborus*.** O. KELLER and W. SCHOBEL (Arch. Pharm., 1927, **265**, 238—243).—*Helleborus niger* (root) contains the two glucosides, helleborein and helleborin. Helleborin has m. p. 269—270°, and analyses (the results are very different from those of earlier authors) indicate that the composition is $C_{28}H_{36}O_6$ or $C_{27}H_{36}O_6$. *Helleborus viridis* (root) contains, together with brown colouring matter and fatty substances, the same two glucosides as *H. niger*, sucrose, and two alkaloids. These two new *bases*, together amounting to only about 0·1% of the dried root, are extracted by Stoll's method (Schweiz. med. Woch., 1921, 23). They differ in carbon content, but both contain about 3% of nitrogen. The one is easily soluble in ether, but sparingly soluble in chloroform; the other sparingly soluble in ether, and easily soluble in chloroform. W. A. SILVESTER.

***Ephredra nevadensis*.** R. E. TERRY (J. Amer. Pharm. Assoc., 1927, **16**, 397—407).—*E. nevadensis* contains no ephredine, which is usually present in the European and Asiatic members of the genus *Ephredra*. The plant contains a water-soluble constituent with a slight diuretic effect, the use of which in medicine is precluded by the large amount of gallotannic acid present in the aqueous extract of the plant. E. A. LUNT.

***Asarum caudatum*.** H. M. BURLAGE and E. V. LYNN (J. Amer. Pharm. Assoc., 1927, **16**, 407—411).—The leaves and petioles of the plant contain little or no volatile oil, the roots and rhizomes as much as 4·06%, depending on the time of harvest. This oil contains a small amount of pinene, 60—75% of methyleugenol or closely related methoxyl compounds, 10% of azulene, and 10% or more of asarone (3 : 4 : 6-trimethoxyallylbenzene). E. A. LUNT.

Glucosides of *Caulophyllum thalictroides*. E. D. DAVY and H. P. CHU (J. Amer. Pharm. Assoc., 1927, **16**, 302—305).—Analysis of the rhizome and roots of *Caulophyllum thalictroides* yielded the alkaloid methylcytisine and a non-crystalline, glucosidal material which differed from that described by Power and Salway (J.C.S., 1913, **103**, 193). On moistening the drug to allow enzyme action to take place before extraction, a crystalline glucoside, m. p. 243—246°, $[\alpha]_D$+45°, sparingly soluble in alcohol, and a non-crystalline glucosidal product, m. p. 230—240°, $[\alpha]_D$+37°, very soluble in alcohol, were isolated. The former may be identical with caulosaponin. W. J. POWELL.

Protoplasm. III. Proteins of the plasmodium of *Fuligo varians*. A. KIESEL (Z. physiol. Chem., 1927, **167**, 141—162; cf. A., 1926, 204; this vol., 382).—The air-dried plasmodium contains crude oil 8·73%, water 9·53%, calcium carbonate 16·35%, organic water-soluble matter 15·35%, residue insoluble in light petroleum, water, or alcohol 50·04%. One of the most important constituents is a nucleoprotein, present to the extent of at least 3·1% of the dry weight, and in addition to the protein-like substance or mixture, "plastin." A. WORMALL.

Glutelins. I. α- and β-Glutelins of wheat. F. A. CSONKA and D. B. JONES (J. Biol. Chem., 1927, **73**, 321—329).—Glutelins can be precipitated from

alkaline solution by concentrations of ammonium sulphate which are too low to precipitate globulins, and may thus be separated from the latter. Wheat flour was freed from starch and gliadin and then extracted with 0·2% sodium hydroxide. Treatment of the extract with ammonium sulphate to 2% saturation precipitated 1% of *α-glutelin*; further addition to the filtrate of ammonium sulphate to 18% saturation yielded about 0·07% of *β-glutelin* (calculated on the weight of the original flour). Both proteins have an isoelectric point at p_H 6·45; figures are given for the nitrogen distribution.

C. R. HARINGTON.

Nitrogen compounds of the rice kernel as compared with those of other cereals. S. L. JODIDI (J. Agric. Res., 1927, **34**, 309—325).—The total nitrogen in oven-dried rice varies from 1·7 to 1·24% in different varieties and different seasons. Polypeptides and free amino-acids occur in the ungerminated rice kernel (brown rice). Amino-nitrogen amounts to 0·75—1·02% of the total nitrogen; corresponding figures for acid amide nitrogen are 0·14—0·23%, and for polypeptide nitrogen, 0·85—1·15%. The percentages of total nitrogen in wheat, oats, rye, maize, and rice decrease in the order named. The proportion of protein nitrogen is smaller in rye, wheat, and oats than in maize or rice, but the absolute quantity is considerably larger. The significance of the non-protein nitrogen compounds during the early stages of seed germination is discussed.

C. T. GIMINGHAM.

Immunological reactions of the globulins from the seeds of leguminous plants. Biological reactions of the vegetable proteins. IX. H. G. WELLS, J. H. LEWIS, and D. B. JONES (J. Infect. Dis., 1926, **40**, 326).—The α-globulin fractions of navy, mung, adzuki, Lima, and Georgia velvet beans have a higher sulphur and a lower nitrogen content than the β-globulins. The globulins from adzuki and mung beans are distinct from those of navy, Lima, and Georgia velvet beans, but the α- and β-globulins of adzuki and mung beans are either identical or similar. Georgia velvet bean globulins are immunologically distinct from the others. CHEMICAL ABSTRACTS.

Portable form of manometric gas apparatus. D. D. VAN SLYKE (J. Biol. Chem., 1927, **73**, 121—126).—A portable form of the apparatus of Van Slyke and Neill (A., 1924, ii, 872) is described and details of technique are given. C. R. HARINGTON.

Carbon dioxide factors for the manometric blood-gas apparatus. D. D. VAN SLYKE and J. SENDROY, jun. (J. Biol. Chem., 1927, **73**, 127—144).—By gasometric analysis of sodium carbonate solutions, the composition of which was independently checked by three different gravimetric methods, factors for the conversion of observed pressure differences into carbon dioxide content in the use of the apparatus of Van Slyke and Neill (A., 1924, ii, 872) have been re-calculated with increased accuracy.

C. R. HARINGTON.

Determination of acetoacetic acid. L. PINCUSSEN (Biochem. Z., 1927, **184**, 359).—A reply to Lorber's criticism (this vol., 372) of the author's micro-methods. R. K. CANNAN.

Determination of lactic acid. T. E. FRIEDEMANN, M. COTONIO, and P. A. SHAFFER (J. Biol. Chem., 1927, **73**, 335—358). **Condenser unit for use in determination of lactic acid.** H. A. DAVENPORT and M. COTONIO (*ibid.*, 359—361).—The oxidation of lactic acid to acetaldehyde is rendered almost quantitative by the addition of manganous sulphate. By utilisation of this observation, development of an improved apparatus, and more rigid determination of the appropriate conditions for the titration of hydrogen sulphite bound by acetaldehyde, an improved modification of the method of Clausen (A., 1922, ii, 593) has been devised. The method is applicable to amounts of lactic acid from 0·045 to 45 mg. with an error of ±5%; the magnitude of the error which may be introduced by the presence of interfering substances in physiological material has been determined in a large number of cases, and methods for the preliminary removal of certain of these substances are indicated.

A technical modification, leading to a more compact apparatus for the above method, is described.

C. R. HARINGTON.

Use of magnesium perchlorate trihydrate and asbestos-sodium hydroxide for determination of water and carbon dioxide in metabolism experiments. M. O. LEE and J. B. BROWN (J. Biol. Chem., 1927, **73**, 69—72).—The quantitative absorption of water and carbon dioxide in metabolism experiments is conveniently accomplished by the use of magnesium perchlorate and asbestos impregnated with sodium hydroxide, respectively, these preparations offering technical advantages over the absorbents commonly employed. C. R. HARINGTON.

Nephelometric determination of small amounts of arsenic. I. Turbidities produced by a new reagent. II. Determination of arsenic in any material. H. KLEINMANN and F. PANGRITZ (Biochem. Z., 1927, **185**, 14—43, 44—62).—I. A reagent prepared by mixing 1 vol. of 1% potassium molybdate with 1 vol. of 2% cocaine and 2 vols. of *N*-hydrochloric acid exhibits a turbidity with minute traces of arsenates. By the use of this reagent, under the specified experimental conditions, amounts of arsenic from 0·06 to 0·0005 mg. can be determined nephelometrically with an error of ±1%. The determination is not affected by the presence of neutral salts up to *N*-concentration.

II. Organic material is dried at 100° and then incinerated with a mixture of sulphuric and nitric acids; the arsenic remaining in the sulphuric acid is reduced by addition of ferrous sulphate; the mixture is then treated with potassium chloride and bromide and distilled, the arsenic trichloride being collected in excess of *N*-sodium hydroxide; the arsenic in the distillate is oxidised by treatment with hydrogen peroxide, and determined nephelometrically. In this way, amounts of arsenic of the order of 0·0005 mg. may be determined in organic material. Methods are described for the removal of traces of arsenic from the reagents employed. C. R. HARINGTON.

BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

SEPTEMBER, 1927.

General, Physical, and Inorganic Chemistry.

Symmetrical character of the terms corresponding with systems containing similar particles, derived by quantum dynamics. F. HUND (Z. Physik, 1927, 43, 788—804).—Mathematical. R. W. LUNT.

Applications of Schrödinger's theory to the structure of spectra. E. WEIGER (Z. Physik, 1927, 43, 624—652).—Mathematical. The characteristic structure of spectra, in particular the laws of series spectra and the Stark and Zeeman effects, have been derived by application of Schrödinger's differential equations. R. W. LUNT.

Orbits and light-radiation of hydrogen electrons. T. ENGSET (Ann. Physik, 1927, [iv], 83, 903—904).—Extensive mathematical corrections to a former paper (this vol., 601) are given.

Number of dispersion electrons for the continuous spectra and series spectra of hydrogen. Y. SUGIURA (J. Phys. Radium, 1927, [vi], 8, 310).—A correction (cf. this vol., 494).

Hydrogen atom with a spinning electron in wave mechanics. C. F. RICHTER (Proc. Nat. Acad. Sci., 1927, 13, 476—479).—It is shown mathematically that Schrödinger's wave mechanics in conjunction with the Uhlenbeck–Goudsmit concept of the spinning electron completely represents the fine structure of hydrogen-like spectra. J. S. CARTER.

Intensities in the helium spectrum produced by a condensed discharge. L. S. ORNSTEIN and H. P. BOUWMAN (Z. Physik, 1927, 43, 839—844).—The intensities of the helium lines 5016, 4922, 4713, 4686, and 4383 Å., excited by a damped wave-train discharge of train frequency 500 per sec., have been measured as a function of the maximum voltage of the wave-trains. The discharge was produced by charging a condenser through a rectifier connected to a high-tension *A.C.* supply at the frequency 500 cycles per sec.; the condenser discharged through an oil-immersed spark gap and the discharge tube containing helium; the inductance of this circuit was made very small in order to increase the frequency of the oscillatory current. In the range 0·5—36 kilovolts the intensities of the lines 5016, 4922, 4713, and 4383 Å. increase to a maximum at approximately 10 kilovolts, diminish rapidly to a minimum in the neighbourhood of 11 kilovolts, and rise again to a second maximum at approximately 25 kilovolts; the relative intensities of these lines remain approximately constant. The intensity of the line 4686 Å. due to He^+ appears to be zero up to approximately 11 kilovolts, and then increases regularly; its intensity relative to the line 5016 Å. increases approximately linearly with the voltage in the range above 11 kilovolts. Intensities were measured by comparison with a standard lamp. R. W. LUNT.

Ionisation potential and the fine line spectrum of hydrogen. K. F. NIESSEN (Z. Physik, 1927, 43, 694—706).—The ionisation potential of hydrogen has been calculated by the use of half quantum numbers assigned to the ion H_2^+; it is shown that some of the fine-line spectrum is attributable to this ion. The value calculated for the ionisation potential is $-1{\cdot}216Rh$(=15 volts), in good agreement with that calculated by Burrau by wave mechanics $-1{\cdot}204Rh$ (=15·4 volts) (Kgl. Danske Videnskab. Selsk. math.-fys. Medd., 1927, 7, 14). R. W. LUNT.

Under-water spark spectra [of beryllium, gold, molybdenum, tantalum, and tungsten]. (Miss) E. J. ALLIN and H. J. C. IRETON (Trans. Roy. Soc. Canada, 1927, [iii], 21, III, 127—131).—The absorption lines observed were (Å.): beryllium, 3321·45, 3321·08, 3131·06, 3130·42, 2650·94. 2650·31, 2494·87, 2494·44, 2350·82, 2348·50, 2175·1; gold, 2700·90, 2641·49, 2387·75, 2376·25, 2352·65, 2129·46, 2126·62, 1938·52; molybdenum, 2045·9, 2038·4, 2018·2, 2013·1; tantalum, 2274·46, 2261·68, 2261·47, 2253·35, 2196·07, 2193·90, 2193·25, 2182·66, 2141·95, 2119·71; tungsten, 2402·43, 2436·61, 2461·60, 2482·21, 2543·43, 2613·07, 2613·86, 2633·10, 2656·56, 2681·40. A. A. ELDRIDGE.

Existence of solid nitrogen in the earth's atmosphere. H. PELZER (Ann. Physik, 1927, [iv], 83, 362—384).—In order to explain the 5577·35 Å. line in the spectrum of aurora borealis, Vegard assumes the existence of a layer of solid nitrogen in the upper atmosphere. The possibility of a temperature below the m. p. of nitrogen (36° Abs.) occurring in the atmosphere with the earth-sun radiation equilibrium has been investigated thermodynamically. It is shown that non-selective absorption of all but a fraction 10^{-1430} of the earth's radiation must occur, or, even if absorption is confined to the infra-red, 99·5% must be absorbed in this region by the deeper atmospheric layers. These conditions do not appear reasonable, and therefore Vegard's hypothesis seems thermodynamically unsound. R. A. MORTON.

Afterglow of active nitrogen. K. F. BONHOEFFER and G. KAMINSKY (Z. physikal. Chem., 1927, 127, 385—400).—Nitrogen, purified by the method of Kaustky and Thiele, exhibits no afterglow; the presence of at least 1% of another gas is necessary before the effect becomes apparent. The characteristic spectrum of the afterglow is independent of the

foreign gas, and the conclusion is therefore reached that the added gas plays no part in the chemiluminescence reaction which is responsible for the afterglow. The homogeneous gas reaction causing the appearance is bimolecular. In the ultra-violet (down to 2100 Å.) and visible regions of the spectrum, active nitrogen exhibits no absorption. Impurities have no influence on the ratio of the intensities of the atomic and molecular spectra, as they have with active hydrogen.

H. F. GILLBE.

Structure of the arc spectra of the elements of the nitrogen group. J. C. MCLENNAN and A. B. MCLAY (Trans. Roy. Soc. Canada, 1927, [iii], 21, III, 63—77).—An examination of existing data leads to the identification of multiplets in the arc spectra of nitrogen, phosphorus, arsenic, antimony, and (tentatively) bismuth. The terms $^4S_2$, $^2D_{23}$, and $^2P_{12}$ are deep, with $^4S_2$ deepest; $^4P_{123}$ and $^2P_{12}$ are the most important of the higher energy terms, with $^4P_{123}$ deeper than $^2P_{12}$. The results accord with the Pauli–Heisenberg–Hund theory. The three outermost electrons of the unionised atom are in each case bound in n_2 orbits; for the most stable of the excited states two are bound in n_2 orbits and one in an $(n+1)_1$ orbit. A. A. ELDRIDGE.

Origin of the auroral green line in the oxygen spectrum. J. C. MCLENNAN, R. RUEDY, and J. H. MCLEOD (Trans. Roy. Soc. Canada, 1927, [iii], 21, III, 27—31).—Parallel evidence is adduced to show that in seeking to fit the auroral green line 5577·341 Å. observed in the oxygen spectrum into the system of energy levels provided for oxygen atoms, "forbidden" as well as "permissible" transitions should receive consideration. A. A. ELDRIDGE.

Explanation of spectra of metals of group II. II. P. K. KICHLU and M. SAHA (Phil. Mag., 1927, [vii], 4, 193—207).—An extension of the previous work of Saha (this vol., 705), in which it is shown that the conclusions of Russell and Saunders (A., 1925, ii, 911) regarding the origin of the p-terms are correct for calcium, barium, and strontium, but should not be accepted as generally applicable to the origins of all dashed terms (cf. following abstract).

A. E. MITCHELL.

Spectrum of neon. M. SAHA (Phil. Mag., 1927, [vii], 4, 223—231).—The results of Hund and of Goudsmit on the spectrum of neon have been utilised according to the author's method for the examination of the spectra of the alkaline earths (cf. preceding abstract). The theory then accounts not only for the fundamental levels, but also for all the higher levels, the Rydberg sequences, and the order of values observed in each case. The treatment leads to the conclusion that whenever from any particular distribution of electrons in potential orbits, F, D, and P terms arise simultaneously they must then have the same combining powers, so that if F and P are treated as ordinary terms then D must be dashed, or if any two terms be treated ordinarily, then the third must be dashed and the choice must depend entirely on the previous knowledge of the spectrum of the element. The theory also explains transitions such as $\Delta K=2$ or 3 which apparently depart from the selection principle. A. E. MITCHELL.

Spectrum of Si^+ II. P. K. KICHLU (J. Opt. Soc. Amer., 1927, 14, 455—459).—The contributions of Fowler and Saha to the structure of the spectrum of Si^+ are discussed and explained on the basis of Hund's theory (A., 1925, ii, 912, 1104); it is shown that the lines $^2P—^4\bar{P}$ are to be expected in the region of 2500 Å., which therefore needs to be investigated further.

R. W. LUNT.

New lines between 3100 and 2400 A. in the arc spectrum of manganese at normal pressure. S. PINA DE RUBIES and J. DORRONSORO (Anal. Fís. Quím., 1927, 25, 211—215).—The wave-lengths, frequencies, and intensities of 135 new lines between 3025 and 2400 Å. in the arc spectrum of manganese are tabulated. The majority of the lines have already been encountered in the spark spectrum.

J. S. CARTER.

Origin of terms of the spectrum of cobalt. N. K. SUR (Phil. Mag., 1927, [vii], 4, 36—49).—The method employed by Saha (this vol., 705) has been applied to the detailed examination of the spectrum of cobalt. Only a small number of fundamental levels and a few levels combining with these have been found. No Rydberg sequence has been discovered. Final settlement is required as to whether the $9M_3$ state is possible or not, since, although according to Bohr and to Stoner the $7M_3—2N_1$ state is the most stable configuration of the electrons in the cobalt atom, the terms due to the $8M_3—1N_1$ state occur prominently in the arc spectrum of cobalt.

A. E. MITCHELL.

Magnetic resolution of the arc spectrum of zinc. E. BACK (Z. Physik, 1927, 43, 309—320).—35 lines of the arc spectrum of zinc (containing 5% of antimony) in the region 6844·2—2268·92 Å. have been resolved in a magnetic field of 39,000 gauss; from the values obtained for the broadening factor g the p, s, and d values have been assigned to the lines according to the theory of Hund (A., 1925, ii, 1104).

R. W. LUNT.

Arc and spark spectra of bromine. L. BLOCH and E. BLOCH (Ann. Physique, 1927, [x], 6, 205—231; cf. A., 1925, ii, 611).—Using an electrodeless discharge tube containing sodium bromide, some 1100 lines have been determined in the region 6700—2250 Å.; of these 700 are reported for the first time. In addition to lines due to neutral bromine atoms, the lines due to singly and doubly ionised atoms have been classified. Some lines are thought to be due to triply ionised atoms. R. W. LUNT.

Wave-length measurements in the arc and spark spectra of zirconium. C. C. KIESS (U.S. Bur. Standards, Sci. Paper 548, 1927, 22, 47—60).—The arc and spark spectra of zirconium as emitte between electrodes of the pure metal have been photographed. The arc spectrum has been trace from 4881 into the infra-red up to 9277 Å. The arc spectrum consists of (1) band spectra originating in a molecule, perhaps of zirconium oxide, (2) line spectra originating in the neutral atom, (3) line spectra originating in the singly ionised atom. The spark spectrum, measured from 2163 to 6115 A., contains, in addition to the foregoing, (4) lines o the doubly ionised atom, (5) lines of the treb y

ionised atom. Tables of wave-lengths of the lines are given. W. E. Downey.

Influence of the magnetic field on the polarisation of the resonance radiation of cadmium. P. Soleillet (Compt. rend., 1927, **185**, 198—199).—The experiments of Wood and Ellett (A., 1924, ii, 715) on the influence of a weak magnetic field on the resonance radiation of mercury have been repeated for the corresponding ray (3261 Å.) of cadmium, and the same qualitative results obtained. The depolarising effect of the magnetic field, however, is considerably greater with cadmium. For a zero magnetic field the polarisation is 73% at 115—170°, but falls to 35% at 210°. J. Grant.

Fine structure of the spectrum lines of cadmium in the ultra-violet. W. Mohammad and S. B. L. Mathur (Phil. Mag., 1927, [vii], **4**, 112—120).—An attempt has been made to analyse the fine structure of the most prominent cadmium lines over the range 4800—2775 Å. In general the results are in agreement with those of MacNair (A., 1926, 986). A. E. Mitchell.

Series in the first spark spectrum of tin. A. L. Narayan and K. R. Rao (Nature, 1927, **120**, 120).—The spectrum of tin in the singly-ionised stage (Sn II) has been investigated. All the terms required by Hund's theory have been found, together with ^4P, a-D, ^2P, and a^2S terms. The second ionisation potential of tin is computed to be about 14·5 volts. About 30 lines in the first spark spectrum have been classified. In general, it closely resembles the spectrum of Si II. A. A. Eldridge.

Electrodeless discharge. Spectra of ionised mercury and of iodine. J. K. Robertson and J. H. Findlay (Trans. Roy. Soc. Canada, 1927, [iii], **21**, III, 89—97).—Sixteen mercury lines between 1942 and 2848 Å. were observed when the discharge was carried by helium at 0·2 mm. pressure, the most intense being 2848, 2837, 2262, 2260, 2225, 2191, 2052, and 1942 Å. Carroll's classification of Hg II (A., 1926, 214) is preferred, and is supported by further study of the line 1942 Å.; the line 2264 Å. probably belongs to Hg III (Kimura and Nakamura, A., 1925, ii, 726). The spectra of pure iodine, iodine and hydrogen, and iodine and helium were also observed. With hydrogen, hydrogen iodide was probably formed, and the spectrum is unlike that obtained in helium; no evidence of combination between helium and iodine was obtained, although the iodine vapour, after discharge, was brown (cf. Boomer, A., 1925, ii, 925). A. A. Eldridge.

Hyperfine structure of lanthanum lines. W. F. Meggers and K. Burns (J. Opt. Soc. Amer., 1927, **14**, 449—454; cf. this vol., 602).—An account of preliminary experiments is given in confirmation of the view that some lanthanum lines have a hyperfine structure. An interferometric method was used in the range 6800—3800 and a grating in the range 0—3800 A. The source used gave sharp and narrow lines and showed little reversal. In the spectrum the line is a quadruplet: 2667·96, 2668·30, 2668·42, and a^4F_4 a doublet: ·4ɔɔ, 3494·633. In the La II spectrum a^1D_2 and a^3D_2 are triplets: 1394·298, 1394·476, 1394·622, and 1894·967, 1895·168, 1895·342; a^3D_3 is a quintuplet: 3250·00, 3250·15, 3250·31, 3250·49, 3250·71; and a^3P_2 and a^1S_0 are doublets: 6227·34, 6227·52, and 7394·48, 7394·59. R. W. Lunt.

Spectrographic junction of the *X*-ray and ultra-violet regions with the aid of ruled gratings. J. Thibaud (Compt. rend., 1927, **185**, 62—64).—By means of a tangent diffraction grating having 1800 lines per mm. (A., 1926, 651) the wave-lengths of the rays Fe$L\alpha$ (17·73 Å.), O$K\alpha$ (23·75 Å.), C$K\alpha$ (44·80 Å.) and Mo$M\alpha$ (65·0 Å.) have been determined within an absolute error of 0·5%. The spectrographic junction between the *X*-ray and ultra-violet regions has thus been attained. J. Grant.

Atomic character of some properties of *X*-rays. E. Delauney (Compt. rend., 1927, **185**, 193—195).—It is shown theoretically, and confirmed by ionisation measurements of the intensity of the radiation of fluorescence produced when mixtures in varying proportions of strontium and barium chlorides were irradiated with *X*-rays, that the intensity of the fluorescence is not an additive property for the two salts. It increases much less quickly in proportion to the amounts of barium chloride present. J. Grant.

Direct and indirect production of characteristic *X*-rays. D. L. Webster (Proc. Nat. Acad. Sci., 1927, **13**, 445—456; cf. Beatty, Proc. Roy. Soc., 1912, **A**, **87**, 511; Balderston, A., 1926, 767).—The characteristic rays from silver are largely of direct origin, the experiments described indicating a ratio of direct to indirect rays equal to 2·4 at all ordinary *X*-ray voltages. Indirect rays do not appear to any appreciable extent in spectra from extremely thin targets, especially when light backing materials are used. The ratio of the probability that a cathode ray will remove a *K* electron from an atom by direct action to the probability that it will radiate a quantum of energy in the continuous spectrum as great as the *K*-ionisation energy, is of the order of unity for silver at 50 kilovolts. The ratio is probably greater for copper under corresponding conditions and may vary with the voltage. J. S. Carter.

Efficiency of *K*-series emission by *K*-ionised atoms. L. H. Martin (Proc. Roy. Soc., 1927, **A**, **115**, 420—442).—Relative values for the efficiency of *K*-emission have been determined in iron, nickel, copper, and zinc for a series of exciting radiations which lie between 0·6 Å. and the respective *K* limits of these elements. In iron, the absolute efficiency has been determined and investigated as a function of the frequency of the ionising radiation. A beam of exciting radiation is totally absorbed in a plate of one of the above metals placed at right angles to it. The ratio of the energy of the total excited *K*-radiation to that of the exciting radiation can be readily deduced from the ratio of the ionisations produced by the total absorption in oxygen of the exciting beam and those excited rays which escape the radiator, if the absorption coefficients for those radiations in the radiator are known. The low values found for the efficiency of emission for *K*-ionised atoms, together with the results of other related experiments, are

explained by the hypothesis that, in some cases, for reasons not yet understood, the excited K-radiation does not escape the atom, but is "internally absorbed" in outer electron shells, giving rise to high-speed electrons. The probability of K-series emission as opposed to its internal absorption is found to be independent of the frequency of the exciting radiation, within the limits of experimental error. The efficiency of K-emission is a function of the atomic number of the excited atom, and it seems probable that similar laws, relating the probability of absorption with atomic number and wave-length, hold for both "normal" and "internal" absorption. L. L. BIRCUMSHAW.

Measurement of the MoK doublet distances by means of the double X-ray spectrometer. B. DAVIS and H. PURKS (Proc. Nat. Acad. Sci., 1927, **13**, 419—422).—Using the double X-ray spectrometer, considerable separations of the Mo$K\alpha$ and $K\beta$ doublets have been obtained. The observed separations, 0·0043 and 0·00058 Å., respectively, are in good agreement with those derived from actual wave-length determinations. The Mo$K\gamma$ doublet could not be separated. J. S. CARTER.

Intensities of soft X-ray lines as a function of the exciting potential. A. JONSSON (Z. Physik, 1927, **43**, 845—865).—The variation of the intensity of X-ray lines as a function of the exciting potential in the range 0—20 kilovolts has been measured using the most recent form of Siegbahn's vacuum spectrograph. Intensities were measured by Geiger's method. The lines measured were Al$K\alpha$, $K\alpha_3$, $K\beta_1$; Ag$L\alpha_1$, Rh$L\alpha_1$, $L\beta_1$, $L\beta_2$, $L\gamma_1$; Mo$L\alpha_1$, $L\beta_1$; Tl$M\alpha$, and W$M\alpha$, $M\beta$. The curves so obtained have been compared with the intensities calculated from the theoretical equations of Bergen–Davis (Physical Rev., 1918, [ii], **11**, 433), and of Rosseland (Phil. Mag., 1923, [vi], **45**, 65). The former does not agree with experiment; if however due allowance be made for anticathode absorption in the application of Rosseland's equation, then a fairly satisfactory agreement with experiment is obtained, at least at low exciting potentials. R. W. LUNT.

X-Ray spectra of the second order. M. J. DRUYVESTEYN (Z. Physik, 1927, **43**, 707—725).—The satellites of the line $K\beta_1$, $K\beta''$, $K\beta_2$, and $K\beta'''$ have been measured for the elements from potassium to iron; the values of $K\beta'''$—$K\beta_1$, expressed as νR^{-1}, agree well with those calculated from data referring to the normal spectra. The satellites of the line $L\beta_2$, $L\beta'_2$ and $L\beta''_2$ have been determined for the elements from niobium to lead; the calculated differences $L\beta'_2$—$L\beta_2$ and $L\beta''_2$—$L\beta_2$ show discontinuities at lead and silver and are always slightly greater than the corresponding experimental values, which lie on a smooth curve. The satellites of the line $L\gamma_1$, $L\gamma_1'$, have been determined for the elements from niobium to tin; the differences $L\gamma'_1$—$L\gamma_1$ lie between the extreme values calculated and so do the differences corresponding with $L\gamma'_{2,3}$—$L\gamma_{2,3}$ for the elements from zirconium to silver. R. W. LUNT.

Emission of soft X-rays by different elements. O. W. RICHARDSON and F. S. ROBERTSON (Proc. Roy. Soc., 1927, **A**, **115**, 280—290; cf. *ibid.*, 1926, **A**, **110**, 273).—An apparatus is described by means of which the efficiency of six different elements as emitters of soft X-rays can be measured in rapid succession under similar conditions without opening up the experimental vessel. The apparatus consists of a quartz tube in which are mounted two filaments, the structure supporting the targets, a pair of nickel condenser plates, a nickel photo-electric plate around which is a nickel electrode, and a nickel earth shield. The thermionic current (*it*) producing the X-radiation was measured, also the photo-electric current (*ip*) produced by a definite portion of that X-radiation when it fell upon a nickel plate, and the ratio *ip*/*it* was plotted against atomic number for the elements carbon, silicon, chromium, manganese, iron, cobalt, nickel, copper, molybdenum, palladium, silver, tungsten, platinum, and gold. For a given element, *ip*/*it* is approximately proportional to the *P.D.* exciting the X-rays. The efficiency appears to be a periodic function of the atomic number, and not, as previously stated (*loc. cit.*), proportional to the square root. L. L. BIRCUMSHAW.

Inverse Zeeman effect in neon lines. H. NAGAOKA and T. MISHIMA (Proc. Imp. Acad. Tokyo, 1927, **3**, 205—207).—Spectrograms are given which show the inverse Zeeman effect in a number of lines of the neon spectrum from 5852 to 6533 Å. The spectrum was excited in the capillary tubing connecting the legs of an H-shaped discharge tube; the field applied varied from 1·8 to 5·8 kilogauss. Careful regulation of the neon pressure and electrode potential is necessary for the production of the phenomenon. R. W. LUNT.

Zeeman effect of the hyperfine structure components of the mercury line 2537. W. A. MACNAIR (Proc. Nat. Acad. Sci., 1927, **13**, 430—432).—In zero magnetic field the positions of the hyperfine structure components of the mercury line 2537 are, taking the central one as reference, —0·0256, —0·0103, 0, +0·0116, and +0·0221 Å., respectively. In magnetic field the last four become triplets with 3/2 the normal separation. The behaviour of the line —0·0256 Å. is more complicated. The perpendicular components behave as the perpendicular components of a 3/2 normal triplet starting at —0·0256 Å., but the parallel component increases in wave-length with increasing field strength. The relative intensities of the five lines in zero field are, in order of increasing wave-length, 13, 8, 10, 10, and 9. In a field of 5000 gauss the relative intensities of the parallel components are 3, 6, 18, 19, and 4, respectively. The anomalous behaviour of the line —0·0256 offers a possible explanation of the incomplete polarisation of resonance radiation of mercury in zero magnetic field. J. S. CARTER.

Transition from ordinary dispersion into Compton effect. I. WALLER (Nature, 1927, 120, 155—156).—A brief account, relating to an atom containing only one electron, is given of the various stages of the transformation. A. A. ELDRIDGE.

Theory of Compton effect. II. G. WENTZEL (Z. Physik, 1927, **43**, 779—787).—The analysis previously developed (this vol., 603) has been extended to a consideration of the inner atomic interference o

scattered radiation whereby a more exact evaluation has been made of the intensities of displaced and undisplaced lines. For the scattering of the $K\alpha$-line of molybdenum (0·708 Å.) the calculated values of the ratio of the normal intensity to that scattered at an angle θ agree satisfactorily with those observed by Woo (A., 1926, 447) for values of θ from 60° to 150°. A more satisfactory agreement between experiment and theory obtains for the $K\alpha$-line of zinc (1·437 Å.). In the case of pure crystal interference of the $K\alpha$-line of ruthenium (0·612 Å.) by sodium chloride for scattering angles from 11° to 60° the analysis leads to values of the ratio of the normal intensity to the intensity according to classical theory, which ratio is identical with the square root of Bragg's form factor, in good agreement with those obtained experimentally (Bragg, Phil. Mag., 1921, [vi], 41, 309; A., 1921, ii, 477). R. W. Lunt.

Duration of resonance phenomenon. E. Fues (Z. Physik, 1927, 43, 726—740).—The duration of resonance has been analysed by wave mechanics, and values have been calculated for argon, krypton, and xenon of the same order of magnitude as those given by Auger. R. W. Lunt.

Ultra-ionisation potentials of mercury. E. O. Lawrence (J. Franklin Inst., 1927, 204, 91—94; cf. this vol., 85).—Ultra-ionisation potentials were detected when mercury vapour was bombarded with electron streams possessing Maxwellian velocity distributions. J. S. Carter.

Thermionic emission from solid and liquid metals. II. The thermionic melting diagram of copper, silver, and gold. A. Goetz (Z. Physik, 1927, 43, 531—562; cf. this vol., 492).—The method is described by which the continuously recording device for emission, temperature, and time was calibrated; the maximum sensitivity is 1·035 amp./mm. The data obtained have been employed to calculate accurately the constants b and b_0 in the Richardson and Richardson–Dushman equations: $I=A\sqrt{T}\times e^{-b/T}$ and $I=A_0T^2e^{-b_0/T}$; from these values A and A_0 have been obtained. The corresponding values of the work of electron evaporation ϕ and ϕ_0 have been calculated from $\phi=bke^{-1}$ and $\phi_0=b_0ke^{-1}$, where k is the Boltzmann constant and e is the electronic charge.

Eighteen measurements were made on silver in the range 1233—1454 °Abs., below which the emission was too low to measure; 17 on gold in the range 1302—1532° °Abs., and 25 on copper from 1276 to 1530 °Abs. For silver the values of ϕ and ϕ_0 increase from 1·89 to 3·43 and from 1·71 to 3·26 volts, respectively; assuming the validity of Dushman's constant A_0 for solid silver, $\phi=4·19$ and $\phi_0=4·03$ volts at 1233 °Abs. ...e emission from gold shows a discontinuity at 1335 °Abs., and the values of ϕ and ϕ_0 increase from ·70 to 4·48 and from 2·51 to 4·30 respectively, whilst he values for solid gold computed as for silver are 4·49 and 4·32 at 1315 °Abs. The emission from copper reaches a maximum at 1360 °Abs., falls suddenly as e metal melts, and then increases. For solid copper s., $\phi=4·50$, $\phi_0=4·33$ volts; in the range 1530 °Abs., ϕ increases from 1·91 to 6·90 and ϕ_0 m 1·79 to 6·69 volts. The work of thermionic evaporation thus diminishes abruptly at the m. p. of these metals, and increases as the temperature rises beyond this point. A number of incidental phenomena associated with the occlusion of gases and with the crystallisation of these metals are also described. R. W. Lunt.

Thermionic emission of incandescent platinum in an atmosphere of iodine. P. Jez (J. Phys. Radium, 1927, [vi], 8, 244—253).—The emission behaves in accordance with Richardson's law of thermionic emission. The negative emission in an atmosphere of iodine is considerably greater than the corresponding emission in air. The positive emission in an atmosphere of iodine is almost zero. It is suggested that the reversible reaction $Pt+2I_2 \rightleftharpoons PtI_4$ takes place on the surface of the platinum, and that a layer of iodide is responsible for the emission. W. E. Downey.

Application of the equations of chemical kinetics to the phenomenon of emission of electrons from red-hot bodies. J. K. Syrkin (J. Russ. Phys. Chem. Soc., 1927, 59, 351—355).—Electrons are assumed to be emitted only from the superficial layer of a hard metal; the emission may therefore be regarded as a heterogeneous chemical reaction of the first order, thus allowing the application of the several well-known equations of chemical kinetics to the various deduced thermodynamical expressions for L, the number of electrons emitted in unit time from unit area of a hot surface. J. Kaye.

Role of circular electrons in paramagnetic phenomena. D. M. Bose (Z. Physik, 1927, 43, 864—882).—An attempt has been made to explain paramagnetic phenomena in terms of quantised electron orbits, thereby avoiding the difficulties associated with the classical theories of Langevin and Weiss. The basic assumptions characterising the analysis now advanced are (1) that of the angular momenta of an electron moving in a closed orbit associated with the s quantum number and the k—1 associated with the k (azimuthal) quantum number, only the former are responsible for paramagnetic phenomena, and (2) that, whatever be the orientation of an atom or ion with an incomplete inner ring to a magnetic field, the resulting magnetic moment is equal to the algebraic sum of the circular angular momenta of all the electrons in the field. From these assumptions the formulæ of Langevin and Weiss have been derived, and the magnetic moments of ions with incomplete inner ring have been calculated as a function of the number of electrons in the M ring. From these values the corresponding numbers of Weiss magnetons have been calculated, in good agreement with experiment, for the following ions: Ti^{+++}, V^{+++}, Cr^{+++}, Fe^{+++}, Mn^{++}, Fe^{++}, Co^{++}, Ni^{++}, and Cu^{++}. R. W. Lunt.

Magnetic study of vanadium tetroxide and trioxide; measurement of the atomic moments of quadri- and ter-valent vanadium. N. Perrakis (Compt. rend., 1927, 185, 111—113; cf. this vol., 288, 717).—The curves relating the variation with temperature of the coefficient of magnetisation of vanadium tetroxide and trioxide indicate that whilst

the former has two atomic moments (8 and 14 magnetons) for two well-defined temperature intervals, the latter has one moment (19·5 magnetons) very near to the dominant moment (9 magnetons) of the V^{IV} ion. The change in moment in the former case has been attributed to dissociation of the tetroxide into the trioxide, since 14 magnetons is the dominant moment of the V^{III} ion. J. GRANT.

Weber's theory of molecular magnetism, and the internal field. W. PEDDIE (Nature, 1927, **120**, 80—81).

Positive-ray analysis of nitric oxide and collisions of the second kind. T. R. HOGNESS and E. G. LUNN (Physical Rev., 1927, [ii], **30**, 26—30).—The ionisation potentials for the formation of NO^+, N^+, and O^+ are 9, 21, and 22 volts, respectively; the heat of dissociation of the molecule of nitric oxide is computed to be 175,000 g.-cal. per g.-mol. The percentages of N^+ and O^+ formed by electron impact increase with increase in pressure from 4 and 1·5% at zero pressure to 9 and 3%, respectively, at 0·01 mm. Some of the NO^+ ions dissociate spontaneously, and others are disrupted into the atomic ions on collision with gas molecules. In presence of argon or helium there is evidence of collisions of the second kind: $NO+A^+=NO^++A$, and $NO+He^+=NO^++He$. A. A. ELDRIDGE.

Influence of neighbouring metal walls on the loss of charge of canal rays. J. KOENIGSBERGER (Z. Physik, 1927, **43**, 883—898).—The discrepancies between the data of Wien, Kutschevski, Ruttenauer, and Ruchardt on the loss of charge and on the mean free path of the particles comprising canal rays are discussed at length with special reference to the effects produced by metal surfaces for which in the particular case of iron capillaries an analysis is developed. Examples are given showing how this analysis leads to values of the concentration of H^+ particles before and after passing through a steel tube (2·5 cm. × 0·8 mm.) which are in good agreement with experiment.

The corrections necessary to evaluate the ratio, w, of the number of positively charged particles to the number of neutral particles in a beam of canal rays are discussed in detail and examples are given. It is shown that for acceleration potentials of approximately 35 kilovolts for H^+ ions in hydrogen the corrected values of w of Ruttenauer and Ruchardt agree approximately. This is because at such potentials the effect of metal capillaries on w is small; at lower potentials the effect is more marked, and in this is to be sought the explanation of the discrepancies in the data of the two workers just mentioned. R. W. LUNT.

Helium compound. D. M. MORRISON (Nature, 1927, **120**, 224).—If orthohelium has one electron relatively far removed from the nucleus with respect to the other, it might be expected to resemble hydrogen in forming a gaseous compound with bismuth or its radioactive isotopes. Experiments in which helium is passed over a strong radioactive source of radium-*B* and radium-*C* and excited by means of an electrodeless discharge indicate that such a gaseous compound is formed. A. A. ELDRIDGE.

Constitution of ordinary lead. F. W. ASTON (Nature, 1927, **120**, 224).—Experiments with lead tetramethyl yield three principal lines, 206, 207, 208, of intensities respectively 4, 3, 7, in good agreement with the at. wt. 207·2. The lines are integral with those of mercury to an accuracy of 1—2 in 10^4. A faint line at 209, and possibly lines at 203, 204, and 205 are also present. The presence in mercury of an isotope 196 (0·04%) is certain. A. A. ELDRIDGE.

At. wt. of scandium. N. H. SMITH (J. Amer. Chem. Soc., 1927, **49**, 1642—1650).—Anhydrous scandium chloride was prepared by passing carbon tetrachloride vapour diluted with nitrogen over pure scandium oxide at 750—850°. The ratio of the fractionally sublimed chloride to pure silver was then determined; the mean of nine analyses gave 45·160 as the atomic weight of scandium (Ag=107·880). A special apparatus for filling a weighing bottle with the chloride in presence of dry air is described. S. K. TWEEDY.

Fundamental at. wts. III. Revision of the at. wt. of silver. Analysis of silver nitrate. O. HONIGSCHMID, E. ZINTL, and P. THILO (Z. anorg. Chem., 1927, **163**, 65—92).—The at. wt. of silver has been redetermined by reduction of silver nitrate with hydrogen. In order to eliminate errors due to adsorption of air on the silver nitrate and on the reduced silver, the analyses were conducted in a vacuum. Taking the at. wt. of nitrogen as 14·008, that of silver is 107·879. H. F. GILLBE.

Fundamental at. wts. IV. At. wt. of potassium. Analysis of potassium chloride. O. HONIGSCHMID and J. GOUBEAU (Z. anorg. Chem., 1927, **163**, 93—104).—The ratios KCl : Ag and Ag : AgCl have been determined by a nephelometric method, giving for the at. wt. of potassium 39·104. H. F. GILLBE.

Fundamental at. wts. V. At. wts. of silver, chlorine, and potassium. E. ZINTL and J. GOUBEAU (Z. anorg. Chem., 1927, **163**, 302—314).—By heating potassium nitrate in hydrogen chloride, the ratio KNO_3 : KCl has been found to be $1{\cdot}356111\pm0{\cdot}000010$. Taking the at. wt. of nitrogen as 14·008, the ratio AgCl : Ag as 1·328668, and the ratio KCl : Ag as 0·691149, the following at. wts. are calculated: silver, $107{\cdot}879\pm0{\cdot}0011$; potassium, $39{\cdot}104\pm0{\cdot}0007$; chlorine, $35{\cdot}456\pm0{\cdot}0003$. R. CUTHILL.

Fundamental at. wts. VI. At. wt. of chlorine. I. Complete synthesis of silver chloride. O. HONIGSCHMID and S. B. CHAN. **II. An incomplete synthesis of silver chloride.** O. HONIGSCHMID and L. BIRCKENBACH (Z. anorg. Chem., 1927, **163**, 315—344).—A weighed amount of liquid chlorine was reduced to hydrogen chloride by means of ammonium arsenite, then caused to react with the equivalent weighed amount of silver, dissolved in nitric acid, and the silver chloride formed weighed. In this way, the ratio Cl : Ag was found to have the value 0·328668, from which, assuming the value 107·880 for the at. wt. of silver, the at. wt. of chlorine is 35·457. Since the weight of silver chloride was equal to the sum of the weights of the constituent elements to within the limits of experimental error, the doubts cast by Guye

on the purity of at. wt. silver (A., 1918, ii, 40) seem unfounded.

An attempt was made to alter the proportions of the isotopes of chlorine in carbon tetrachloride by fractional distillation. The chlorine in the two extreme fractions was converted into hydrogen chloride by passing the carbon tetrachloride over glowing quicklime, precipitating the calcium with ammonium carbonate, and distilling the concentrated filtrate with sulphuric acid. The acid was then used to precipitate a weighed amount of silver. In neither case was the result different from that obtained using ordinary hydrochloric acid. R. CUTHILL.

Special effects of polonium, solar radiation, and high tension on lead. (MLLE.) S. MARACINEANU (Compt. rend., 1927, **185**, 122—124; cf. A., 1926, 879; this vol., 710).—The ionisation-currents obtained from a lead strip 0·1 mm. thick on the back of which polonium had been deposited, were determined before and after exposure to positive or negative tensions of 120,000 volts, and to the sun, with or without the high tension. In all cases the ionisation was small at first, increasing rapidly to a maximum and slowly falling off exponentially. The unexposed strips and those exposed to high tension only produced greater ionisation-currents than those exposed to solar radiation with or without exposure to a high tension, the effects of the high tension (especially of the negative type) and of the sun being to lower and raise the ionisation-currents, respectively. The radiation which is not due to the polonium itself is of the α-particle type, although exposure to a negative tension causes the appearance of a β-radiation also. The phenomena are attributed to the formation of a new radio active substance in the lead. J. GRANT.

[Special effects of polonium, solar radiation, and high tension on lead.] H. DESLANDRES (Compt. rend., 1927, **185**, 124—125).—The α-particles of polonium may give rise to a more penetrating radiation of protons when they are stopped by the lead, the effect of which may be modified by the nature of the subsequent exposure. J. GRANT.

Vaporisation of polonium. P. BONET-MAURY (Compt. rend., 1927, **185**, 204—206).—By means of the apparatus previously described (this vol., 606) it has been shown that the curve obtained when the percentage of polonium vaporised is plotted against r/d follows the cosine law to within 2%. The ratio r/d is known as the "reduced ray," r being the radius of the circle enclosing the number of polonium atoms concerned, and d the distance between a centre of symmetry situated on the normal to the emitting surface, and the centre of the disc bearing the deposits. J. GRANT.

Theory of luminescence in radioactive luminous compounds. J. W. T. WALSH (Proc. Physical Soc., 1927, **39**, 318—333).—Determinations of the brightness curves of radioactive luminous compounds over a period of about 4000 days show that the brightness–time relationship is of the form $\log\{B/(b+B)\}+kt+a=0$, where a, b, and k are constants, and B is the brightness after time t. The results are in accord with Rutherford's theory of the destruction of active centres combined with a hypothesis of progressive increase in the light absorption of the material. The rate of destruction of active centres is 6—9 times that of the ionisation of inactive molecules, and in the new material 20—50% of the molecules are in the active state. J. S. G. THOMAS.

New scheme for atom-building. M. N. SAHA (Physikal. Z., 1927, **28**, 469—473; cf. *ibid.*, 221; this vol., 705).—The principles laid down in the earlier paper are given a new graphical form. The optical, *X*-ray, and periodic properties of the atoms are co-ordinated in terms of the new scheme. W. E. DOWNEY.

Wave mechanics and atomic structure of matter and of radiation. L. DE BROGLIE (J. Phys. Radium, 1927, [vi], **8**, 225—241).—Schrödinger's mechanics represents dynamic phenomena by continuous waves. It is shown that these continuous solutions give only a statistical view of dynamical phenomena. For a more exact description of the phenomena, it is necessary to take into account singular solutions. This conception gives a clear view of Schrödinger's equation. W. E. DOWNEY.

Hypothesis that light quanta and electrons are discrete elements. G. BECK (Z. Physik, 1927, **43**, 658—674).—The Compton and photo-electric effects, diffraction, polarisation, interference, and the general theory of electrodynamics are analysed and discussed from the point of view of the following hypothesis: matter and radiation are to be conceived as discrete elements; to each fundamental characteristic of radiation there is a corresponding characteristic of matter. R. W. LUNT.

Quantum mechanics of magneton electrons. W. PAULI, jun. (Z. Physik, 1927, **43**, 601—623).—The characteristic-function method of Schrödinger and the Dirac–Johnson transformation theory have been employed to derive the quantum mechanics of electrons responsible for magnetic phenomena. R. W. LUNT.

Application of wave mechanics to the quantising of black-body radiation. E. GUTH (Z. Physik, 1927, **43**, 653—657).—Mathematical. R. W. LUNT.

Radiationless quantum changes. G. WENTZEL (Z. Physik, 1927, **43**, 524—530).—The probability of a radiationless change has been analysed by wave mechanics for the special case in which an electron from an *L*-orbit is transferred to a *K*-orbit which is previously ionised: the calculated ratio of the number of $K\alpha$ quanta emitted to the number of *L* electrons transferred is in good agreement with the data of Auger (A., 1926, 1188) and of Robinson (Proc. Roy. Soc., 1926, **A**, **113**, 282). R. W. LUNT.

Magnetic hydrogen atoms and non-magnetic molecules. W. A. NOYES (Proc. Nat. Acad. Sci., 1927, **13**, 377—378).—The magnetic character of hydrogen atoms and the non-magnetic character of hydrogen molecules suggest the following possibilities: Isolated hydrogen atoms may orient themselves loosely in pairs with the rotation of their electrons in the same direction, but will be prevented from combining by the repulsion between the nuclei and also between the electrons. Under the catalytic effect of a metal the orbits of the electrons may be assumed to

take opposite directions, with the two nuclei between the planes of the two orbits. There will be magnetic repulsion between the orbits, but the electrons will be held to their orbital positions by their attraction for the nuclei and will fall closer to these since there are now two nuclei instead of one. This accounts for the large dissipation of energy when two hydrogen atoms unite to form a molecule. The formation of helium atoms is possible by the approach of two hydrogen molecules with the four nuclei between the planes of two electrons, which will fall very close in, whilst the two other electrons will assume orbits at a greater distance. Since the mass of a helium atom is less than that of four hydrogen atoms, the energy evolved in such a process will be of a different order from that involved in the formation of a hydrogen molecule. J. S. CARTER.

"Pendulum" orbits in atomic models. R. B. LINDSAY (Proc. Nat. Acad. Sci., 1927, **13**, 413—419).—Although "pendulum" orbits are usually ruled out of the systems of actual orbits since they apparently involve collision of the electron with the nucleus, such orbits are, however, plausible on the assumption of a repulsive force operative only in the immediate vicinity of the nucleus. Assuming this force to obey an inverse cube law, it is shown that the calculated distances are of a not unreasonable order of magnitude. J. S. CARTER.

Structure of the helium atom. I. J. C. SLATER (Proc. Nat. Acad. Sci., 1927, **13**, 423—430).—The success of the method of perturbations in the calculation of spectra depends entirely on finding a soluble problem to serve as the unperturbed solution which is itself a sufficiently close approximation to the actual case. A method of finding such an approximation is presented and applied to helium, where even the soluble, unperturbed problem gives results in good agreement with experiment. The applicability of the present method to various other problems is indicated. J. S. CARTER.

Coupling of electronic and nuclear motions in diatomic molecules. E. U. CONDON (Proc. Nat. Acad. Sci., 1927, **13**, 462—466).—The new quantum mechanics offers at least a qualitative explanation of phenomena conditioned by the quantum mechanical coupling between the motion of the nuclei and of the electrons in diatomic molecules. J. S. CARTER.

Wave mechanics and the normal state of the hydrogen molecule. E. U. CONDON (Proc. Nat. Acad. Sci., 1927, **13**, 466—470).—Burrau's data (Kgl. Danske Videnskab. Selsk. math.-fys. Medd., 1927, 7, 14) for the energy of an electron moving under the influence of two fixed centres of Coulomb attraction as a function of the distance apart of these centres are used to give a semi-quantitative discussion of the neutral hydrogen molecule. On the assumption that the electrons have no mutual influence, the moment of inertia and the heat of dissociation are $2{\cdot}7\times10^{-41}$ g.cm.^{2} and 24·36 volts respectively. On correction for electronic interaction these quantities become $4{\cdot}26\times10^{-41}$ g.cm.^{2} and 4·4 volts respectively. The latter value agrees to within 0·1 volt with the band spectrum value of Witmer (A., 1926, 552) and of Dieke and Hopfield (this vol., 89). J. S. CARTER.

Energy computations in a simple four-body system. K. F. NIESSEN (Z. Physik, 1927, **43**, 675—693).—The energetics of a simple four-body system have been analysed by classical mechanics with special reference to the application of half quantum numbers to the excited hydrogen molecule. R. W. LUNT.

Absolute intensities in the hydrogen chloride rotation spectrum. R. M. BADGER (Proc. Nat. Acad. Sci., 1927, **13**, 408—413).—The absorption of hydrogen chloride in the region of 80 μ has been determined at four pressures and the absolute absorption curves have been obtained. The value of $B_{5,6}$ calculated from the absorption coefficient as indicated by Tolman and Badger (A., 1926, 451, 555) and using the *a priori* probabilities for the respective quantum states given by the new theories is $4{\cdot}7\times10^{16}$, whilst that demanded by the new quantum theory is $1{\cdot}12\times10^{18}$. The lack of agreement between the experimental and theoretical transition probabilities suggests that, whilst the predictions of the new quantum theory may apply to some ideal system, they do not describe the conditions observed with hydrogen chloride. J. S. CARTER.

Absorption of ozone in the visible spectrum. G. COLANGE (J. Phys. Radium, 1927, [vi], **8**, 254—256).—The values of the absorption coefficient of ozone between 4350 and 6400 Å. have been determined by photographic photometry. The maximum value of the coefficient occurs at about 6070 Å. W. E. DOWNEY.

Absorption and emission spectra of nitric oxide in the ultra-violet. M. LAMBREY (Compt. rend., 1927, **185**, 382—384).—The spectral data of pure nitric oxide have been determined by the method previously described (this vol., 489). Under a feeble dispersion the absorption spectrum appeared as a series of narrow doublets (1948—2267 Å.), but with greater dispersion the components of the first two doublets were found to be double. The moment of inertia of the NO molecule was calculated and found to be $0{\cdot}22\times10^{-39}$ c.g.s.u. and the distance apart of the constituent atoms $0{\cdot}45\times10^{-8}$ cm. An electrodeless discharge produced a mauve illumination the emission spectrum of which included the first two absorption doublets and contained numerous rays in the visible and ultra-violet spectra (2348—2855 Å.). An analogy is indicated between nitric oxide and carbon monoxide. J. GRANT.

Band spectrum of water vapour. D. JACK (Proc. Roy. Soc., 1927, **A**, **115**, 373—390; cf. Watson, A., 1925, ii, 349; Dieke, *ibid.*, 927).—A summary is given of the work of previous investigators on the water-vapour bands 3064, 3122, 2811, and 2875. Experimental evidence as to the nature of the emitter is discussed and shown to be in favour of the hydroxyl ion. Details are given of the band 2608, which is similar in structure to the others. For any definite value of m, it gives the same final value for the moment of inertia as the bands 2811 and 3064, whilst the initial value is the same as that for the band 2875. The scheme of bands suggested by Dieke

(*loc. cit.*) has been extended, and the addition of the band 2608 allows of the scheme being verified by taking differences of the wave-numbers of the null lines in the various bands. The band at 3428 also fits into the scheme. The doublet separations are found to be the same for bands giving the same final value for the moment of inertia. The possibility of explaining the formation of the doublets by the application of the Kratzer–Kramers–Pauli theory is discussed. A series of single lines near the head of the band 2811 has also been measured, and found to fit reasonably well into a parabolic formula. The series bears a strong resemblance to the singlet series measured by Watson. L. L. Bircumshaw.

Interpretation of molecular spectra. III. Rotational and vibrational spectra of molecules containing more than two atoms. F. Hund (Z. Physik, 1927, **43**, 805—826; cf. this vol., 495).—The analysis has been applied to the spectra of water, methane, and ammonia, and in general to molecules containing four or more atoms; its incidence on optical isomerism is discussed. R. W. Lunt.

Molecular spectra of sodium, potassium, and sodium-potassium mixtures. P. Pringsheim and E. Rosen (Z. Physik, 1927, **43**, 519—523).—From observations of the resonance spectrum of potassium, the band spectrum has been analysed, and the nuclear frequencies have been determined. These frequencies for sodium and potassium are inversely proportional to the atomic number. The frequencies characteristic of a mixture of sodium and potassium lie between those of these two metals, and are thought to afford evidence of the existence of the compound NaK. R. W. Lunt.

Deformation of the ionisation curve of pure argon by the addition of oxygen. M. A. Da Silva (Compt. rend., 1927, **185**, 65—67; cf. A., 1926, 877).—Ionisation curves have been constructed to show the progressive deformations of the normal curve of spectroscopically pure argon (ionised by polonium) when mixed with 0·03, 0·3, 2·4, and 4·0% of oxygen by volume. Above 4% no further deformation is produced. J. Grant.

Transparency of fused silica to ultra-violet radiations. Tsukamoto (Compt. rend., 1927, **185**, 55—57).—The absorption of ultra-violet radiations of short wave-length by fused silica varies from one sample to another, probably according to the purity. The absorption coefficient of the purest product obtainable has been measured between the wave-lengths 1862 and 2182 Å. The absorption increases rapidly for wave-lengths below 2100, and is greater than that of crystalline quartz. Extrapolation of the results indicates an appreciable transparency at 1500 Å. J. Grant.

Instantaneous spectra of the alkaline earths. H. Nagaoka, D. Nukiyama, and T. Futagami (Proc. Imp Acad. Tokyo, 1927, **3**, 208—211).—By using a rotating film with a peripheral speed of 655 cm./sec. spectrograms have been obtained of the spectra emitted by magnesium, calcium, strontium, and barium produced by the oscillatory discharge of a condenser of 1·3 microfarads, charged to 25 kilovolts across electrodes of these metals. The inductance of the leads was 34 microhenries, and the resulting frequency $4{\cdot}54\times10^4$ cycles per sec.; the maximum instantaneous current was computed to be $9{\cdot}4\times10^3$ amp. Numerous lines are emitted during the first half cycle, others at a later stage, and some persist for 10^{-4} sec. The magnesium line 2852 ($1S-1P$) is reversed from the initial stage and increases in width to 60 Å., which is thought to be due to the formation of magnesium oxide. The lines 3337, 3332, 3330 ($1p-2s$), initially faint, become stronger; 2942, 2939, 2937 ($1p-3s$) are strong and broadened to 12 Å.; 2782, 2778, 2776 ($1p-4s$) show weak reversal; the triplet 3838, 3832, 3829 shows initial reversal, and 3097, 3093, 3091 shows sharp reversal. The mean line from ionised magnesium 4481 ($2\delta-3\phi$) is strong, and 2803, 2796 ($1\sigma-1\pi$) shows weak reversal. The calcium line 4227 ($1S-1P$) shows strong reversal and is suddenly broadened to 220 Å. The lines 3285, 3274, 3269 ($1p-4s$), 4455, 4435, 4426 ($1p-2d$), 3644, 3631, 3624 ($1p-2d$), 3362, 3350, 3344, ($1p-4d$), 3226, 3215, and 3209 ($1p-5d$) show faint reversal. The lines from the ionised atom 3968 and 3934 show strong and sharp reversal as also for a short duration do 3181, 3179, 3159. The only strontium line showing distinct reversal is 4078 ($1\pi_1-1\sigma$); other lines recorded are 4305, 4161, 4216, 3475, 3464, and 3381. No barium line shows reversal and the following lines are strong: 4554, 4934, 4166, 4131, and 3893. R. W. Lunt.

Reversal of magnesium lines in different gases. H. Nagaoka, D. Nukiyama, and T. Futagami (Proc. Imp. Acad. Tokyo, 1927, **3**, 212—213).—Using the method of excitation described in the preceding abstract, the reversal of magnesium lines has been examined in a partial vacuum of a few cm. in air, nitrogen, oxygen, carbon dioxide, and coal gas at 76 cm., and in air at 152 cm. The principal features are described, and indicate that there are two stages of excitation: one in which the lines are all excited, and the other after 3×10^{-5} sec. in which the combination series lines vanish and the lines 4703, 4352, 4168, 4057 broaden and increase in intensity. The reversal is very much diminished at reduced pressures. R. W. Lunt.

Instantaneous spectrograms of alkali metals by disruptive discharge. H. Nagaoka, D. Nukiyama, and T. Futagami (Proc. Imp. Acad. Tokyo, 1927, **3**, 258—261; cf. preceding abstracts).—The method of obtaining spectrograms previously described has been applied to lithium, sodium, potassium, and rubidium. W. E. Downey.

Instantaneous spectrograms of the alkali chlorides. H. Nagaoka, D. Nukiyama, and T. Futagami (Proc. Imp. Acad. Tokyo, 1927, **3**, 262—264; cf. preceding abstracts).—The reversals observed in spectra obtained by the disruptive discharges of different elements are not observed in the spectra of the salts even although the temperature is high enough to cause complete dissociation of the salts. W. E. Downey.

Absorption spectra of complex ferro- and ferri-cyanides in aqueous solution. L. Cambi and L. Szego (Atti R. Accad. Lincei, 1927, [vi], **5**, 636—641).—The extinction coefficients of the following

complex cyanides in aqueous solution have been determined in the range 5000—2000 Å.: $K_4[Fe(CN)_6]$, $Na_3[Fe(CN)_5,H_2O]$, $Na_3[Fe(CN)_5NH_3]$, $Na_4[Fe(CN)_5NO_2]$, $Na_4[Fe(CN)_5AsO_3]$, $Na_5[Fe(CN)_6SO_3]$, $NaK_3[Fe(CN)_5NO_2]$, $Na_2[Fe(CN)_5,H_2O]$, $Na_2[Fe(CN)_5NH_3]$, $Na_2[Fe(CN)_5NO]$, and $K_3Fe(CN)_6$. The changes in the absorption of a solution of $Na_3[Fe(CN)_5,H_2O]$ in acid and alkaline solution are thought to correspond with the equilibrium $[Fe(CN)_5,H_2O]'''+OH'=[Fe(CN)_5OH]''''+H_2O$. R. W. LUNT.

Absorption spectrum of bromine in solution. BOVIS (Compt. rend., 1927, **185**, 57—59).—Solutions of bromine in water, carbon tetrachloride, chloroform, ethyl alcohol, and carbon disulphide always show two absorption bands (in the violet and ultra-violet). Their sizes and positions are practically constant, the former being 0·106 and 0·036 μ, and the latter 0·414 and 0·260 μ for the violet and ultra-violet, respectively. Comparison with the absorption spectra of gaseous and liquid bromine (A., 1924, ii, 712) shows that the band 0·414 μ is obtained in all cases, whilst the band 0·260 μ is characteristic of bromine in solution only. The opacity of liquid bromine increases regularly from the radiation 0·350 μ (where its optical density is a minimum) towards the radiation 0·240 μ. The observations are complicated by the presence of impurities and by changes in the strengths of the solutions. J. GRANT.

Continuous and band spectra of mercury. H. VOLKRINGER (Compt. rend., 1927, **185**, 60—62).—The author has extended his method (this vol., 178) to the study of the ultra-violet portion of the spectrum obtained when mercury vapour at 240° is excited by an electrodeless, oscillating discharge, the intensities (calculated by the method of Chalonge and Lambert) being plotted against the wave-lengths. The continuous spectrum comprised a large band (0·37—0·30 μ) with a maximum intensity at 0·336, and a smaller band with a maximum at 0·265 μ. A minimum was obtained at 0·260 μ followed by a sharp rise to 0·2537 μ (the resonance ray) when the spectrum ceased sharply. The wave-lengths of the maxima of the numerous diffuse bands between 0·305 and 0·265 μ have also been determined. The distribution of energy as a function of wave-length is similar to that of the radiation from a black body at 2233°. As with cadmium, the wave-lengths of the maxima are almost 2 and 4/3 times that of the resonance ray for the visible and ultra-violet regions, respectively. J. GRANT.

Ultra-violet spectroscopy of engine-fuel flames. G. L. CLARK and A. L. HENNE (J. Soc. Automotive Eng., 1927, **20**, 264—269).—The spectra of radiation during the four quarters of a stroke were observed for straight-run petrol under detonating and non-detonating conditions for the same fuel using lead tetraethyl, aniline, and iodine as knock-suppressors, and for cracked-petrol blends. During detonation the first-quarter spectrum extends far into the ultra-violet, and the second-quarter spectrum a smaller distance; the third and fourth quarters are characterised by very little radiation energy. During normal explosion, or when knock suppressors are used in the engine under detonating conditions, the spectra of all four quarters have the same length and intensity. From lead tetraethyl, lead emission lines appear only in the first quarter. CHEMICAL ABSTRACTS.

Absorption spectra of naturally occurring benzophenone derivatives. T. TASAKI (Acta Phytochim., 1926, **2**, 199—205).—The absorption spectra of certain naturally occurring benzophenone derivatives have been investigated. Maclurin, hydrocotoin, methylhydrocotoin, protocotoin, and methylprotocotoin all show similar absorption, with a single wide band with maximum at 3250 Å. Protocotoin is regarded on spectrochemical grounds as 6-hydroxy-2 : 4-dimethoxy-3′ : 4′-methylenedioxybenzophenone. L. M. CLARK.

Absorption spectra of coumarin derivatives. T. TASAKI (Acta Phytochim., 1927, **3**, 21—29).—The absorption spectra of the following derivatives of coumarin in 0·0001*M*-alcoholic solution have been determined for wave-numbers (λ^{-1} in cm.) from 2000 to 5000: coumarin, hydroxy- and methoxycoumarin, dihydroxycoumarin, æsculin, æsculetin, acetylcoumarin, diacetylæsculetin, and methylenedioxyphenylcoumarin. Coumarin shows two absorption maxima in this region at 3200, 3600 Å. When one or two hydroxyl groups are introduced into the benzene nucleus of coumarin the substance shows only one absorption maximum. E. A. LUNT.

Impact fluorescence of zinc. J. G. WINANS (Physical Rev., 1927, [ii], **30**, 1—10).—The fluorescence radiation obtained when a mixture of zinc vapour at 16 mm. and mercury vapour at 0·28 mm. pressure is illuminated by light of various wave-lengths from the hot and cold quartz mercury arcs and the aluminium spark contains several zinc lines which require more than 4·9 volts for their excitation (cf. A., 1926, 102, 768). It is assumed that mercury atoms in the 2^1P_1 and 2^3S_1 or 3^3D states are effective in impacts of the second kind; a collision between an excited mercury atom and a normal zinc atom appears more likely to be one of the second kind if the energy of the excited mercury atom only slightly exceeds that needed to excite the zinc atom. A band at 2770 Å. may be due to an HgZn molecule. A. A. ELDRIDGE.

Transition of fluorescence into phosphorescence. E. GRAVIOLA and P. PRINGSHEIM (Z. Physik, 1927, **43**, 384—393).—With a rotating phosphoroscope and a Graviola fluorometer the time of duration of the luminescence of the following substances has been determined (time in 10^{-9} sec.): rhodulin-orange in sugar $4\pm0·7$, in gelatin $4·5\pm0·4$, in glycerol $4·3\pm0·4$, in gelatin at −180° with a green filter $4·9\pm0·7$, with a red filter 6·2; uranin in glycerol 4·4; rhodamine-*B* in gelatin $4·6\pm0·2$, in glycerol 4·2; ruby >15; uranium glass >15, uranyl nitrate 5·1, uranyl sulphate in sulphuric acid 1·9. All these substances, except ruby and uranium glass, which exhibit only phosphorescence, show a momentary fluorescence followed by a weaker and relatively slowly diminishing phosphorescence. After a review of the subject, it is concluded that the phenomena of photoluminescence can be classified as follows: (1) Pure fluorescence in which the time interval is of the order o 3×10^{-9} sec. If the exciting light is polarised, the

secondary radiation is unpolarised, or only partly polarised according to the nature of the solute and solvent. (2) Fluorescence followed by phosphorescence in which the time interval is of the order of 10^{-8} sec. For polarised incident light, the fluorescent and phosphorescent emissions are either both unpolarised, or both equally polarised. (3) Pure phosphorescence in which the polarisation of the secondary radiation does not depend on that of the incident beam, but is determined by the crystal structure of the phosphorescent substance. It is also concluded, in agreement with the results of Vavilov and Pringsheim, that no transition of fluorescence into phosphorescence is to be observed.

R. W. LUNT.

Luminescence phenomena during oxidation reactions in aqueous solutions. L. MALLET (Compt. rend., 1927, **185**, 352—354).—Numerous oxidation reactions, even in dilute solutions, are accompanied by the production of visible light, or by a radiation detectable photographically, or made visible by the addition of fluorescent substances. A number of such reactions are described. J. GRANT.

Dissociation of hydrogen by electrons. A. L. HUGHES and A. M. SKELLETT (Physical Rev., 1927, [ii], **30**, 11—25).—Dissociation of hydrogen by electrons begins when the electrons have an energy corresponding with 11·5 volts. With 100-volt and 20-volt electrons, the rate of diminution of pressure (the atomic hydrogen produced being condensed on the walls of the tube which was immersed in liquid air) is directly proportional to the pressure; hence the dissociation is probably produced as a direct result of the impact of an electron on the molecule.

A. A. ELDRIDGE.

Current density in the normal cathode-fall. R. SEELIGER and M. REGER (Ann. Physik, 1927, [iv], **83**, 535—564).—With different cathode-metals but the same gas, the normal current density (j_n) in a discharge tube is smaller as the normal cathode-fall (V_n) is greater; with different gases but the same metal j_n increases as the normal cathode-fall increases. With plane cathodes j_n varies as the square of the pressure, but with cylindrical cathodes of small diameter j_n varies directly as the pressure. Using an improved technique, j_n has been determined for 21 different cases, the variables being (*a*) hydrogen, nitrogen, neon; (*b*) Aluminium, iron, zinc, copper, silver, gold, platinum; (*c*) pressure: 3—10 mm. The results are expressed by means of the relation

in which a and b are constants characteristic of each metal and each gas: the values for a vary between 0·006 and 0·350, whilst those for b vary between 1·00 and 2·05. A comparison is made between the results with the normal current density and other processes with which the cathode is concerned, viz. the normal cathode-fall V_n and the thickness d_n of the cathode dark space. Reasons are given against the validity of quantitative relationships have been suggested for these magnitudes, but it is regarded as legitimate to group the results in series V_n, Al<Zn<Fe<Pt≤Ag<Cu<Au. b, Al>Zn>Fe>Pt>Ag≤Cu. j_n, Al>Fe>Zn>Pt>Au>Cu≤Ag.

Measurements have been carried out with mixtures of gases. Using mixtures of hydrogen and neon and a copper cathode, b falls from 1·86 for 100% hydrogen at first slowly to 1·7 for 75% neon and then rapidly to 1·06 at 100% neon; a is 0·125 at 100% hydrogen, about 0·12 at 25% neon, and 0·024 at 100% neon. In the case of hydrogen–nitrogen mixtures, using an iron cathode the results differ widely: a at 100% hydrogen is 0·14 and at 100% nitrogen 0·325, and between the limits 25% and 100% nitrogen it is greater than 0·325, reaching a maximum at values roughly given by a=0·55, 65% nitrogen. The magnitudes V_n and b show minima in the same region of gaseous composition, whilst d_n shows a less pronounced minimum near 75% nitrogen.

All of the results apply only to cylindrical cathodes 3 mm. in diameter. They are even more complicated than would have been expected, but a more exhaustive discussion will be possible if accurate values for the cathode-fall can be obtained. R. A. MORTON.

Electron affinity of some stable molecules at high temperatures. G. PICCARDI (Z. Physik, 1927, **43**, 899—920).—A stationary potential is established between a platinum gauze and plate by allowing a Bunsen flame of constant length to burn through the gauze and impinge on the plate mounted above the gauze. This potential, which arises from a difference between the electron emissions of the gauze and plate due to a constant difference in temperature, causes a constant current to flow through a reflecting galvanometer which connects the gauze to the plate; since its resistance is low compared with that of the flame it serves as an ammeter. When a bead of a volatile salt on a platinum wire is introduced into the flame between the gauze and plate the galvanometer registers an increased current due to the ions formed from the volatilised salt. From the observed current increase and from the rate of loss in weight of the bead the equilibrium constant K of the dissociation $A \longrightarrow A^+ + e$ can be calculated, $K=[A^+]^2[A]^{-1}=[e]^2[A]^{-1}$. Data, referring to sodium, barium, and lithium salts, are given to illustrate that K is sensibly constant over a wide range of concentration of metal atoms in the flame.

By assuming that the ionisation potential U is independent of the temperature, the integrated form of the van 't Hoff isochore, $\log K$ — — has been used to calculate the ionisation potentials of the following metals from the values of $\log K$ determined in the Bunsen flame: cæsium 3·89, potassium 4·32, sodium 5·13, calcium 6·09, barium 5·19, strontium 5·67, thallium 6·04, silver 7·54, and copper 7·69 volts. In a similar way the ionisation potentials of the rare earths have been determined. The following values were obtained: lanthanum 5·49, cerium 6·91, praseodymium 5·76, neodymium 6·31, samarium 6·55, gadolinium 6·65, terbium 6·74, dysprosium 6·82, ytterbium 7·06.

It is shown that the electron affinity of the anions, or their decomposition products, liberated by the salts used for the above determinations are too low to have any appreciable effect on the galvanometer reading. The electron affinities of bromine and of iodine have been determined from the diminution of

the galvanometer reading and the corresponding values of log K when ethyl bromide and methyl iodide are introduced in known amounts into the flame. The values obtained are 3·58 and 3·76 volts, respectively. It can be shown that electron affinities are proportional to log K. The electron affinities, at a constant flame temperature, of hydrogen sulphide, sulphur and selenium dioxides, and of molybdenum trioxide have been calculated from the ratios of the corresponding values of log K to that corresponding with iodine; the values obtained are 2·83, 2·78, 2·3, and 2·7 volts, respectively. Approximate data only have been obtained for chlorine and for phosphoric, arsenious, boric, tantalic, niobic, and tungstic oxides.

R. W. LUNT.

Dielectric constant of atomic hydrogen in undulatory mechanics. P. S. EPSTEIN (Proc. Nat. Acad. Sci., 1927, **13**, 432—438).—Application of the principles of wave mechanics shows that in weak fields the orientation of atoms is arbitrary; in strong ones it has a relation to the field. The dielectric constant of atomic hydrogen in the normal state is 1·000224. J. S. CARTER.

Dielectric constant of atomic hydrogen from the point of view of Bohr's quantum theory. (MISS) E. F. AYLESWORTH (Proc. Nat. Acad. Sci., 1927, **13**, 438—445; cf. preceding abstract).—Application of the Bohr theory leads to a similar dependence of orientation on field strength, and to an expression for the dielectric constant identical with that for the limiting value of the refractive index. J. S. CARTER.

Dielectric constants and magnetic susceptibilities in the new quantum mechanics. II. Application to dielectric constants. J. H. VAN VLECK (Physical Rev., 1927, [ii], **30**, 31—54; cf. this vol., 609).—The Debye formula applies to asymmetrical models with three unequal moments of inertia, as well as to symmetrical models. The influence of a magnetic field on the dielectric constant, and the relation of dielectric constant to index of refraction are discussed. The limit of accuracy of the Debye formula in the quantum mechanics is investigated, and a general classical derivation of the formula is given. A. A. ELDRIDGE.

Molecular and atomic volumes. XV. Indium halides. III. Densities of solid indium trihalides. W. KLEMM (Z. anorg. Chem., 1927, **163**, 235—239).—The values of d_4^{25} for the indium trihalides are: trichloride 3·46, tribromide 4·77, triiodide 4·66. If the molecular volumes are plotted against those of the corresponding potassium halides, the resulting curve is not rectilinear (cf. Biltz, A., 1921, ii, 437), the nature of the deviation indicating that the solid trichloride and tribromide are constituted of ions, whereas the tri-iodide consists of molecules. R. CUTHILL.

Additivity of volumes in inorganic compounds. IV. Volume of hydrogen in hydrides. E. MOLES (Anal. Fís. Quím., 1927, **25**, 204—210).—Calculations of the molecular volumes at absolute zero of hydrides of elements in groups IV, V, VI, and VII of the periodic classification show that in each group the volume occupied by the hydrogen atom increases with the atomic volume of the element forming the hydride. The atomic volume of hydrogen in its various compounds with a given element is remarkably constant. The volume occupied by hydrogen in various halogenated hydrocarbons varies with the atomic volume of the halogen. For methyl compounds of metals, however, the volume occupied by the methyl group is independent of the metal.

J. S. CARTER.

Volume relationships in formation of solid compounds. J. SASLAVSKY (J. Russ. Phys. Chem. Soc., 1926, **58**, 659—663).—An attempt to deduce a connexion between the molecular and atomic volumes of a compound and its constituents by empirical methods. The change of volume of a compound on formation from its elements is expressed by: $C=MV/\Sigma AV$, where MV and AV are the molecular and atomic volumes, and C is the "compression constant." In the case of hydrogen, nitrogen, oxygen, fluorine, chlorine, bromine, and iodine the density data were referred to absolute zero. The systematic study of halides, oxides, sulphides, hydroxides, and several oxy-salts of metals (cf. A., 1925, ii, 933) demonstrates that analogous compounds show a parallelism in the degree of compression. The theories of Schroder, Kopp, Ephraim, and Biltz are shown to follow from the above conclusions, and the influence of the acidic and metallic residues on the properties of the compound are discussed.

M. ZVEGINTZOV.

Scattering of light by liquid surfaces. L. A. RAMDAS (Indian J. Phys., 1927, **1**, 199—234).—Gans' theory of the scattering of light by liquid surfaces (Ann. Physik, 1924, [iv], **74**, 231; 1926, [iv], **79**, 204) is found to account for the main features observed experimentally. The optical behaviour of the surface of liquid carbon dioxide near the critical temperature has been studied experimentally.

W. E. DOWNEY.

Circular dichroism of the alkali cuprotartrates. R. DE MALLEMANN and P. GABIANO (Compt. rend., 1927, **185**, 350—352; cf. this vol., 543).—In addition to the compounds $C_4H_4O_6CuNH_4.H_2O$ and $C_4H_4O_6CuNa,H_2O$ the compound $C_4H_4O_6CuNa_2,2HO$ has been isolated from a solution of 1 g.-mol. of pure neutral copper tartrate and 2 g.-mols. of sodium hydroxide, the solution being evaporated in a vacuum in the dark in presence of sulphuric acid. The crystals were blue; the dichroism and rotatory power of their solutions increased rapidly with the concentration, but diminished when the crystals were allowed to deliquesce under the influence of air and light. The compositions of the crystals and of the mother-liquor were confirmed by analysis and by optical measurements. The circular dichroism of these three compounds is most marked in the disodium derivative. J. GRANT.

Dispersion of ultra-violet rays by organic substances. H. VOELLMY (Z. physikal. Chem., 1927, **127**, 305—357).—The molecular refractions have been measured of methyl, ethyl, propyl, butyl, amyl, and allyl alcohols, amylene, *iso*pentane, *cyclo*hexene, *cyclo*hexane, hexane, methyl*cyclo*hexene, methyl*cyclo*hexane, diethyl ether, anisole, prop-

aldehyde, *iso*butaldehyde, glycol, glycerol, acetone, methyl ethyl ketone, 2-methyl*cyclo*hexanone, *cyclo*hexanol, *cyclo*hexanone, benzene, toluene, *o*-xylene, fluoro-, chloro-, bromo-, and iodo-benzene, and mesitylene, at wave-lengths between 6560 and 2100 Å. In all cases the molecular refraction increases, at first slowly and then more rapidly, with decrease of wave-length. The results indicate that the molecular refraction is not a simple additive property, and that in many cases there exist wide deviations from the additive law. The nature of the curves obtained by plotting refraction against wave-length for any individual group or linking is not constant, but dependent on the compound investigated. In general the refraction due to a group or linking increases on the long wave-length side of an absorption band, and becomes negative on the other side, approaching zero again as the wave-length decreases still further; a faint absorption band thus produces an inflexion on the refractivity–wave-length curve. The refraction of a molecule could thus be calculated additively from the refractions of the various groups and linkings at any specified wave-length. When, therefore, a substance possessing no absorption band is converted by the addition of a group into another compound which is also colourless, the normal value will be obtained for the refractivity of the group. This theory is well supported by the measurements made on the aliphatic hydrocarbons, none of which possesses absorption bands in the range investigated, and for which the additive law is valid. The deviations which occur when a colourless group is introduced into a coloured molecule, a coloured group into a colourless molecule, and a coloured group into a coloured molecule, are in agreement with the theory that the deviations are caused by variations of the refractivity of a group in the immediate neighbourhood of an absorption band. H. F. GILLEE.

Dispersion in the liquid state at extreme temperatures. W. HERZ (Z. anorg. Chem., 1927, 163, 217—220).—The refractive indices and dispersions of a large number of liquids at absolute zero and at the critical temperature have been calculated from existing data. At −273° the dispersion is always less than, and at the critical temperature greater than, that at ordinary temperatures. The differences in the refractive indices at the two temperatures are greatest for the *F* line and least for the *C* line. In series of similar compounds the differences increase with increasing mol. wt. H. F. GILLBE.

Optical rotatory dispersion. III. The rotatory dispersion of quartz in the infra-red, visible, and ultra-violet regions of the spectrum. T. M. LOWRY and W. R. C. COODE-ADAMS (Phil. , 1927, A, 226, 391—466; cf. *ibid.*, 1912, A, 212, 261).—The measurements of the optical rotatory power of quartz have been extended into he ultra-violet and infra-red regions. The infra-red erm previously added to Drude's equation is now ep aced by a small constant, and both the dispersion and rotation constants of the ultra-violet erms are modified. The rotatory dispersion of 20° is $\alpha = 9{\cdot}5639/(\lambda^2 - 0{\cdot}0127493) - 2{\cdot}3113/(\lambda^2 - 0{\cdot}000974) - 0{\cdot}1905 \pm 0{\cdot}002°$ per mm. The square roots of the dispersion constants represent two bands of selective absorption at 1130 and 310 Å., but have not yet been determined by direct measurement. The validity of these numbers is confirmed by the deduction of an accurate formula for the refractive dispersion of quartz. C. J. SMITHELLS.

Double refraction and thixotropy of aluminium hydroxide sols. M. ASCHENBRENNER (Z. physikal. Chem., 1927, 127, 415—445).—The influence of sol concentration and of the presence of electrolytes on the appearance of double refraction in aluminium hydroxide hydrosols has been investigated in a roughly quantitative manner. A minimum concentration of electrolyte is necessary for the appearance of double refraction, which thereafter at first increases with increase of concentration, reaches a maximum, and then falls; at the optimum concentration the refractivity reaches a steady value within a few minutes, whereas at higher or lower concentrations days or weeks may be required. At high concentrations of electrolyte the sol sets to a jelly, which is not doubly refracting and cannot be liquefied again by shaking. There is thus a well-defined range over which the sol is doubly refracting, and simultaneously it exhibits thixotropy, *i.e.*, the reversible sol–gel transformation which takes place on shaking the fluid sol. The influence of electrolytes increases very rapidly with the valency and adsorbability of the active ion. Double refractivity is inhibited by protective agents such as gelatin and amino-acids.

Heating the sol in presence of electrolytes arrests the double refractivity, but the normal value is regained on cooling; in absence of electrolytes the effect is reversed: heating the sol causes the double refractivity to increase very considerably, but the addition of a minute quantity of electrolyte causes the property to vanish. The effect of dialysis is very similar to that of heat. If the viscosity of the sol be reduced by shaking, the liquid becomes more strongly doubly refracting, but with more violent shaking the sol reverts to its original condition. Although double refraction and thixotropy are strongly influenced by the same factors, and to roughly the same extent, neither is necessary for the appearance of the other. It is probable that the change in the nature of a sol which is produced by electrolytes is governed by two factors, viz., the number of particles forming an aggregate and the nature of the linking between the particles; both these factors act in the same manner on the viscosity, whereas the appearance of double refractivity is favoured by the one and hindered by the other. H. F. GILLBE.

Constitutions of the hydroborons [boron hydrides]. J. D. MAIN SMITH (Chem. News, 1927, 135, 81—88).—The constitutions of all the known boron hydrides have been worked out on the basis of the author's scheme of atomic structure, utilising the conception of a chemical linking of a single electron. If a hydrogen atom is directly replaceable by a halogen atom it is bound by a two-electron linking, and inferentially, if it is not so replaceable it is bound by a single linking. Thus, if it is bound to a boron atom by a one-electron linking, a second hydrogen atom is similarly attached to the same atom. The configurations

are based wholly on Stock's experimental results, and it is contended that diborane-diammine does not exist, and that the compound isolated is monoboran-ammine, BH_3,NH_3. The confusion arises from the formation of the ammine during the determination of the mol. wt. of diborane in liquid ammonia.

J. GRANT.

Relation of the octet of electrons to ionisation. W. A. NOYES (Proc. Nat. Acad. Sci., 1927, **13**, 379—380).—According to the octet theory the atom of an ion assumes a noble gas structure but with the difference that in an ion the positive nuclear charge is greater or less than the number of electrons in the shell by a whole number of units. In solution, in spite of the static attractions between ions of opposite sign, the external shells of electrons exert so great a repulsion on close approach that ions will separate and maintain their independent existence after collision. The fact that hydrogen compounds are ionised to a much smaller extent than the corresponding alkali metal compounds is doubtless due to the fact that the hydrogen ion has no external electron and may approach much closer to a negative ion and may even be actually included within the orbits of a pair of electrons belonging to the negative ion.

J. S. CARTER.

Electron-sharing ability of organic radicals. R. M. HIXON and I. B. JOHNS (J. Amer. Chem. Soc., 1927, **49**, 1786—1795).—On the electron theory of valency, the properties of any polar group must depend on the electron-sharing ability of the radical or element to which it is attached. It is shown that the dissociation constants and free energies of ionisation in the series $R{\cdot}NH_2$, $R{\cdot}CO_2H$, $R{\cdot}CH_2{\cdot}CO_2H$, $R{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H$, can be expressed as exponential functions of such an electron-sharing ability, and that an exponential equation of the same general form holds for the change in dissociation constant brought about by the interposition of successive $\cdot CH_2\cdot$ groups between the radical R and the polar group. The bearing of this relationship on Langmuir's results (A., 1917, ii, 525) is discussed.

F. G. WILSON.

Illinium, the new rare earth. B. S. HOPKINS (J. Franklin Inst., 1927, **204**, 1—11).—A *résume* of the American investigations which led to the discovery of the element 61.

J. S. CARTER.

Eka-manganese. N. SELJAKOV and M. KORSUNSKI (Physikal. Z., 1927, **28**, 478—479).—Polemical against I. and W. Noddack's work on rhenium (this vol., 532).

W. E. DOWNEY.

Improvements in the Debye-Scherrer technique. G. KURDJUMOV (Z. Physik, 1927, **43**, 921—933).—Following an analysis of the relation between the shape of an object, the divergence of the incident X-ray beam, and the line width of the X-ray spectrogram, a modified form of slit is described to be used in conjunction with a cylindrical object whereby a line width of 0·15 mm. is readily obtained. Thus, for example, a steel wire 1 mm. in diameter gave lines with a width of 0·16 mm. The exposure necessary, however, is approximately three times that corresponding with the usual procedure.

R. W. LUNT.

Crystal system of α-thallium. G. ASAHARA and T. SASAHARA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1926, **5**, 79—81).—Comparatively perfect crystals of thallium were prepared by the electrolysis of a saturated solution of thallous sulphate using a current density of 0·05 amp./dm.^{2} at 3 volts. The crystals appear to belong to the hexagonal holohedral class, isomorphous with magnesium, and have an axial ratio of 1·63.

C. J. SMITHELLS.

Crystal structure of α-thallium. T. SASAHARA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1926, **5**, 82—94).—The crystal structure of α-thallium prepared by electrolysis (preceding abstract) has been determined from Laue and rotating-crystal photographs. The crystal is hexagonal close-packed, space-group D^4_{6h}; the unit cell contains 2 atoms arranged at $\frac{1}{3},\frac{2}{3},\frac{1}{4}$; $\frac{2}{3},\frac{1}{3},\frac{3}{4}$; its dimensions are $a=3{\cdot}41_5$, $c=5{\cdot}54_0$ Å., $c/a=1{\cdot}62_2$.

C. J. SMITHELLS.

Crystal structure of α-manganese. A. J. BRADLEY and J. THEWLIS (Proc. Roy. Soc., 1927, A, **115**, 456—471).—The crystal structure of α-manganese has been investigated by the powder method, using the precision camera of Westgren and Phragmén (A., 1925, ii, 1035). The specimen contained 0·4% Al, 1·3% Fe, and 1·5% Si, and was alloyed with 0·35% C. The number of atoms in the unit cell is 58, not 56 as stated by Westgren and Phragmen. By a lengthy process of elimination, the only atomic arrangement capable of explaining the experimental results has been selected from 21 alternative structures. The space-group is probably T^3_d, and there are four groups of equivalent positions, containing respectively 2 X, 8 A, 24 D_1, and 24 D_2 atoms. The exact positions of the atoms are defined by five parameters, 0·317, 0·356, 0 042, 0·089, and 0·278, respectively. The structure is based on a single body-centred cubic lattice, but each lattice point is represented by a cluster of 29 atoms with tetrahedral symmetry. The interatomic distances range from 2·24 to 2·96 A., indicating that the electrons are distributed unequally between the various atoms. This implies the presence of something more closely related to a compound than to a true element in the α-manganese structure.

L. L. BIRCUMSHAW.

Crystal structure of ammonium fluoride. W. ZACHARIASEN (Z. physikal. Chem., 1927, **127**, 218—224).—The crystal structure of ammonium fluoride has been determined by means of the Laue and Debye diagrams, and is of the zinc oxide type; u is $\frac{3}{8}$ approx. The hydrogen atoms are arranged in a manner which permits the easy decomposition of ammonium fluoride into ammonia and hydrogen fluoride.

H. F. GILLBE.

Precise measurements of the lattice constants of magnesium oxide, sulphide, and selenide and manganous oxide and selenide. E. BROCH (Z. physikal. Chem., 1927, **127**, 446—454).—The lattice constants of magnesium oxide, sulphide, and selenide, and of manganous oxide and selenide, mixed with sodium chloride, have been determine by the powder method. The values of α_ω are magnesium oxide 4·208±0·001 for one preparation and 4·207±0·002 Å. for a second, magnesium sulphide 5·190±0·002 and 5·190±0·003 Å., magnesium

selenide 5·452±0·002 Å., manganous selenide 5·448±0·002 Å. These results are obtained using the $K\alpha$ copper line of wave-length 1·539 Å. Employing the $K\alpha$ iron line of wave-length 1·934 Å., the figures obtained are: magnesium selenide, 5·451±0·001, manganous oxide, 4·435±0·002 Å. The method of calculating the limiting error of the measurements is given. H. F. GILLBE.

Zinc blende–wurtzite lattice and ionic lattices. G. VON HEVESY (Z. physikal. Chem., 1927, **127**, 401—414).—The electrical conductivity of substances in the crystal and in the molten states may be employed to differentiate between lattices composed of ions or of uncharged particles. Both kinds of particles are usually present in one and the same crystal, as is indicated by quantum theory considerations. For beryllium oxide the X-ray diagram gives no indication as to whether the lattice is atomic or ionic, but conductivity measurements demonstrate, in agreement with Grimm and Sommerfeld and with Goldschmidt, the existence of uncharged particles in the crystal lattice. The α-AgI lattice is ionic, whilst that of the β-form is atomic; the apparent invalidity of Grimm and Sommerfeld's considerations to the case of silver iodide is thus explained. The appearance of metallic conductivity is due to the presence of uncharged lattice particles. The relationship between the breaking down of the crystal lattice and the appearance of polymorphic transition is demonstrated.
H. F. GILLBE.

Compounds of the lattice type of pyrrhotine (FeS). W. F. DE JONG and H. W. V. WILLEMS (Physica, 1927, **7**, 74—79).—The following lattice data are recorded: CrS: a 3·44, c 5·67 Å., 4·85. CrSe: a 3·59, c 5·80 Å., $d_{calc.}$ 6·74. CrAs (solid solution): a 4·14, c 5·51 Å., $d_{calc.}$ 7·08. MnS and MnSe are regular. MnAs: a 3·74, c 5·75 Å., $d_{calc.}$ 6·20. MnSb, which can dissolve much manganese or antimony: a 4·14, c 5·90 Å., $d_{calc.}$ 6·71. FeS: a 3·43, c 5·71 Å., $d_{calc.}$ 5·01. FeAs, rhombic. FeSb: a 4·06, c 5·13 Å., $d_{calc.}$ 8·05. CoS: a 3·37, c 5·14 Å., $d_{calc.}$ 5·98. CoSe: a 3·60, c 5·27 Å., $d_{calc.}$ 7·78. CoTe: a 3·89, c 5·36 Å., $d_{calc.}$ 8·85. CoSb: a 3·91, c 5·20 Å., $d_{calc.}$ 8·72. NiS: a 3·42, c 5·30 Å., $d_{calc.}$ 5·61 NiSe: a 3·66, c 5·33 Å., $d_{calc.}$ 7·41. NiTe: a 3·95, c 5·36 Å., $d_{calc.}$ 8·55. NiAs: a 3·57, c 5·10 Å., $d_{calc.}$ 7·88. NiSb (solid solution): a 3·94, c 5·14 Å., $d_{obs.}$ 8·42, $d_{calc.}$ 8·69. Ante, Ni(As,Sb), a mixed crystal: a 3·80, c 5·20 Å., 7·19. The action radii of the metals and metalloids in the compounds are tabulated.
CHEMICAL ABSTRACTS.

Existence and preparation of some oxides of the platinum metals. Amorphous oxides. G. LUNDE (Z. anorg. Chem., 1927, **163**, 345—354).—Various supposed oxides of the platinum metals have been examined by X-ray methods to ascertain whether they represent one or more crystalline substances. The substance obtained by heating ruthenium in oxygen is a mixture of the metal and the oxide, so also is the product obtained by heating the trihydroxide. The trioxide does not seem capable of existence in the anhydrous crystalline state. The lattice constants of palladium monoxide are: a 3·029±0·005 Å., c 5·314±0·005 Å. Claus' iridium trioxide (J. pr. Chem., 1847, **42**, 359) is a mixture of the metal and the dioxide. Attempts to prepare crystalline cobaltic oxide have proved futile, the methods described in the literature giving either cobaltocobaltic oxide or cobaltous oxide.
R. CUTHILL.

Atomic structure of AuSn. G. O. PRESTON and E. A. OWEN (Phil. Mag., 1927, [vii], **4**, 133—147).—X-Ray examination of the compound AuSn by the powder and Laue methods show that the compound crystallises on a hexagonal lattice of side 4·307 Å.; the axial ratio is 1·276, which requires two molecules of AuSn per unit cell. The space-group is D^1_h, C^4_{6v}, or D^4_{6h}, it being impossible to differentiate further. The intensities of reflexion are in agreement with a structure having the gold atoms at the points (0, 0, 0) and (0, 0, $\frac{1}{2}$) with the tin atoms at the points ($\frac{1}{3}$, $\frac{2}{3}$, $\frac{1}{4}$) and ($\frac{2}{3}$, $\frac{1}{3}$, $\frac{3}{4}$).
A. E. MITCHELL.

Grating deformation in precipitated mixed crystals. L. VEGARD (Z. Physik, 1927, **43**, 299—308).—Earlier work (this vol., 504) on the grating deformation in mixed crystals of mercurous chloride and bromide has been extended to a quantitative determination of the deformation. In mixed crystals the grating constants a and c increase linearly from 6·320 to 6·585 and from 10·907 to 11·122 Å., respectively, as the molecular percentage of mercurous bromide is increased from 0 to 100. The mixed crystals are formed either by mixing concentrated solutions of mercurous nitrate, potassium bromide, and potassium chloride, or by dropping mercurous nitrate solution slowly into the solution of potassium bromide and chloride; in both cases a is greater than the values corresponding with the mixed crystals formed in the solid state, and c is less except in the range 30—70% mercurous bromide when precipitated from concentrated solutions. The deviation in the case of slowly precipitated crystals is small.
R. W. LUNT.

Chemistry of solid substances. Forms of mercuric sulphide and sulphur. H. W. KOHLSCHUTTER (Koll. Chem. Beihefte, 1927, **24**, 319—364).—The characteristic features of reactions of solids are discussed, and the transitions of polymorphic substances are regarded as ideal cases of topochemical reactions. Experiments were carried out on the polymorphic changes of mercuric iodide, the observations being carried out on single crystals. Suitable crystals of the yellow variety for both macroscopical and microscopical observations can be prepared by subliming mercuric iodide under a pressure of 14 mm. in an electric oven kept at 230°, and afterwards falling to 130°. Too rapid heating causes the formation of dendritic structures. Alternatively, a slow stream of an indifferent gas may be used during the sublimation. When kept at the ordinary temperature, the originally lemon-yellow crystals gradually become a pure bright yellow, and then the transition to the red form commences. This change first travels in a straight fine line parallel to the prism base, then gradually broadening out until the whole of the crystal is involved. In the smallest crystals, the transition sets in at a corner of the crystal and spreads radially. Larger crystals

change to the red variety more rapidly than do the smaller crystals. When the red crystals are heated at 129—130°, they change suddenly throughout the entire crystal to the yellow form. The accepted transition temperature of 127° has always been determined on the finely divided material. The accelerating influence of light on the change from the yellow form to the red was also found to depend on the state of subdivision of the particles. Tammann's observations (A., 1920, ii, 315) on a white form of mercuric iodide were confirmed, but it was not possible to establish this as a definite allotropic modification. On the other hand, a definite tetragonal orange modification of striking stability appears to be formed by slow cooling of the vapour. This retains its colour even at the temperature of liquid air. By similar methods, Muthmann's sulphur (S_{III}) was prepared in the dry way and the transition to rhombic sulphur observed. E. S. HEDGES.

Crystal structures of *n*-octane, *n*-hexane, and *n*-pentane. J. C. MCLENNAN and W. G. PLUMMER (Trans. Roy. Soc. Canada, 1927, [iii], 21, III, 99—113; cf. Müller and Saville, A., 1925, ii, 367).—A modified Debye-Scherrer apparatus was employed. Each hydrocarbon exists in one of two forms, according to the conditions of solidification, both sets of spacings usually appearing in the photographs. *n*-Octane, orthorhombic, has *a* 3·50, *b* 4·36, *c* 15·0 Å., *d* 0·82 g./c.c.; monoclinic, *a* 3·87, *b* 4·72, *c* 14·4 Å., β 120°. *n*-Hexane, orthorhombic, has *a* 3·51, *b* 4·26, *c* 11·6 Å., *d* 0·80 g./c.c.; monoclinic, *a* 3·87, *b* 4·61, *c* 12·0 Å., β 120°. *n*-Pentane, orthorhombic, probably has *a* 3·35, *b* 4·31, *c* 10·3 Å., *d* 0·90 g./c.c.; monoclinic, *a* 3·86, *b* 4·61, *c* 10·0 Å., β 120°. Calculated values of the smallest number of mols. per unit cell are, respectively, 0·98, 0·99; 0·98, 1·04; 1·00, 1·03. The respective "long spacings" for the rhombic forms of *n*-octane (15·0 Å.), *n*-hexane (11·6 Å.), and *n*-pentane (10·3 Å.) correspond with that of a straight chain of carbon atoms terminating with hydrogen atoms. A. A. ELDRIDGE.

Dielectric investigations on anisotropic molten *p*-azoxyanisole. W. KAST (Ann. Physik, 1927, [iv], 83, 391—417; cf. this vol., 498).—Particles of fluid anisotropic *p*-azoxyanisole are oriented in a magnetic field, so that their axes are parallel to the field. This corresponds with anisotropy in dielectric properties. It is known from optical experiments that the particles adhere to the walls of the containing vessel. New experiments are interpreted in terms of this adhesion effect and it is found that the magnetic moment of *p*-azoxyanisole is about 10^5 Bohr magnetons, whilst the dielectric anisotropy ($\varepsilon_1-\varepsilon_2$) is −0·112 at a temperature near the m. p. (119°), as the temperature approaches the clarifying point this magnitude rapidly decreases. The size of the elementary particles in the nematic state may be determined from the magnetic moment. It is shown that a close relationship exists between crystal structure and the structure of the units in the nematic phase (cf. following abstract). R. A. MORTON.

X-Ray investigations on solid crystalline and molten anisotropic *p*-azoxyanisole. W. KAST (Ann. Physik, 1927, [iv], 83, 418—426).—The *X*-ray pattern of the nematic phase of *p*-azoxyanisole in a magnetic field consists of two diffuse interference maxima in a direction at right angles to the direction of the field. The molten aggregates are arranged so that the long axes of the molecules are parallel to the force-lines. The *X*-ray diagram of a polycrystalline preparation shows complete orientation of the crystallites when care is taken to avoid the effect of the walls of the containing vessel in influencing the growth of crystals from a magnetically oriented fluid. The crystal of *p*-azoxyanisole is monoclinic with β 107° 34′, *a* 10·18, *b* 7·74, *c* 16·72 Å. There are 4 molecules in the unit cell. The axial ratios are 1·32 : 1 : 2·21. R. A. MORTON.

X-Ray diffraction patterns from liquids and colloidal gels. G. L. CLARK (Nature, 1927, 120, 119—120).—For unstretched rubber latex films the spacings calculated by the Ehrenfest formula from the two principal rings are 6·03 and 14·76 Å.; for purified caoutchouc the spacings are 5·97 and 11·15 Å. Bragg's formula $n\lambda=2d\sin\theta$ is preferred to Ehrenfest's expression. Values for the spacings of the inner and outer rings in cellulose nitrate, fresh, aged by light, and aged by heat, are tabulated. Swelling or combination of molecules with solvent or oil has a much greater effect than ageing. Percentage changes, referred to the spacings of raw, liquid china-wood oil, are tabulated for the oil on polymerisation and drying. No indication has been found of long spacings such as are obtained with solid carbon chain compounds and liquid primary normal alcohols. Similar results have been obtained with cumar, resins, and varnishes. A. A. ELDRIDGE.

Unusual micro-structure in iron and tungsten. C. J. SMITHELLS and H. P. ROOKSBY (Nature, 1927, 120, 226—227).—An unusual micro-structure, resembling that observed by Tritton in cast electrolytic iron, has been observed in tungsten. The small grains formed by the sub-boundaries have a nearly uniform orientation in each crystal. The sub-boundaries may be formed under the influence of stresses set up during the rapid cooling of the metal. A. A. ELDRIDGE.

Recrystallisation phenomena in aluminium. A. E. VAN ARKEL and M. G. VAN BRUGGEN (Z. Physik, 1927, 42, 795—806).—An extension of previous work. The number of new crystals formed in aluminium after stretching is greatly diminished, for the same percentage stretching, at 500°. The results are discussed at length with reference to the mechanical properties of aluminium. R. W. LUNT.

Heat-motion of crystal atoms in relation to the intensity, position, and sharpness of spectral lines. I. WALLER (Ann. Physik, 1927, [iv], 83, 153—183).—Earlier work on the Doppler effect (Z. Physik, 1923, 17, 398) is in agreement with the results of von Laue (Ann. Physik, 1926, [iv], 81, 877). It is shown that a fraction amounting to several % of the whole measured intensity of a spectral line corresponds with scattering due to heat motion. This deduction throws light on the relation between temperature and the sharpness

of X-ray spectral lines. The cubic term is evaluated in the expression for the potential energy of the lattice in atom displacements. Both classical statistical mechanics and quantum considerations lead to the same result for the connexion between temperature, heat expansion of the lattice, and the shift of X-ray lines. In the special case of a lattice with free marginal atoms the assumption that each atom is influenced only by its six nearest neighbours enables the heat expansion to be expressed as a homogeneous distortion of the lattice. The treatment is extended theoretically in other directions.

R. A. MORTON.

Relation between the surface of crystals and their mass and volume. K. HRYNAKOVSKI (Bull. Soc. amis sci. Poznan, 1927, **1**, 49—53).—The ratio between the actual surface area and the area of the equivalent sphere is constant during the growth of a crystal. It decreases as the crystal symmetry increases. The relative rate of growth of the faces is dependent on the mass of the crystal.

CHEMICAL ABSTRACTS.

Scattering of electrons from single crystals of nickel. A. L. PATTERSON (Nature, 1927, **120**, 46—47).—In Davisson and Germer's investigations (this vol., 492) the alteration in intensity, with varying voltage, of the reflexion with maximum at 50° in the (111) azimuth for 54-volt electrons can be explained by the control provided by a second cross grating beneath the first, the position of the maximum requiring the spacing between the gratings to be $Ka/\sqrt{3}$, where $K=0{\cdot}66$ or $1{\cdot}16$ and $a/\sqrt{3}$ is the normal spacing of the (111) planes of a face-centred cubic lattice of constant a. Calculated and observed maximum intensities for voltages in the neighbourhood of 54 are compared. The variation of intensity with azimuth has also been calculated. The assumption of the existence of faces (111) would explain the reflexion in the (111) azimuth. A. A. ELDRIDGE.

Mechanism of the electrical conductivity of metals. N. S. NAZAROV (Bull. Univ. Asie Centrale, 1926, No. 12, 83—87). CHEMICAL ABSTRACTS.

New theory of crystal detectors. W. OGAWA (Radio-nonihon [Japan], 1927, **4**, 114—115, 270—272).—The rectifying action of a crystal detector is ascribed to (1) difference of electron emissions from each electrode, and (2) an appropriate resistance to minimise metallic conduction at real contact points and make electron emission possible through the adjacent narrow free space. The activation of synthetic galena by silver sulphide is ascribed to the formation of metallic silver.

CHEMICAL ABSTRACTS.

l effect a bismuth crystal. C. W. HEAPS (Physical Rev., 1927, [ii], **30**, 61—65).—The Hall effect was measured in plates cut in different directions from a single crystal of bismuth.

A. A. ELDRIDGE.

Thermo-electric phenomena with thin metallic —ns. T. TERADA, S. TANAKA, and S. KUSABA (Proc. Imp. Acad. Tokyo, 1927, **3**, 200—203).—A preliminary account of the thermo-electric effects u oy local heating of thin films of silver, bismuth, and antimony, deposited chemically, or by sputtering, on glass. When the image of a 300 candle-power filament lamp is focussed on such films, voltages of the order of 10^{-7} volt were observed with silver and of 10^{-5} volt with bismuth and antimony.

R. W. LUNT.

Physical properties of molybdenum at high temperatures. C. ZWIKKER (Physica, 1927, **7**, 71—74).—Determinations were made between 1200° and 2400° Abs. of the following physical properties: spectral emissive power (λ 0·652), black temperature (λ 0·652), emissive power (λ 0·541), pseudo-emissive power, colour temperature, specific resistance, total radiation, light emission, heat conductivity, and linear expansion coefficient. Expressions are given for the thermo-electric emission, rate of evaporation, and vapour pressure. The Thomson effect is negligible. The heat of vaporisation is 154,000 g.-cal. per g.-atom, and the sublimation point at 1 atm. is 4780° Abs. CHEMICAL ABSTRACTS.

Vibration frequencies of binary compounds. W. HERZ (Z. anorg. Chem., 1927, **163**, 221—224).—The vibration frequencies of a large number of binary compounds have been calculated from existing data and the results compared with the sum of the vibration frequencies of the atoms composing the molecule. In all cases the latter bears a simple numerical relationship to the vibration frequency of the compound.

H. F. GILLBE.

Electric differential method for measuring the specific heat C_v of gases. M. TRAUTZ (Ann. Physik, 1927, [iv], **83**, 457—497).—The principles underlying the differential method for measuring C_v are considered in detail and equations are deduced and expressed in such a form that experimental data can be conveniently inserted. On the assumption that the experimental technique and the theoretical considerations are mutually consistent it is shown that C_v may be measured to within 0·04%. Various sources of error are discussed. The high degree of accuracy attainable by the method opens up a new field for investigation. By measuring C_v accurately for mixtures, it is possible to evaluate C_v for any material the vapour pressure of which is a few mm. of mercury at 0° or the ordinary temperature, if nitrogen or argon is first saturated with the vapour. The specific heats of vapours determined in this way are likely to be trustworthy to within 1—5%, a degree of accuracy which has been hitherto attained only with pure gases. R. A. MORTON.

Specific heat of the hydrogen molecule. D. M. DENNISON (Proc. Roy. Soc., 1927, **A**, **115**, 483—486).—The values for the moment of inertia of the hydrogen molecule and the ratio of the weights of the symmetrical group of states to the asymmetrical group, obtained by Hund (this vol., 495), are not in agreement with the observed features of the band spectra of hydrogen. On the assumption that the time of transition between a symmetrical and an asymmetrical rotational state of the hydrogen molecule is very long compared with the time in which the observations of the specific heat are made, a specific heat curve is obtained which follows the observed curve within the limits of experimental error. Moreover, the constants I (moment of inertia)

and ρ (proportion of symmetrical to asymmetrical molecules) are in good agreement with the values of these constants as found in the band spectrum of hydrogen. L. L. BIRCUMSHAW.

Relation between specific heat, thermal expansion, and velocity of sound in liquids. B. N. SREENIVASAIAH (Indian J. Phys., 1927, **1**, 255—266).—Theoretical. An extension of Ray's work (Physical Rev., 1920, [ii], **15**, 24). W. E. DOWNEY.

Connexion between heat of fusion and specific heat. K. LICHTENECKER (Physikal. Z., 1927, **28**, 473—475; cf. Skaupy, Verh. Physikal. Ges., 1916, **18**, 302) —It is shown that the heat of fusion of ice is equal to the integral of the specific heat from —273° to 0° plus the heat of compression due to the change in volume at the m. p. W. E. DOWNEY.

Physico-chemical studies on tin. IX. Transition temperature grey tin ⇌ white tin. E. COHEN and K. D. DEKKER (Z. physikal. Chem., 1927, **127**, 178—182).—The transition temperature of grey tin into white tin lies between 12° and 14·3°, the most probable temperature being 13°. H. F. GILLBE.

Metastability of elements and compounds as a result of enantiotropy or monotropy. X. True specific heats of chemically and physically pure white and grey tin. E. COHEN and K. D. DEKKER (Z. physikal. Chem., 1927, **127**, 183—217).—Chemically pure grey tin has been prepared from white tin of known purity. The physical purity of the grey modification was controlled by density measurements with the pyknometer and by *X*-ray observations. For pure white tin d_4^{18} is 7·285, and for the grey form 5·765. The true specific heats of pure grey and white tin have been determined by means of the electric adiabatic calorimeter of Cohen and Moesveld. The specific heat between 8° and 13° of grey tin is 0·0493± 0·0002, and of white tin 0·0537±0·0003. Further evidence has thus been obtained for the untrustworthiness of physical data given in the literature, since the measurements have in many cases been made on physically impure substances. H. F. GILLBE.

Determination of transition points with the aid of a thermocouple. D. CANNEGIETER (Chem. Weekblad, 1927, **24**, 350—351).—The two transition points, at 60° and 180°, found dilatometrically for lead by Travers and Houot (A., 1926, 893) have been investigated, using a lead–copper thermocouple. The transition point at 60° could not be confirmed, and the second one was found to be at 182·5° after the metal had been heated for 36 hrs. or longer at 240°. S. I. LEVY.

Density of carbon dioxide. S. W. PARR and W. R. KING, jun. (Univ. Illinois Eng. Exp. Sta. Circ., 1926, **13**, 1—21).—The earlier table (A., 1909, ii, 234) is revised, values having been recalculated from more accurate data. Between 10° and 30° the revised values are 0·0004—0·0016 mg. per c.c. smaller than the former values. CHEMICAL ABSTRACTS.

Method for measuring vapour densities. P BLACKMAN (Chem. News, 1927, **135**, 97—100).—The apparatus consists of a short graduated tube drawn off and open at one end, to the other end of which is joined a long side tube leading to a bulb, and bent into the form of an inverted and an upright U-tube. The bulb is almost filled with mercury, and a small weighed amount of substance inserted through the inlet, which is then sealed. The substance is completely vaporised by immersion of the bulb in a suitable liquid, and the levels of the mercury in the bulb and graduated tube are noted. A calculation is given for the determination of the vapour density, due allowance being made for the mercury remaining in the bulb. Satisfactory results were obtained for a number of simple organic liquids. J. GRANT.

Germanium. XIX. Vapour pressure of germanium tetrabromide. F. M. BREWER and L. M. DENNIS (J. Physical Chem., 1927, **31**, 1101—1105).—The vapour pressure of germanium tetrabromide determined over the range 0° to b. p. by the method of Laubengayer and Corey (A., 1926, 931) gives the value of 186·5° for the b. p. L. S. THEOBALD.

Vapour pressure of acetone at low temperatures. E. H. ARCHIBALD and W. URE (Trans. Roy. Soc. Canada, 1927, [iii], **21**, III, 133—144).—Values of the vapour pressure of acetone between —105° and 20° are tabulated and plotted (*e.g.*, 74·92 mm. at 0°, 185·57 mm. at 19·89°). The results accord with the equation: $\log P=-(a/T)+b\log T+cT+dT^2+e$, where the logarithms of the constants *a*, *b*, *c*, *d*, and *e* are, respectively, 4·4022197, 2·9123338, 0·2140094, 3·0784842, and 3·2374543. An equation expressing the variation of the latent heat with the temperature has also been obtained. An abnormal maximum value at 4·6° indicates association followed by dissociation. A. A. ELDRIDGE.

Theory of the state of matter. K. M. STAKHORSKI (Bull. Soc. chim., 1927, [iv], **41**, 775—787).—The molecular pressures, *i.e.*, the quantity a/v^2 in van der Waals' equation, at $0{\cdot}50T_c$ and $0{\cdot}64T_c$, *i.e.*, temperatures in the vicinity of the f. p. and b. p., respectively, of a number of normal liquids have been calculated by three methods, and the relation $B=k\gamma T/T_c$, where *B* is the molecular pressure, γ the surface tension, and *k* a constant, has been confirmed. Theoretical relationships between the molecular pressure and various physical constants, *e.g.*, specific cohesion, vapour pressure, latent heat, ebullioscopic constant, etc., are derived and it is shown that Trouton's rule, the f.-p. and b.-p. capillary relations of Walden (A., 1908, ii, 1014) and Kistiakovski (A., 1906, ii, 655), respectively, and Beckmann's expression for the ebullioscopic constant, $k=0{\cdot}00096MT$, where *M* is the mol. wt., are all particular cases of much more general relationships. J. S. CARTER.

Theory of the state of matter. VIII. Internal pressure and the theorem of corresponding states. F. SCHUSTER (Z. Elektrochem., 1927, **33**, 244—245; cf. this vol., 103).—The internal pressure, p_i, has been calculated for various substances by relation $p_i=94{\cdot}47T_cT(\log p_c/p)/V(T_c-T)$, where is any temperature, *p* the corresponding vapo pressure, *V* the molecular volume in c.c., T_c the cri temperature, and p_c the critical pressure. coefficient dp_i/dT at the b. p. has a value betwe and 3 for many normal substances, but it decreas

with increasing T_c for compounds of a given type. Higher values are obtained for associated substances and substances with unsaturated subsidiary valencies, so that this coefficient may also be related to p_c, which is high in such cases. H. J. T. ELLINGHAM.

Solution of the ammonium chloride problem. A. SMITS (Rec. trav. chim., 1927, **46**, 445—452).—The vapour pressure of ammonium chloride is lowered by intensive drying. Although internal transformations are not thereby inhibited, the equilibrium position is altered, the shift being greater the higher the temperature; the effect vanishes completely at temperatures above about 310°. Association increases with decrease of temperature, becoming appreciable at 286°. The phase relationships are explained on the assumption that double molecules exist in the vapour phase. H. F. GILLBE.

New equation of state for fluids. I. Application to gaseous ethyl ether and carbon dioxide. J. A. BEATTIE and O. C. BRIDGEMAN (J. Amer. Chem. Soc., 1927, **49**, 1665—1667).—The equation $p=[RT(1-\varepsilon)(v+B)-A]/v^2$ is proposed, where $A=A_0(1-a/v)$, $B=B_0(1-b/v)$, and $\varepsilon=c/vT^3$, A_0, a, b, and c being constants. This, it is claimed, is readily amenable to mathematical manipulation and accurately represents the known data. The constants are easily and accurately calculated from pressure–volume–temperature data. For ethyl ether the constants are (atm.; c.c./g.): R 1·10777, B_0 6·1350, b 1·6137, A_0 5700·0, a 1·6775, c $4·5\times10^6$; for carbon dioxide: R 1·8650, B_0 2·3810, b 1·6443, A_0 2586·0, a 1·6210, c $15·0\times10^6$. The average deviation from the observed data is 0·07% for ethyl ether and 0·08% for carbon dioxide. The equation is flexible, and A, B, and ε can be expanded, if necessary, without altering the form of the equation. S. K. TWEEDY.

Poisson's theorem and Hugoniot's equation. O. KLUSENER (Z. Physik, 1927, **43**, 597—600).—An expression for the maximum temperature attained during a compression wave in a gas has been derived in terms of the pressure–volume relations in the gas immediately before and after the passage of the wave-front, by considering the frictional losses and the changes produced in thermal conductivity and capacity. It leads to values in good agreement with those derived by Becker (*ibid.*, 1922, **8**, 321) in which the more general equation of Hugoniot (J. école polytechn. Paris, 1887, **57**; 1889, **58**) was employed to analyse pressure data obtained experimentally. R. W. LUNT.

Factorial functions in entropy calculations. M. MASIUS (Physical Rev., 1927, [ii], **30**, 84—86).—Mathematical. A. A. ELDRIDGE.

Reflexion of atomic hydrogen from ice crystals. T. H. JOHNSON (Nature, 1927, **120**, 191).

Le Chatelier viscosity law. P. LASAREV (Compt. rend., 1927, **185**, 106—107).—The Le Chatelier formula for the variation of the viscosity of glass with the temperature (cf. A., 1925, ii, 280) is in agreement with results of other workers, and also viscous liquids (*e.g.*, amyl alcohol and solutions of sugar in glycerol). J. GRANT.

Viscosity of liquids above their b. p. II. T. TITANI (Bull. Chem. Soc. Japan, 1927, **2**, 161—171; cf. this vol., 616).—The usually-accepted definition of molecular viscosity is held to be inadequate. The distance between the sliding and stationary surfaces should be taken as $V^{1/3}$, V being the molecular volume, and not as unity. According to the new definition the true molecular fluidity Φ is related to the conventional fluidity ϕ by the expression $\Phi=\phi/V^{1/3}$. The following relationships are proposed: $\Phi=K(V^{2/3}-B^{2/3})$; $(\Phi_c-\Phi)=C(T_c-T)^{1·5}$, where K, B, and C are constants, T_c is the critical temperature (Abs.), and Φ_c the molecular fluidity at the critical temperature. Agreement with experiment is usually good, but the behaviour of water, mercury, acetic acid, and alcohols is abnormal. J. S. CARTER.

Vapour pressure and specific gravity of aqueous hydrocyanic acid solutions. G. BREDIG and M. SHIRADO (Z. Elektrochem., 1927, **33**, 209—211).—Measurements have been made of the specific gravity and of the total and partial vapour pressures of aqueous solutions containing from 5 to 100% of hydrogen cyanide. Partial vapour-pressure data were obtained by determining the weights of water vapour and hydrogen cyanide carried by a stream of electrolytic gas passed through the solution. H. J. T. ELLINGHAM.

Binary mixtures of volatile liquids. F. MICHAUD (Compt. rend., 1927, **185**, 108—110; cf. this vol., 730).—The author's theory is extended to cases in which the two components have normal vapour densities and form a compound (ether and chloroform). By analogous methods the partial vapour pressures of the two components and of the compound have been determined. If the solution is saturated with a non-volatile substance (acetanilide) the mass action constant is higher than for the pure mixtures. J. GRANT.

New binary azeotropes. VI. M. LECAT (Ann. Soc. scient. Bruxelles, 1927, **47**, *B*, [i], 63—71; cf. this vol., 617).—142 New binary mixtures of organic liquids have been examined of which 52 give positive azeotropes, 4 negative azeotropes, and 42 eutectic mixtures. The remaining 44 are non-azeotropic. The b. p. of each constituent and the b. p. and composition of the azeotropic and eutectic mixtures are tabulated. The experimental numbers usually agree well with previous generalisations. Some errata in the preceding lists are corrected. H. E. F. NOTTON.

Dielectric constants of binary mixtures. II. Electric moments of certain organic molecules in benzene solution. J. W. WILLIAMS and I. J. KRCHMA (J. Amer. Chem. Soc., 1927, **49**, 1676—1686).—The dielectric constants, refractive indices, and densities at 25° of mixtures of *p*- and *o*-xylene, phenol, carbon tetrachloride, ethyl ether, toluene, chlorobenzene, and chloroform with benzene are recorded (cf. A., 1926, 1000). Benzene has no electric moment, hence in each case the moment of the solute molecule can be calculated by an application of Debye's expression for the molecular polarisation of a binary mixture (Marx, "Handbuch der Radiologie," 1925, **6**, 625), which is based on the

Clausius–Mosotti formula. For the first five solutes the molecular polarisation is proportional to the mol. fraction in the solution. The electric moment of each solute is calculated; in the case of carbon tetrachloride and *p*-xylene it is zero.

S. K. TWEEDY.

Electrical resistance of molten metals and alloys. Y. MATUGAMA (Sci. Rep. Tôhoku Imp. Univ., 1927, **16**, 447—474).—The specific resistance of mercury, tin, bismuth, cadmium, lead, zinc, antimony, aluminium, and silver, and of binary alloys containing tin, bismuth, cadmium, lead, zinc, antimony, and copper has been determined at various temperatures. The resistance of the pure metals increases linearly with the temperature, but with mercury the increase is more rapid. The resistance–concentration and temperature coefficient–concentration curves of alloys are smooth when there is no compound formation, but otherwise breaks are found at points which correspond with the compounds formed. Increased dissociation of a compound in the liquid phase with rise of temperature is said to be indicated by a negative temperature coefficient.

F. S. HAWKINS.

Electrical and thermal conductivities of carbon steel and cast iron. H. MASUMOTO (Sci. Rep. Tôhoku Imp. Univ., 1927, **16**, 417—435).—The measurements were made by an improved Kohlrausch method (A., 1925, ii, 503). The specific electrical resistance and the thermal conductivity can be expressed as linear functions of the amounts of impurities by the equations $\sigma=1{\cdot}044+0{\cdot}548C+1{\cdot}572Si+0{\cdot}718Mn$; $1/\lambda=5{\cdot}744+2{\cdot}432C+5{\cdot}087Si+2{\cdot}461Mn$, when the total impurity is small. With a larger carbon content, the rate of decrease of the two conductivities becomes smaller, and the ratio of thermal to electrical conductivity slowly increases. Measurements made on chill-cast iron before and after annealing show that the conductivities increase after treatment, but further annealing causes no change until graphite separates, when a considerable increase in both the conductivities and their ratio occurs. Measurements were also made on K.S. magnet steel and gold.

F. S. HAWKINS.

Solid solubility of antimony in lead as determined by conductivity measurements on cold-worked alloys. E. E. SCHUMACHER and G. M. BOUTON (J. Amer. Chem. Soc., 1927, **49**, 1667—1675).—The solid solubilities of antimony in lead were determined by conductivity measurements on severely cold-worked alloys: 146°, 0·70%; 100°, 0·52%; 70°, 0·48%; 40°, 0·32%; and 25°, 0·24%. Cold working causes the precipitation of excess of antimony from the supersaturated solution in a few hours; normally, this process takes years. A revised phase diagram for the lead end of the lead–antimony system is given.

S. K. TWEEDY.

Solubility of natural hemihydrate of gypsum after heating at various temperatures. A. J. SWORYKIN (Z. anorg. Chem., 1927, **163**, 178—184).—The solubility of the natural hemihydrate of calcium sulphate, determined by measurements of conductivity, decreases with rise of temperature of ignition. An increase in the solubility after ignition at 1000° is due to a change in the molecular structu and to partial dissociation of the gypsum.

H. F. GILLBE.

Solubility of chromic hydroxide in alkalis. R. B. COREY (J. Chem. Education, 1927, **4**, 532—533).—The view that chromic hydroxide and excess o aqueous alkali form a colloidal solution and not a chromite is supported by the observation that after segregation of the chromic hydroxide from such "solution," the liquid fails to respond to a test fo chromium.

CHEMICAL ABSTRACTS.

Sucrose crystallisation. I. A. KUKHARENKO and G. S. BENIN (Zapiski [Russia], 1926, **4**, 75—77, 86—91; cf. B., 1927, 567).—The solubility of sucrose in aqueous potassium sulphate solutions (0·5—2·0%) at 50° diminishes with increase in the salt concentration. The speed of crystallisation of sucrose at 50° is not affected by the potassium sulphate, which is a negative molasses former.

CHEMICAL ABSTRACTS.

Lactic acid. IV. Partition of lactic acid between water and ether, and between water and amyl alcohol. R. DIETZEL and E. ROSENBAUM (Biochem. Z., 1927, **185**, 275—286).—The observed partition coefficients are corrected for the degree of dissociation of lactic acid. For water : ether at 20° the coefficient varies from 11·3 to 8·7 between 0·931 and 0·201 mol. per litre and for water : amyl alcohol it varies from 2·13 to 2·42 according to the concentration. Variation in temperature from 0° to 25° has little effect. In the case of amyl alcohol and water, the presence of 30% of anhydride (lactyl-lactic acid) in the lactic acid used lowers the partition coefficient to about 1·75.

C. R. HARINGTON.

Adsorption of carotin by charcoal and inorganic salts. S. G. WILLIMOTT (J. Biol. Chem., 1927, **73**, 587—592).—The discrepancy between the results of Palmer ("Carotinoids and Related Pigments," 1922, 270) and those of Stephenson (A., 1921, i, 295) is explained by the varying capacity of different samples of charcoal to adsorb carotin. The amounts required to adsorb the carotin from 100 g. of butter fat ranged from 3·5 g. with Norit (vegetable charcoal) to 40 g. with ordinary decolorising charcoal. Various inorganic compounds were found to be poor adsorbents for carotin, but red antimony trisulphide was as active as the poorer grades of charcoal, whilst black antimony trisulphide was quite inactive.

C. R. HARINGTON.

Heat of adsorption of gases by charcoal. S. J. GREGG (J.C.S., 1927, 1494—1512).—For the adsorption of nitrous oxide, acetylene, ethane, carbon monoxide, sulphur dioxide, carbon dioxide, ethylene, and nitrogen by charcoal, measurements have been made of the heat change, the equilibrium pressure, and the quantity adsorbed. Most of the experimen s were conducted at 0°, employing the Bunsen ice calorimeter, whilst others were carried out at 40·55°, using phenol in the calorimeter. For the integra heat of adsorption Q, the relationship ho ds, where x is the quantity of gas adsorbed, and k and are constants. For all gases except those with a hig critical temperature, the Williams–Henry equatio $\log x/p=A_0-A_1x$ is valid, p being the equilibriu

pressure and A_0 and A_1 constants which depend on the temperature. With the same restrictions, the modified Iljin equation $Q=B \log (p/\alpha+1)+A$ is also applicable; in this α is a constant which increases as the van der Waals constants a and b decrease.

H. F. GILLBE.

Sorption of hydrogen by palladium on various carriers. T. SABALITSCHKA (Arch. Pharm., 1927, 265, 416—424; cf. Sabalitschka and Moses, this vol., 427).—The absorption of hydrogen by palladium deposited on blood, beech, sponge, and bone charcoals, barium sulphate, and kieselguhr has been examined. All the carriers, freshly cleansed, were loaded with palladium to 2·5% of their weight. No distinction is drawn between hydrogen simply absorbed and hydrogen taken up as palladium hydride. The carriers alone show a definite saturation capacity on repeated treatment, thus: blood charcoal, 1·35 c.c. per g.; beech, 0·94; sponge, 0·84; bone, 0·72; barium sulphate, 0·00; kieselguhr, 0·26, but when the palladium is present the absorptive capacity is not constant but rises to a maximum and then (after the third or fourth treatment, with interposed exhaustion at 300°) shows a decline. For the various systems, the figures (at this maximum) are 7·49, 2·20, 10·46, 5·27, 8·18, and 1·91, respectively. These correspond with the following when referred to the palladium present: on blood charcoal, 2924 c.c. per g. Pd, beech, 867; sponge, 4581; bone, 2167; barium sulphate, 3895, kieselguhr, 910. These results agree with such earlier ones as can be compared. The rise of the absorptive activity to a maximum and the subsequent decline are due to the gradual conversion of the palladium from the amorphous into the crystalline form. W. A. SILVESTER.

Adsorption isothermals. H. BRADLEY (Nature, 1927, 120, 82).—The formula $a=[f(T)p^{T/273x}]/[1+\phi(T)p^{T/273x}]$, where a is the amount adsorbed, $f(T)$ and $\phi(T)$ are functions of T°Abs., and p is the equilibrium pressure of the gas, is in good agreement with various series of experimental results when x is unity, or a small integer. When combined with Gibbs' adsorption formula $a=-(c/RT)d\sigma/dc$, an equation is obtained which reduces to Szyszkowski's empirical formula for $T=273$ and $x=1$. A. A. ELDRIDGE.

Adsorption from solution by ash-free adsorbent charcoal. IV. Non-inversion of sucrose by adsorbed acids and its significance for theories of adsorption and catalysis. E. J. MILLER and S. L. BANDEMER (J. Amer. Chem. Soc., 1927, 49, 1686—1697; cf. A., 1925, ii, 656).—Inorganic, aliphatic dicarboxylic, and aromatic acids irreversibly adsorbed on ash-free charcoal are unable to invert sucrose at 80°. This is an extreme example of negative catalysis in which both reactants are adsorbed. Experiments on the adsorption of dextrose from sucrose solutions indicate that strong adsorption of the reaction products is not the cause of this negative catalysis. Inversion always occurs when the acid is reversibly adsorbed and a portion is displaced by the sugar, the change being produced by the displaced part. Charcoal containing acid and water adsorbed from salt solutions (A., 1924, ii, 664) is incapable of inverting sucrose, suggesting that both the acid and sucrose, and possibly the water also, are "bound" in some manner. The adsorption of acids does not imply a high concentration of hydrogen ions around the adsorbent, the adsorbed acid being probably in an undissociated and unoriented state.

S. K. TWEEDY.

Adsorption. XIX. Adsorption of electrolytes by manganese dioxide. Freundlich adsorption formula. M. N. CHAKRAVARTI and N. R. DHAR (J. Physical Chem., 1927, 31, 997—1033).—The adsorption of various cations by a sol of negatively charged manganese dioxide during coagulation has been measured, and shows that, contrary to the views of Bancroft (A., 1915, ii, 424) and Weiser (A., 1925, ii, 855), but in agreement with the work of Ghosh and Dhar (A., 1925, ii, 511) and others, the higher the valency of an ion the less is the adsorption, the order of decreasing adsorption being silver, potassium, copper, lithium, barium, strontium, cerium, aluminium, and thorium. The high adsorption observed for sols of manganese dioxide and of ferric, aluminium, and chromium hydroxides is due more to the adsorption of electrolytes by the freshly coagulated mass than to charge neutralisation, and the interpretation of the Schulze–Hardy law (that the greater is the valency the less is the adsorption) should be strictly applicable only to cases in which adsorption is due to charge neutralisation. Experiments on the adsorption of cations by a sol and by freshly precipitated manganese dioxide give results in agreement with this interpretation. Manganese dioxide, being acidic, adsorbs hydroxyl more readily than hydrogen ions. The value of the constant in the usual Freundlich equation depends on the strengths of the organic acids adsorbed by the hydroxides of iron, chromium, and aluminium. When the adsorbent remains the same or chemically similar, the value of the exponent changes little when the substances adsorbed are similar. With electrolytes, however, it varies with concentration.

The chief factor in adsorption with a positively charged sol of manganese dioxide is the chemical affinity of the coagulum, and in this case the ratio of positive to negative ion adsorbed is always greater than unity and decreases with a decrease in concentration of the sol.

The whole investigation supports the view that chemical affinity is the preponderating factor in adsorption phenomena. L. S. THEOBALD.

Effect of inorganic salts on the adsorption of inorganic acids and bases. L. R. PARKS and P. G. BARTLETT (J. Amer. Chem. Soc., 1927, 49, 1698—1709).—The adsorption of 0·01N-hydrochloric and -nitric acids by pure active sugar charcoal increases rapidly with increasing concentration of the corresponding sodium salt until the latter reaches 0·75N, after which the amount of acid adsorbed is a linear function of the salt concentration. A maximum is never attained. Nitric acid is adsorbed to a greater extent than hydrochloric acid. Similar relationships hold for 0·01N-sulphuric acid except that, contrary to the results of Michaelis and Rona (A., 1920, ii, 168), the adsorption diminishes with increasing concentration of sodium sulphate. Experiments with salts having no common ion are also described.

Mixtures of two acids show an adsorption which lies between the values for the separate acids. Experiments with blood charcoal gave results similar to the above; sodium hydroxide is more strongly adsorbed as the sodium chloride concentration rises and the adsorption of sodium hydrogen sulphate is rapidly depressed by the addition of sodium sulphate, which is contrary to the results of Michaelis. The phenomena of adsorption from solution are explained on the basis of the attraction of ions by colloid particles. Neutral inorganic salts are not hydrolytically adsorbed in presence of inorganic acids or bases.

S. K. TWEEDY.

Adsorptive properties of cellulose. H. TAMIYA and N. ISHIUCHI (Acta Phytochim., 1926, 2, 139—192).—Pure filter-paper adsorbs cations from a solution of electrolyte, whereby the acidity of the solution is correspondingly increased. If the cellulose itself contains electrolytic impurity, cations are transferred to the solution, with consequent decrease in acidity. These two opposed effects lead to amphoteric behaviour of cellulose and filter-papers therefore show variation in their reaction towards p_H indicators. The p_H tests thus give valuable information as to the purity of filter-papers. The adsorption of dyes on cellulose is influenced by the amount of electrolyte both in the cellulose and in solution. Enzymes are adsorbed on cellulose in very different amounts. Diastase, urease, emulsin, and invertase are but little if at all adsorbed, whereas trypsin, pancreatin, catalase, and pepsin are strongly adsorbed. This provides evidence for the difference in sign of the electric charge carried by the enzyme colloid. Non-electrolytes are apparently not adsorbed on cellulose, even when they possess strong surface activity. The presence of the electric double layer on the cellulose micelle surface, to which the adsorptive power of the cellulose is to be ascribed, was demonstrated by an electric endosmose apparatus. The electro-potential on the cellulose surface is affected by electrolytes in solution, the effect being determined by the valency of the ions concerned and by the p_H of the solution.

L. M. CLARK.

Surface phenomena and adsorption at the contact of two liquid phases. R. DUBRISAY (Rev. gen. Colloid., 1927, 5, 533—539; cf. this vol., 618).—An account is given of previous experiments on adsorption at benzene–soap solution surfaces (using sodium laurate and sodium glycocholate) in presence of 1% of sodium chloride (cf. A., 1926, 672), which support the hypothesis that electrolytes which diminish the concentration of the soap increase the amount adsorbed at the interface. This receives further support from measurements of the adsorption of various dyes from aqueous solution by sand, cotton, kieselguhr, etc., in presence of small quantities of coagulating substances. The author's theory that the less soluble of two substances, dissolved at the same molecular concentration in the same solvent, is the more strongly adsorbed is discussed, and shown to follow from the thermodynamic adsorption theory of Gibbs. A summary is given of earlier work (A., 1918, ii, 368; 1923, ii, 741; 1924, ii, 154, 731), and applications of the results to colloid-chemical problems are indicated. L. L. BIRCUMSHAW.

Adsorption and surface charge. I. Metallic oxides. P. BARY (Rev. gén. Colloid., 1927, 5, 517—522).—It is supposed that the phenomena of adsorption and of surface electric charge have a common origin, and are due to the chemical action of the medium on the solid particles in contact with it. The view that the oxides of multivalent metals are in general polymerised is discussed, with special reference to ferric and aluminium hydroxides. The electric charge which the oxides assume in contact with water and aqueous solutions, no matter whether the oxide are in colloidal solution, in suspension, or present as a porous mass, arises from the electrolytic dissociation of a complex compound formed between the oxide and the solvent. The hypothesis of adsorption is thus avoided, and the question may now be considered as consisting of a simple hydration of the oxide, using the primary valencies of the new compound formed by the rupture of molecular chains. The oxides of this type must be regarded as never absolutely pure, every molecule, whatever its length, having polar groups, such as H and OH, or H and Cl, or Na and OH, at its extremities. L. L. BIRCUMSHAW.

Effect of water on the formation and spreading of fatty oil films. L. AUER (Koll.-Chem. Beihefte, 1927, 24, 268—318).—The process of the drying of fatty oils is discussed. When exposed to air, absorption of oxygen and water takes place, and the oil increases in weight. The curves obtained by Weger, connecting the increase of weight of the oil with time, are not true adsorption curves, since a simultaneous loss of weight occurs, due to the formation of volatile products. From experiments with the oil spread on plates of glass contained in a series of desiccators kept at constant temperature, each desiccator containing a different mixture of water and sulphuric acid, giving a definite pressure of water vapour, it is concluded that the apparent adsorption curves of Weger cannot be resolved into two independent curves, representing the absorption of oxygen and of water vapour, as formerly supposed. The effect of water appears to be entirely physical, the irregularities in the vapour-pressure isotherms being ascribed to secondary complications. The experiments performed in a vacuum gave results in best agreement with those expected in a swelling process. The gas coagulation theory and the adsorption theory are regarded as working hypotheses which are not free from objection.

E. S. HEDGES.

Reactions in the solid state. B. GARRE (Z. anorg. Chem., 1927, 163, 43—48).—The compactness of compressed powders, both before and after heating at a moderately high temperature, has been studied. Dry quartz powder cannot be compressed into a pellet under the conditions employed, but with increasing percentages of water the compactness of a pellet, formed under a constant pressure, increases. If the pellet be heated at 500°, in which case the water is replaced by air, the compactness decreases with increase of the initial water content; heating at 900° reverses the effect owing to change of crystal structure. The weight of quartz in a pellet of constant dimensions decreases with increase of water content. The binding power of the water is thus es-

than the reduction of compactness caused by the decrease of density. Similar results have been obtained for a number of other powders: the compactness of organic powders, formed under constant pressure, increases very rapidly with temperature as the m. p. is approached. H. F. GILLBE.

Friction of solids. A. MALLOCK (Nature, 1927, 120, 44—46).—The coefficients of friction between various metals and alloys and sapphire for pressures up to the limiting pressure (except for steel) are tabulated. The differences between the values for the various metals are small. When the pressure is high, the presence of a lubricant nearly always increases the coefficient of friction.

A. A. ELDRIDGE.

Natural rotatory dispersion in the ultra-violet of aqueous solutions of the neutral tartrates of sodium, potassium, and ammonium. R. DESCAMPS (Compt. rend., 1927, **185**, 116—119).—The dispersion of solutions of tartaric acid has been determined at various stages of neutralisation by alkali hydroxides, for wave-lengths of 5780—2536Å. The Darmois lines were found to intersect at points which lie on a straight line, and not in a single point as is indicated by Vellinger's measurements in the visible spectrum (this vol., 500). J. GRANT.

Colloidal iodine. W. L. CHANDLER and E. J. MILLER (J. Physical Chem., 1927, **31**, 1091—1096; cf. Amann, A., 1912, ii, 751).—Stable suspensions of colloidal iodine have been prepared by rapidly acidifying with concentrated hydrochloric acid a dilute solution of sodium hypoiodite in the presence of gum arabic at 0°. The colour varies with the conditions of formation from brick-red, light brown, or chocolate. The size of particles is approximately 0·2 μ. The iodine is probably in the form of an emulsion in water. Concentration of the emulsion to a dry condition can be effected by the addition of sufficient dextrose or gum arabic. Re-dispersion in water is unaffected by this treatment.

The possible uses and advantages of colloidal iodine as an antiseptic are indicated. L. S. THEOBALD.

Aerosols. V. KOHLSCHUTTER (Kolloid-Z., 1927, 209—223).—A general survey of the properties and conditions of stability of aerosols. The points of resemblance and the differences between aerosols and hydrosols are discussed. A distinction is drawn between true aerosols and dust clouds, based on the electrical properties of the latter. The aggregation of particles in smokes is considered, together with methods for measuring their size and density. Experiments are described dealing with the behaviour of oxide smokes and the formation of smoke gels.

L. L. BIRCUMSHAW.

Atmospheric disperse systems and their physico-chemical and electrical properties. A. STAGER (Kolloid-Z., 1927, **42**, 223—229).—Various atmospheric disperse systems are described, and methods for investigating them are outlined. The origin of the electric charge on ionised air particles and dust particles, etc., is discussed.

L. L. BIRCUMSHAW.

Sedimentation of colloidal particles. F. W. LAIRD (J. Physical Chem., 1927, **31**, 1034—1049).—Mainly theoretical. The conception of sedimentation equilibrium is discussed with reference to the work of previous investigators. Additional data on a mercury sol support the conclusions of Burton (A., 1924, ii, 459) and of Porter and Hedges (A., 1923, ii, 743). L. S. THEOBALD.

Röntgenographical investigation of inorganic colloids. J. BÖHM (Kolloid-Z., 1927, **42**, 276—284).—The theory and practice of the Debye-Scherrer method of investigation are discussed, and its applicability to the study of colloidal systems is considered, with special reference to colloidal gold, silver, platinum, and stannic acid, and aged sols of ferric hydroxide and vanadium pentoxide.

L. L. BIRCUMSHAW.

Increase of Brownian movement by light. W. POSPÍSIL (Ann. Physik, 1927, [iv], **83**, 735—752).—Experiments on the dependence of the Brownian movement on the intensity of the applied illumination show that in the case of substances which do not absorb the light (*e.g.*, mastic), no detectable change is observed when the intensity of the illumination is varied a thousandfold. In the case of light-absorbing substances (carbon, gamboge) the movement increases appreciably with increasing intensity of illumination. The observed phenomena cannot be explained on the basis of the kinetic theory. It is suggested that the assumption of a photoelectric or a radiation effect offers a plausible explanation.

J. S. CARTER.

Solubility and particle size. IV. D. BALAREV [with A. KOVANDJIEV and K. KULELIEV] (Z. anorg. Chem., 1927, **163**, 213—216).—Colloidal barium sulphate has been prepared from barium chloride or acetate in aqueous alcoholic solution by the addition of sulphuric acid. The size of the smallest particle is about 0·1 and a saturated aqueous solution at 25° has a conductivity of 3·3—$3·5\times10^{-6}$; the conductivity of a saturated solution of the ordinary form is about $2·86\times10^{-6}$. Electrolytes adsorbed on the sol particles have a large influence on the stability of the sol and therefore on the apparent solubility. Fine crystals of barium sulphate having a minimum particle size of about 0·2 μ have been prepared by the addition of dilute sulphuric acid to a boiling dilute solution of barium chloride; the conductivity of a saturated solution of this form is $2·89—3·0\times10^{-6}$.

Temperature fluctuations in the neighbourhood of 20° cause the rapid disappearance of the smallest particles from an aqueous suspension of finely-divided gypsum, whilst at 38°, at which temperature the solubility curve of gypsum is nearly horizontal, temperature fluctuations have no effect. The ratio of the rate of crystallisation to the rate of dissolution of gypsum in the neighbourhood of the saturation point at 25° is about 8 : 1. The determination of both velocities is affected considerably by the influence of temperature changes on the disappearance of the smaller particles. The long period required for equilibrium to be attained in the system finely-divided gypsum–water cannot be entirely explained by the differences in the surface tensions of the different-sized particles. Stirring a suspension of

gypsum in water causes at first an increase in the number of the smallest particles, and only after prolonged stirring is a suspension obtained in which the smallest particles are larger than those existing in the suspension before stirring.

Neither by breaking down crystalline particles nor by precipitation from colloidal solution can exact determinations be made of the solubility of very small particles. H. F. GILLBE.

Optical behaviour of protein solutions. C. V. RAMAN (Nature, 1927, **120**, 158).—The variation of the Tyndall effect in gelatin solutions with p_H and temperature is explicable according to the general thermodynamic theory of light scattering, whereby the scattering power of a colloidal solution is connected with the osmotic pressure P of the particles by the relation $[\pi^2RT/2N\lambda^4][k(\delta\varepsilon/\delta k)^2\rho/m]/(\delta P/\delta k)$, where k is the concentration of the dispersed material, ε is the optical dielectric constant of the solution, and ρ/m is practically unity for a dilute solution, for the osmotic pressure becomes very small at the isoelectric point.

A. A. ELDRIDGE.

Dispersoidological investigations. XII. Cellulose dispergation in concentrated aqueous solutions of calcium iodide. P. P. VON WEIMARN and H. HORI. **XIII. Strontium iodide.** P. P. VON WEIMARN and K. JUNA. **XIV. Barium iodide.** P. P. VON WEIMARN and S. KATOKA. **XV. Potassium, sodium, and lithium iodides.** P. P. VON WEIMARN and K. JUNA. **XVI. Lithium bromide.** P. P. VON WEIMARN and T. YONEDA (Rep. Imp. Ind. Res. Inst. Osaka, 1926, **7**, No. 17, 7—18, 19—26, 27—36, 37—44, 45—51; cf. A., 1926, 576).—Dispersions of cellulose (3%) prepared by boiling filter-paper with saturated calcium iodide solution for 10 min. gelatinised, on cooling, at a higher temperature than when calcium thiocyanate was used. Thus calcium iodide has a smaller dispergating power than calcium thiocyanate, but greater than that of calcium bromide. Alkalis retard and acids accelerate the dispergation. Strontium salts are in the descending order: thiocyanate, iodide (< calcium iodide), bromide, chloride. Barium iodide is intermediate between the bromide and thiocyanate. The alkali iodides are in the descending order of dispergating power: lithium, sodium, potassium. The lithium salts are in the descending order: iodide, bromide, chloride.

CHEMICAL ABSTRACTS.

Platinum hydride hydrosol and its dehydrogenation by metallic mercury. C. PAAL and C. AUERSWALD (Ber., 1927, **60**, [*B*], 1648—1654).—A solid, colloidally soluble preparation of platinum (33·88% Pt) protected by sodium lysalbate is dissolved in water and the solution is alternately saturated with hydrogen and exposed for varying periods to the air. The largest quantity of hydrogen is absorbed by the original material which, during the process of drying, is freely exposed to the air during several days. Under these conditions it appears to absorb 2·03% of oxygen, equivalent to 305 vols. of the gas per vol. of metal. If the platinum hydride hydrosol is shaken with mercury it becomes slowly transformed into platinum amalgam hydrosol and free hydrogen. H. WREN.

Non-liquid disperse systems of the fatty oils. L. AUER (Kolloid-Z., 1927, **42**, 288—292).—Systems containing no non-oily constituents are considered. Cases of "film" formation and of the solidification of the oil to a jelly are discussed. For some oils (*e.g.*, wood oil), a disperse phase and dispersion medium are already present, but in many raw, unboiled, fatty oils a disperse phase must be formed, or, if present, must be concentrated before gel-formation can occur. The action of gases in film-formation is explained on the assumption that they not only behave as coagulators, but are also responsible for the formation of the micelles of the disperse phase.

L. L. BIRCUMSHAW.

Whetham's law and the law of mass action, and their application to the coagulation of colloidal platinum. S. W. PENNYCUICK (Austral. J. Exp. Biol., 1927, **4**, 99—112).—By the application of the mass law to the coagulation of colloids by electrolytes it is shown that Whetham's law, and also the law of mass action when based on similar principles to those on which Whetham's law is based, lead to quantitative relations which are not in accord with experimental facts, and it is concluded that Whetham's law is theoretically unsound. Assuming that coagulation occurs when the charge on the colloid is wholly or partly neutralised by combination with an ion carrying the opposite charge, the proportionality $p_1:p_2:p_3=1:1/C_1:(1/C_1^2)$ is deduced, p_1, p_2, p_3 being the coagulating powers of uni-, bi-, and ter-valent ions, and C_1 the corresponding coagulating concentration. The deduction of Whetham's law on comparable lines leads to the same relation. By adopting Robertson's assumption that one colloid particle combines with one univalent ion, and two colloid particles with one bivalent ion, etc. (cf. "The Physical Chemistry of the Proteins," 1920, 116), the relation $p_1:p_2:p_3=1:Q:Q_2$ is deduced, Q being the colloid concentration. A large number of coagulation experiments were made, using very pure colloidal platinum and a series of electrolytes with uni-, bi-, and ter-valent cations, but none of the above relations could be confirmed. The theoretical and observed results differ so greatly as to suggest that the theoretical relations give no quantitative indication of the relative coagulating powers. L. L. BIRCUMSHAW.

Physico-chemical properties of Japanese acid clay. I. Ultramicroscopic observations. K. KOBAYASHI and K. YAMAMOTO (J. Soc. Chem. Ind. Japan, 1927, **30**, 431—435).—Ultramicroscopic photographs of several acid clays, colloidal carbons, silica gels, etc., have been taken by means of a cardioid ultramicroscope and the sizes of the particles determined by using a slit ultramicroscope. The acid clay is composed of extremely minute particles compared with other clays; the radius of the particles which remain in suspension after centrifuging at 4000 revolutions per minute fell between 1×10^{-5} and 2×10^{-5} cm. The acid clay when calcined at 300° shows no perceptible change of structure, but at 500° the colloidal character disappears. K. KASHIMA.

Influence of concentration of colloidal solutions on the quantity of electrolyte necessary for flocculation. A. Boutaric and (Mlle.) G. Perreau (J. Chim. phys., 1927, 24, 496—506).—The minimum quantity α of different electrolytes which produces flocculation in ferric hydroxide and arsenious sulphide sols of a definite concentration has been determined. The ratio of the values of α for two different electrolytes varies with the concentration of the sol when the coagulating ions differ in valency, but remains practically constant for ions of the same valency. Schultze's rule is obeyed qualitatively but not quantitatively. Kruyt's theory is discussed, and it is shown that the results, in the case of ferric hydroxide sols, are in direct contradiction to it. The limiting quantities of electrolyte necessary for flocculation per g. of colloid have been compared. In the case of ferric hydroxide coagulated by a salt with a multivalent anion, the curve connecting the time t with the quantity q of electrolyte has three branches with asymptotes at $q=a$, b, and c, and two zones of precipitation, one for values of q between a and b and the other for values of q greater than c. The ratios of a, b, and c to the concentrations C of sol for the coagulation of ferric hydroxide sol by sodium phosphate, sodium citrate, and potassium ferrocyanide have been determined. Whilst a/C and b/C increase as C increases, c/C diminishes.

M. S. Burr.

Hofmeister series. E. H. Buchner (Rec. trav. chim., 1927, 46, 439—444).—The salting-out influence of various salts on gelatin sols has been determined, and the variations of the salting-out effect with temperature and sol concentration have been measured. All inorganic univalent ions promote the swelling of gelatin, whereas the majority of multivalent ions have the reverse effect.

H. F. Gillbe.

Behaviour of alcohol-soluble proteins in mixed solvents. III. Denaturation of wheat gliadin. M. J. Gottenberg and C. L. Alsberg (J. Biol. Chem., 1927, 73, 581—586).—The critical peptisation temperature, *i.e.*, the temperature at which turbidity first appears on cooling the solution, is raised on keeping solutions of gliadin in 20—30% alcohol for some days at temperatures of 4—58°, and is lowered by keeping the solution in 70—90% alcohol under similar conditions. Solutions in intermediate concentrations of alcohol undergo no change.

C. R. Harington.

Swelling of isoelectric gelatin in water. I. Equilibrium conditions. J. H. Northrop (J. Gen. Physiol., 1927, 10, 893—904).—Experiments on the swelling of isoelectric gelatin confirm the view that it consists of a network of insoluble elastic fibres enclosing a more soluble material, the osmotic pressure of which causes the elastic fibres to expand until equilibrium is reached (cf. A., 1926, 1098). If the expansion is large so that the expansion is considerable the elastic limits may be exceeded and a permanent swelling then occurs which may go on indefinitely. A loss of elasticity is also observed if a block of gelatin, after attaining equilibrium in water, is heated in air and replaced in water, when secondary swelling occurs. A mathematical expression is obtained for the amount of swelling at equilibrium in terms of the elastic constant of the gelatin.

W. O. Kermack.

Swelling of isoelectric gelatin in water. II. Kinetics. J. H. Northrop and M. Kunitz (J. Gen. Physiol., 1927, 10, 905—926).—On the basis of the mechanism for the swelling of isoelectric gelatin previously described (see preceding abstract), equations are deduced for the kinetics of swelling which agree well with experiment. The effects of the size and the shape of the block of isoelectric gelatin can in this way be accounted for, and the permeability of gelatin to water, calculated indirectly from swelling experiments, has been verified by direct experiment. Equations are also deduced which describe the secondary swelling which occurs as a result of elastic fatigue of the gelatin, and these equations are also found to agree with the experimental facts.

W. O. Kermack.

Cataphoresis in mixed solvents. Theory of coagulation. J. J. Bikerman (Kolloid-Z., 1927, 42, 293—295; cf. A., 1925, ii, 522).—Measurements have been made of the cataphoresis of colloidal solutions of arsenic trisulphide in water–propyl alcohol mixtures in presence of calcium nitrate solution. The viscosity and dielectric constant of the mixtures varied in the ratio 1 : 3·5 and 1 : 4, respectively. Precipitation occurs at a critical potential which is practically independent of the solvent and of the concentration of the sol. This confirms the results previously obtained by the author (*loc. cit.*).

L. L. Bircumshaw.

Diffusion of water into lecithin–collodion membranes. H. A. Abramson and S. H. Gray (J. Biol. Chem., 1927, 73, 459—462).—The rate of diffusion of water into collodion sacs containing solutions of sodium sulphate or calcium chloride was not affected, between p_H 2 and 12, by the presence of 50% of lecithin in the collodion.

C. R. Harington.

Effect of hydrogen- and hydroxyl-ion concentration on water transport through a collodion membrane. P. J. Jurišić (Biochem. Z., 1927, 185, 423—426).—The rate of transport of water across a collodion sac, containing sodium sulphate solution and dipping into water, is delayed by addition of acid and accelerated by addition of alkali, in concentrations of $N/20{,}480$ and upwards, to the sodium sulphate solution, the maximum effect being reached at $N/80$. The potential difference set up between inner and outer solutions is increased by addition of acid and reduced by addition of alkali.

C. R. Harington.

Capillary action of filter-paper. L. Jendrassik and A. Czike (Biochem. Z., 1927, 185, 470—476).—Rapid stroking of the surface of an aqueous solution with a piece of filter-paper raises the surface tension, if this was originally lower than that of water. Prolonged contact of the filter-paper with the solution lowers the surface tension, the effect being due either to impurities in the paper (which may be removed by extraction with alcohol), or, in the case of such solutions as those of alkaloid salts, to the acid-binding power of the paper.

C. R. Harington.

Influence of the orientation of the molecules in the clogging of filters and ultrafilters. G. GÉNIN (Rev. gen. Colloid., 1927, **5**, 523—532).—The results obtained by Wilson and Barnard (cf. B., 1922, 929A) in their investigation of the influence of the nature of the capillary wall and of the liquid on the rate of flow of liquids through capillary tubes are explicable on the basis of the Langmuir–Harkins orientation hypothesis. The phenomenon of clogging in ultrafiltration may be explained in the same way. The rate of flow of a given oil through a cellulose nitrate membrane is found to decrease rapidly when a laboratory ultrafilter is used, whereas with an industrial ultrafilter the decrease is much less marked. Moreover, the effect is much greater in the case of vegetable oils than with mineral oils or aqueous liquids. It is assumed that the pores of the filter become lined with layers of oriented molecules of fatty acids (supposed to be always present in the oil, however highly purified it may be), which decrease the size of the pores and eventually, in some cases, cause complete obstruction to the passage of the liquid. The fact that with the industrial apparatus the effect is only slight is attributed to the more rapid circulation of the oil, which might prevent orientation of the molecules and their consequent adsorption on the filter surface. The influence of clogging in ordinary filtration is considered, and the application of the orientation hypothesis to a number of filtration problems is discussed.

L. L. BIRCUMSHAW.

Law of capillary flow in the case of colloids. A. W. PORTER and P. A. M. RAO (Trans. Faraday Soc., 1927, **23**, 311—314).—Determinations have been made by the capillary tube method of the flow, under various pressure-gradients, of starch sols of different concentrations. An equation has been deduced connecting flow with longitudinal pressure-gradient, the radius of the tube, and the viscosity, and also an expression showing approximately the dependence of viscosity on concentration. M. S. BURR.

Electro-endosmosis of aqueous solutions through a diaphragm of sintered glass powder. F. FAIRBROTHER and H. VARLEY (J.C.S., 1927, 1584—1589).—Electro-endosmosis experiments with a diaphragm of sintered glass in water and in dilute hydrogen chloride solution show that in water, after an initial period, the amount of electro-endosmosis decreases with time, the glass becoming less negative; in 0·01*N*-hydrogen chloride solution reversal is observed. The permeability of the glass to water also decreases with time. The suggestion is made that these effects are due to swelling of the glass surface, whilst to account for the reversal it is suggested that the distribution of potential at the interface is that described by Freundlich ("Kapillarchemie," 1922, 342). H. F. GILLBE.

Kinetics of osmosis. J. H. NORTHROP (J. Gen. Physiol., 1927, **10**, 883—892).—By combining the laws for osmotic pressure and rate of diffusion, an expression is obtained for the rate of osmosis, and this has been verified experimentally in the case of a collodion membrane containing a solution of egg-albumin or of gelatin. W. O. KERMACK.

Hydrodynamics and the kinetic theory of gases. Y. ROCARD (Ann. Physique, 1927, [x], **8**, 5—120).—A brief description is given of the classical method which leads to equations for the motion of the particles of a perfect gas according to the kinetic theory. Adopting the results obtained by Chapman (Phil. Trans., 1916, **A**, **211**, 337) and Jones (*ibid.*, 1922, **A**, **223**, 1) in their work on the function for the distribution of the velocities, the equations of the motion are given in an explicit form. The first approximation gives the equations of viscous flow, whilst the following approximation yields the complementary terms which, among other properties, contradict Lagrange's theorem. An analogous study is made for gaseous mixtures, and in the equations for the motion a new term is inserted which expresses the influence on the complete motion, or on that of each constituent considered separately, of variations of composition of the gaseous mixture by diffusion processes. An attempt is made to construct a "hydrodynamics" of compressed gases on the basis of the kinetic theory. The calculations are possible only in the case of gases which obey van der Waals' criteria. An analysis is made of the new terms which appear in the equations of the motion of a compressed gas, and express the influence on the motion of intermolecular forces and of molecular impacts. The former give a precise meaning to the terms $\delta P/\delta x$, $\delta P/\delta y$, $\delta P/\delta z$, of classical hydrodynamics; the latter deal with the viscous properties, and are, in effect, a correction to the coefficient of viscosity, for which a rigorous expression is obtained as a function of the specific volume. For the hydrodynamic treatment of this problem it is necessary to know, besides the equations of motion and the equations of state, the equations of heat transfer. In simple cases this reduces to the adiabatic hypothesis, but in the case of compressed gases new terms appear which lead to a rigorous expression for the coefficient of thermal conductivity as a function of the specific volume. The results obtained are obviously only remotely comparable with the experimental data, but by considering an arbitrary molecular model, consisting of a molecule having a very intense force of attraction acting over a very small range, satisfactory comparisons with experiment are obtained for the variation in the coefficient of viscosity of carbon dioxide with pressure. L. L. BIRCUMSHAW.

Dissociation of carbon dioxide at high temperatures. R. W. FENNING and H. T. TIZARD (Proc. Roy. Soc., 1927, **A**, **115**, 318—333).—A simple relation is shown to exist between the composition of the carbon monoxide–air mixture giving maximum pressure on explosion and the dissociation of carbon dioxide at the maximum explosion temperature. If the initial composition and the composition at the maximum temperature are represented by the expressions $2(1+a)CO+O_2+bN_2$ and $2(1-x)CO_2+2(a+x)CO+xO_2+bN_2$, respectively, then $x=a/b$ when P_e, the maximum pressure observed after explosion, is a maximum. Thus the dissociation of carbon dioxide at high temperatures may be determined by adding carbon monoxide in varying quantities to a standard mixture of nitrogen and oxygen, an

measuring the pressures reached on exploding the different mixtures. The value of a when the explosion pressure is a maximum is read off from the curve representing the results, x is given by a/b, and K_p by the equation $K_p=[(a+x)/(1-x)]^2\times x/(2+2a+x+b)\times P_e$. By varying the proportion of nitrogen to oxygen, the dissociation has been determined over a wide temperature range, and the constants found from the explosion experiments by this method agree closely with those deduced from the same experiments by a method which, in principle, has been previously used by Bjerrum and others. The results obtained for the dissociation of carbon dioxide at high temperatures are considerably lower than the accepted values. The reasons for this are discussed. It is pointed out that the relation $x=a/b$ at the maximum temperature applies also to flames. L. L. Bircumshaw.

Dissociation of carbon dioxide at high temperatures. W. T. David (Nature, 1927, 120, 157).—Fenning and Tizard's assumption (cf. preceding abstract) that chemical equilibrium is established by the time the maximum pressure is reached in explosions is considered to be erroneous. Investigations indicate that even with pure gases (carbon monoxide and hydrogen) chemical equilibrium is far from being attained at maximum pressure. A. A. Eldridge.

Soret effect. A. W. Porter (Trans. Faraday Soc., 1927, 23, 314—316).—Theoretical. Mathematical expressions are deduced connecting the concentration gradient of a solution with the temperature gradient, and applied to Tanner's data (this vol., 204) for electrolytes. M. S. Burr.

Formation of a complex ion in aqueous solutions of silver nitrate and phenol. K. Endo (Bull. Chem. Soc. Japan, 1927, 2, 147—155).—Measurements of the partition of phenol between benzene and aqueous solutions of silver nitrate show that silver nitrate differs from the salts previously studied (this vol., 729) in that it increases the solvent power of water for phenol. Measurements of f.-p. depression show that this abnormal behaviour is due to the formation of the complex ion $[Ag{\cdot}C_6H_6O]^+$. J. S. Carter.

Titration curves of taurine and of cysteic acid. S. Andrews and C. L. A. Schmidt (J. Biol. Chem., 1927, 73, 651—654).—Titration curves are given for taurine and cysteic acid; taurine has K_a $1{\cdot}8\times10^{-9}$, K_b 3×10^{-13}; cysteic acid has K_a $1{\cdot}3\times10^{-2}$ (assuming K_b to be 2×10^{-13}), and K_{a_2} 2×10^{-9}. C. R. Harington.

Influence of adsorbing materials on chemical equilibria in solution. R. Dubrisay and J. Bravard (Compt. rend., 1927, 185, 385—386).—The effects of kieselguhr (treated with hydrochloric acid and washed with hot and then cold water till neutral), of Fontainebleau sand, silica, and china and other clays on the solubility of calcium carbonate in contact with a solution of ammonium chloride, have been determined at 17°, 41°, and 35° in solutions of various concentrations ($4N$- to $N/16$-ammonium chloride). The adsorbing material increases the solubility of the calcium carbonate according to the equation $2NH_4Cl+CaCO_3=(NH_4)_2CO_3+CaCl_2$, the effect being less marked in warm than in cold solutions. J. Grant.

Second law of thermodynamics. E. Denina (Gazzetta, 1927, 57, 415—451).—The analyses advanced in the author's recent contributions to thermodynamics (cf. this vol., 314, 316) have been summarised and co-ordinated. The fundamental concept is the definition of the second law in the following form: that for any reversible cycle associated with a change of energy, dW, there exists a quantity P such that the integral $\int P^{-1}dW$ throughout the cycle is zero. P is termed the potential factor of the system. Alternatively, $P^{-1}dW$ is a function of a quantity C, termed the capacity factor of the system, and is a complete differential. The application of this form of the second law, for which unification and simplification are claimed, is discussed at length for all types of systems. R. W. Lunt.

Influence of concentration and the activity of the hydrogen ions on the rotatory power of aqueous solutions of electrolytes. (Mlle.) J. Liquier (Ann. Physique, 1927, [x], 8, 121—203).—An electrometric investigation of aqueous acid or basic solutions of weak optically active electrolytes (nicotine, quinine, and asparagine) shows that the rotatory power may be expressed as a function of the p_H of the solution. The variation of the rotatory power, and the anomalous dispersion observed in certain cases, may be explained by the hypothesis of the superposition of the rotatory dispersions of two or more active constituents (*i.e.*, neutral molecules and the ions formed on dissociation). The experimental curves, $[\alpha]=f(p_H)$, have the S-shape of the curves which are associated with saturation of weak acids or bases by strong bases or acids, and they coincide with the theoretical curves obtained by applying the classical laws governing dilute solutions of weak electrolytes to the substances under consideration. The relation between the dissociation constants and the degree of acidity or basicity shown by the electrolytes may be determined with great accuracy from the curves $[\alpha]=f(p_H)$. The degree of hydrolysis of the salts formed may also be accurately calculated.

The measurements of rotatory power have been extended to solutions of asparagine in presence of strong electrolytes. From a consideration of the rectilinear diagrams of Darmois (cf. A., 1923, i, 299, 535, 751) for the visiblo and ultra-violet spectra, it is concluded that the active constituents of these salt solutions are the same as those of aqueous solutions of variable acidity, *i.e.*, the neutral asparagine molecule and corresponding anion and cation. The properties of asparagine are thus, both in salt and aqueous solution, a function of its degree of dissociation. The law of mass action is applicable to these solutions, provided that it is generalised by the introduction of the coefficients of activity of the ions present in the solution. Knowing the rotatory power and the activity of the hydrogen ion for a given salt solution, the coefficients of activity of the ions formed by dissociation may be calculated. It is proved that these coefficients vary in the directions indicated by the Debye–Huckel theory of strong electrolytes. The facts observed constitute a qualitative verification of this theory, and it is shown in

particular that they may be interpreted in terms of the diminution of the dielectric constant of the solvent due to the addition of salts. L. L. BIRCUMSHAW.

Recent advances in the ionisation theory as applied to strong electrolytes. V. K. LA MER (Amer. Electrochem. Soc., May, 1927. Advance copy. 54 pp.).—In a review of the anomaly of strong electrolytes, the theory of Debye and Hückel is presented and discussed at length. The influence of the mathematical approximations in the present form of the theory is shown to be most marked for ions of small size. This question and its relation to Bjerrum's hypothesis of ion association (A., 1926, 1101) are developed in some detail. Most of the discrepancies between theory and experiment vanish when the mathematical development is extended to include the case for ions of small size and high valency. Bronsted's principle of specific interaction (A., 1924, ii, 94) is discussed and the significance of the true degree of dissociation of strong electrolytes is considered. It is claimed that the extension of the Debye–Hückel theory to concentrated solutions, as given by Hückel (A., 1925, ii, 513), assuming that the dielectric constant is a linear function of the ionic concentrations, is not justified. The agreement with Hückel's equation found by Scatchard (A., 1926, 911) and by Harned (A., 1926, 354) is stated to be illusory and values of the dielectric constant required by Hückel's equation do not agree with the experimental data of Walden, Ulich, and Werner (A., 1925, ii, 773). Gronwall and the author have shown that values of the dielectric constant chosen so as to fit in with vapour pressure and *E.M.F.* data in concentrated solutions are in agreement with Walden's results. It is claimed that a thermodynamic error is involved in the derivation of Huckel's equation and an equation derived by Gronwall and the author is put forward in its place. H. J. T. ELLINGHAM.

Electrochemistry of solutions of mixed electrolytes. H. S. HARNED (Amer. Electrochem. Soc., May, 1927. Advance copy. 34 pp.).—The determination of the activity coefficient of an electrolyte in solutions of other electrolytes is discussed and recent work on the subject is reviewed. The thermodynamic behaviour of hydrogen and hydroxyl ions is compared with their catalytic effects in the light of recent experimental measurements.

H. J. T. ELLINGHAM.

Transference number and activity of sodium hydroxide in aqueous solution. A. L. FERGUSON and A. W. SCHLUCHTER (Amer. Electrochem. Soc., May, 1927. Advance copy. 11 pp.).—The activity coefficient of sodium hydroxide in aqueous solutions ranging from 0·01 to 2·8 g.-mol. per kg. of water has been determined by measuring the *E.M.F.* of the concentration cells, $H_2|NaOH(C_1)|Na_xHg|NaOH(C_2)|H_2$ and $H_2|NaOH(C_1)|NaOH(C_2)|H_2$. From the data obtained transference numbers have been calculated over the given concentration range. The value for the cation varies from 0·203 in the most dilute to 0·153 in the most concentrated solution.

H. J. T. ELLINGHAM.

Mixed solutions of electrolytes and non-electrolytes. G. SCATCHARD (Amer. Electrochem. Soc., May, 1927. Advance copy. 14 pp.).—Recent work on the activity coefficients of electrolytes in solutions of non-electrolytes is reviewed and the theoretical treatment of such systems discussed.

H. J. T. ELLINGHAM.

Ionic partition coefficients. I. N. BJERRUM and E. LARSSON (Z. physikal. Chem., 1927, 127, 358—384).—The partition coefficients of a number of ions between water and ethyl alcohol have been determined by *E.M.F.* measurements. The partition exponent P, defined as the logarithm of the partition coefficient, is composed of an electrical term P_e dependent on the ionic charge, a term P_u due to molecular forces, and a third term P_s dependent on the different degrees of solvation of the ion in the two solvents. P_e may be calculated if the valency and radius of the ion and the dielectric constants of the two solvents be known, and P_u may be considered to be of the same magnitude as the partition exponent of a similar but neutral molecule. P_s is equal to the logarithm of the equilibrium constant of the solvation in the two media. The calculated values of the partition exponents and the extent of the agreement with the experimental figures are discussed. The application of the partition exponent in the analytical treatment of the Soret phenomenon and of thermoelectric forces in solutions of electrolytes are discussed. H. F. GILLBE.

Factors influencing the solubility of strong electrolytes. I. Reciprocal solubility effects of homoionic alkali salts. I. J. F. HOLLUTA and S. MAUTNER (Z. physikal. Chem., 1927, 127, 455—475).—The influence of sodium chloride and of potassium nitrate on the solubility of potassium chloride, of potassium chloride on that of sodium chloride, and of potassium chloride on that of potassium nitrate, in aqueous solution at 18·5°, have been measured up to the highest possible concentration of the added salt. A series of equations, which hold only for non-electrolytes and assume complete ionisation of all strong electrolytes, have been applied to the results; discrepancies are discussed, and a general relationship is proposed between the magnitude of the solubility effect and the solubility and chemical nature of the two salts concerned. Equations are given for calculating the solubility effect at any concentration of the added salt.

Rothmund's equation for the reciprocity of the solubility effect has been tested; on the assumption of complete ionisation, discrepancies of considerable magnitude exist between the theoretical and experimental figures. H. F. GILLBE.

Mol. wt. determinations and solubilities in liquid chlorine. K. H. BUTLER and D. MCINTOSH (Trans. Roy. Soc. Canada, 1927, [iii], 21, III, 19—26).—The following anhydrous compounds produce no rise in the b. p. of, and are consequently insoluble in, liquid chlorine: Potassium aluminium sulphate, aluminium acetate, ammonium chloride, sulphate, and thiocyanate, antimony trichloride and oxide, barium chloride, bismuth nitrate, boric acid, cadmium chloride, cæsium chloride, calcium carbonate and fluoride, chromium sulphate and trioxide, cupric sulphate, cuprous chloride, ferric chloride and

sulphate, iodine trichloride, lead chloride and sulphate, lithium chloride, mercuric iodide, mercurous chloride, nickel chloride, potassium chloride, chlorate, dichromate, ferricyanide, ferrocyanide, iodate, iodide, and nitrate, phosphorus chloride, selenium dioxide, silver nitrate, sodium arsenate, arsenite, hydrogen sulphite, bromide, phosphate, and stannate, strontium chloride, uranyl acetate, zinc chloride and sulphate. The following hydrated salts have no influence on the b. p.: cadmium sulphate, ferrous sulphate, magnesium chloride and sulphate, stannic chloride, stannous chloride. Silver, copper, zinc, sulphur, and arsenic are unaffected by boiling liquid chlorine, although attacked by the gas; aluminium reacts readily, tin and iodine violently, and phosphorus explosively. The most probable value of the ebullioscopic constant is 1·73, corresponding with a latent heat of 66·0 g.-cal. per g. Bromine molecules appear to dissociate in, but not to form a compound with, liquid chlorine. A. A. ELDRIDGE.

Solubility of acids in salt solutions. I. E. LARSSON (Z. physikal. Chem., 1927, **127**, 233—248).—The solubility of benzoic, cinnamic, hippuric, *o*-nitrobenzoic, benzilic, and salicylic acids in dilute salt solutions has been determined and the results have been compared with those obtained by Loven for the solubility of a sparingly soluble monobasic acid in a solution of a salt of another monobasic acid. In dilute salt solutions the ion activity coefficients do not influence the solubility when both acids are monobasic. At higher concentrations it would be expected that the activity coefficients of the molecules would influence the sparingly soluble acid, but measurements of the solubility of benzoic acid in solutions of sodium acetate, sodium formate, and sodium monochloroacetate at concentrations up to *M* show that no such effect takes place. The ions present, therefore, appear to have opposing influences on the activity of the benzoic acid molecule. More probably, sodium benzoate increases the solubility of benzoic acid, whilst the other three salts act as salting-out agents. The solubility of benzoic acid in sodium chloride solution is smaller, and in sodium benzoate solution greater, than in water. Equations are proposed by which the solubility of a monobasic acid in a solution of a salt of a polybasic acid may be calculated, but these are applicable only at infinite dilution. H. F. GILLBE.

Influence of neutral salts on acid–salt equilibria. I. Standard value for calculating the activity exponent of the hydrogen-ion concentration. I. M. KOLTHOFF and W. BOSCH (Rec. trav. chim., 1927, **46**, 430—438).—It is suggested at p_{aH} of the standard solution 0·01*N*-HCl+KCl be taken as 2·075, whence $p_{aH}=p_H+0·037$. Neutral salts decrease the hydrogen-ion activity in hydrogen chloride solutions, but at higher concentrations have the reverse influence. The effect produced is independent of the anion. H. F. GILLBE.

Solubility in water of 4-dimethylamino-1-phenyl-2:3-dimethyl-5-pyrazolone [pyramidone]. D. CHARONNAT (Compt. rend., 1927, **185**, 286). The solubility data between 0° and 200° give a looped curve which is attributed to the existence of a second form of pyramidone (β-pyramidone), which has not been isolated. The transformation $\alpha \longrightarrow \beta$ is said to account for the rapid increase in the solubility at 65—70°. J. GRANT.

Equilibrium between the hydrates of calcium sulphate. D. BALAREV [with A. SPASSOV] (Z. anorg. Chem., 1927, **163**, 137—140).—The process of dehydration of the hemihydrate of calcium sulphate above 80° is reversible, but the dehydration does not take place spontaneously. Below 80° the water-vapour pressure of the system lies below 2 mm. of mercury. The decomposition of the hemihydrate into a mixture of dihydrate and anhydrous salt is therefore thermodynamically impossible, as the regeneration of the hemihydrate could not take place. Such a decomposition is possible only if two forms of the soluble anhydrous salt exist, viz., an α form stable below 72° and incapable of existence in equilibrium with the hemihydrate, and a β form stable above 72° and stable in the presence of hemihydrate. Dilatometric measurements confirm the existence of the two forms; the transition $\alpha \rightleftharpoons \beta$ occurs at 82°, and is rendered evident also from the nature of the heating and cooling curves, the β form being produced from the α with the evolution of heat.

Contradictions in the literature concerning the crystal form of anhydrous calcium sulphate may most probably be referred to the existence of the two forms. H. F. GILLBE.

Systems: $CoCl_2$–MCl or MCl_2–H_2O. A. BENRATH (Z. anorg. Chem., 1927, **163**, 396—404).—The equilibria in the above ternary systems at 25° have been studied. Together with the evidence obtained by Mazzetti (this vol., 22) and by Foote (*ibid.*, 313) the results indicate that the blue colour of cobalt chloride solutions containing chlorides of sodium, potassium, ammonium, or the alkaline-earth metals cannot be ascribed to the existence of complex compounds. The colour cannot be due to the formation of lower hydrates of cobalt chloride, since the lowest hydrate obtained under the experimental conditions was the dark violet dihydrate. It seems probable that the compound $CoCl_2,RbCl,2H_2O$ reported by Foote was a mixture. A blue *compound*, $CoCl_2,4LiCl,10H_2O$, has been obtained. From the red solutions of cobalt chloride containing zinc chloride and cadmium chloride, the *compounds* $2ZnCl_2,CoCl_2,12H_2O$ and $2CdCl_2,CoCl_2,12H_2O$ have been isolated, and it is probable that mercuric chloride yields a similar compound. R. CUTHILL.

Complex chemical behaviour of beryllium. V. R. FRICKE and O. RODE (Z. anorg. Chem., 1927, **163**, 31—39).—The thermal diagram of the system beryllium chloride–*iso*hexonitrile shows the existence of three eutectics, viz., at about 154°, 125°, and −53°, and of three compounds containing 2, 3, and 4 *iso*hexonitrile groups combined with one molecule of beryllium chloride. Beryllium chloride–propionitrile and beryllium chloride–*p*-toluonitrile both yield complexes containing 2, 3, 4, 5, and 7 nitrile groups per molecule of beryllium chloride. The results for *p*-toluonitrile are confirmed by conductivity measurements. H. F. GILLBE.

Organic binary equilibria. System glyceryl trinitrate–trinitrotoluene. V. TAMBURRINI (Annali Chim. Appl., 1927, **17**, 275—282).—The cooling curve for this system with initial separation of solid trinitrotoluene shows scarcely any supercooling, but this phenomenon is clearly marked when glyceryl trinitrate separates first as solid. With eutectic crystallisation pronounced superfusion occurs. The existence of a compound is improbable.

T. H. POPE.

Binary pharmaceutical mixtures. A. ANGELETTI (Annali Chim. Appl., 1927, **17**, 269—275).—Examination by Rheinboldt's method (A., 1926, 25) has given the following eutectic points. Acetanilide–pyramidone, 58·5°, 41% acetanilide; acetanilide–phenacetin, 82·5°, 58% acetanilide; pyramidone–phenacetin, 78·5°, 68% pyramidone; salol–benzonaphthol, 34°, 86·9% salol. In the last case, mixtures containing 80—90% of salol would undergo partial fusion in hot weather and are hence "incompatible."

T. H. POPE.

System: iron–silicon. T. MURAKAMI (Sci. Rep. Tohoku Imp. Univ., 1927, **16**, 475—489).—The magnetic transformation which occurs at 450° in alloys containing more than 16% of silicon is not due to a change of phase, and the evolution of heat at 1020° is due to the formation of Fe_3Si_2 from the α phase and FeSi. The existence of a compound melting at 1225° is confirmed by *X*-ray analysis, and it is found to dissolve up to 1% of silicon, forming a solid solution which gives a eutectic point with FeSi at 1220°. This is so close to the m. p. of $FeSi_2$ that discrimination of the two changes by means of cooling curves is impossible. Silicon forms a solid solution which may contain up to 4% of iron. F. S. HAWKINS.

System: iron–cobalt–nickel. T. KASE (Sci. Rep. Tohoku Imp. Univ., 1927, **16**, 491—513).—The system has no ternary eutectic and there is no evidence of compound formation. The relations suggest a continuous series of solid solutions, except for a small range on the iron side, where there is a discontinuous change from one solid solution to another. Magnetic, dilatometric, scleroscopic, and microscopic observations indicate the occurrence of one magnetic and two polymorphic changes in the solidified alloy. The polymorphic change on the iron side is the transition from γ- to α-solution, and that on the cobalt side from γ-solution to a hexagonal lattice solution. The magnetic change involves no change of phase. F. S. HAWKINS.

Three-component system copper–aluminium–manganese, and its magnetic properties. W. KREINGS and W. OSTMANN (Z. anorg. Chem., 1927, **163**, 145—164).—The system shows no ternary compound, nor could the existence of the compound Al_3Mn be confirmed; Al_4Mn, however, is present. The ternary diagram may be divided into three regions: (1) the triangle Al–$CuAl_2$–Al_4Mn in which there exists at 536° a ternary eutectic which contains 29·6% of copper and 3% of manganese; (2) an area of ternary mixed crystals, which undergo transition in the solid state and may be isolated by rapid cool-

(3) a polyphase area lying between (1) and (2), which has not been investigated further. When less than 45% of copper is present two liquid layers are formed.

The maximum susceptibility of Heusler's alloys lies at the point of intersection of Cu_3Al and $AlMn_3$. Alloys containing more than 30% of manganese, which have not been previously investigated, are also magnetic. The increase and decrease of magnetic properties are accompanied by changes of structure, which have been studied by the aid of photomicrographs.

In contradistinction to Heusler's alloys, which attain their maximum magnetic susceptibility after being heated at 144° for a long period, alloys of high manganese content exhibit their maximum magnetic properties after ageing at a high temperature, whereas ageing at 144° causes all magnetic effects to vanish. H. F. GILLBE.

Ternary system methyl benzoate, methyl alcohol, water. E. C. GILBERT and B. E. LAUER (J. Physical Chem., 1927, **31**, 1050—1052).—The solubility isotherms for 15°, 25°, and 35° have been determined by the method of Walton and Jenkins (A., 1924, i, 156). An equation of the type $X/Y^n=K$ is shown to hold at the lowest temperature, but there is increasing divergence from experiment with a rise of temperature. Methyl benzoate and water are practically immiscible at the ordinary temperature, and a large proportion of methyl alcohol is required to produce a one-phase mixture. The solubility surface rises abruptly. L. S. THEOBALD.

Systems uranyl sulphate, alkali sulphate, water, at 25°. A. COLANI (Compt. rend., 1927, **185**, 273—275).—Solubility data for the systems, uranyl sulphate and water, with ammonium, potassium, and sodium sulphates at 25° show the existence of a number of complex *salts*. The following have not been previously described: $(NH_4)_2(UO_2)_2(SO_4)_3,5H_2O$, $K_2(UO_2)_2(SO_4)_3,5H_2O$, and $Na_4(UO_2)(SO_4)_3,3H_2O$. All the compounds obtained behave as true double salts, but anomalies are shown by the sodium sulphate system. J. GRANT.

Solubility of silver halides in concentrated halide solutions. L. DEDE and T. WALTHER (Z. anorg. Chem., 1927, **163**, 185—194).—The solubilities have been determined of silver chloride in concentrated solutions of the chlorides of potassium, ammonium, sodium, calcium, lithium, and hydrogen, and of silver bromide in concentrated solutions of potassium, calcium, and hydrogen bromides, at 20°, 40°, 60°, and 80°. In all cases the temperature coefficient is large. The increase of solubility produced by the presence of the various salts is in the order given, being greatest for potassium halides and least for the hydrogen halides. This order is not the same as that of the activity coefficients of the salts.

H. F. GILLBE.

Systematic doctrine of affinity. XXXIX. Indium halides. II. Heats of formation of indium chlorides. W. KLEMM and M. BRAUTIGAM (Z. anorg. Chem., 1927, **163**, 225—234; cf. A., 1926, 669).—The heats of formation of the solid indium chlorides from the metal and gaseous chlorine at 18° are: monochloride, 44·6±0·1; dichloride, 86·8±0·3, trichloride, 128·5±0·1 kg.-cal. CUTHILL.

Systematic doctrine of affinity. XL. Indium halides. IV. Ammines of indium halides. W. KLEMM (Z. anorg. Chem., 1927, **163**, 240—252).—Isothermal decomposition experiments indicate the existence of *compounds* of indium trichloride with 15(?), 7, 5, 3, 2, and 1 molecules of ammonia. The tribromide forms compounds with 15(?), 7, 5, and 3 molecules of ammonia, and the tri-iodide with 21(?), 13, 9, 7, 5, 2, and 1(?) molecules. For a few of the compounds, the dissociation pressures at various temperatures have been determined, and the results used to calculate the partial heats of formation. In some cases, the heat of dissolution in hydrochloric acid has been determined, and the total heat of formation calculated from it. From these measurements, assuming the heat of formation of indium trichloride to be 128·5 kg.-cal., the heats of formation of the tribromide and tri-iodide are found to be 97·1 and 56·4 kg.-cal., respectively. Addition of ammonia to the monochloride causes it to decompose into the metal and the ammonia compounds of the trichloride, but on removal of the ammonia the triammine passes directly to the ammonia-free monochloride without formation of a diammine or monammine. R. CUTHILL.

Systematic doctrine of affinity. XLI. Uranium oxides. W. BILTZ and H. MÜLLER (Z. anorg. Chem., 1927, **163**, 257—296).—The relation between the valency of uranium in its oxides and their energy contents has been investigated. For preparations varying in composition from UO_3 and U_3O_8, the dissociation isotherms between 438° and 650° are continuous, so that the solid phase, the *X*-ray diagram of which shows the lattice of uranoso-uranic oxide, consists of a solid solution. The pressures actually observed are apparently not quite equal to the true equilibrium pressures. This is probably due to the great chemical resistance to the passage of part of the amorphous trioxide into mixed crystals. Under ordinary conditions, the reverse transformation of uranoso-uranic oxide into the trioxide does not occur, although it seems to have occurred in some minerals, and does actually take place with very finely-divided preparations such as are obtained by ignition of uranyl oxalate (cf. Lebeau, A., 1922, ii, 302). From the tensimetric data, the heat of the reaction $2U_3O_8 + O_2 = 6UO_3$ is calculated by means of Nernst's approximate equation for the dissociation pressure of oxides to be 32 kg.-cal. In the passage of uranoso-uranic oxide into the dioxide, the equilibrium pressure is rapidly established, and the process is completely reversible. Between the compositions $UO_{2\cdot61}$ and the pressure at constant temperature is constant, corresponding with the existence of conjugate uranoso-uranic oxide and the dioxide. At 1000°, the mixed crystals have an appreciable vapour pressure, and sublimation occurs. Neither the tension curves nor *X*-ray diagrams yield any evidence for the existence of the pentoxide, U_2O_5. For the reaction $3UO_2 + O_2 = U_3O_8$ is calculated 77 kg.-cal. by the van 't Hoff isochore, and [illegible] kg.-cal. by Nernst's equation. The densities at 0°/0° of uranium oxides between $UO_{3\cdot069}$ and $UO_{1\cdot99}$ have been [illegible]. Between UO_2 and $UO_{2\cdot26}$, oxygen is taken up without any change in the volume of the oxide, the latter composition corresponding with the solubility of uranoso-uranic oxide in the dioxide. Beyond this point, the volume increases regularly, the curve showing no discontinuity at the composition corresponding with uranoso-uranic oxide (cf. preceding abstracts). R. CUTHILL.

Relation between unit electrolytic conductivity and Faraday's law. M. EPPLEY (J. Franklin Inst., 1927, **204**, 95—96).—The relation is expressed in the statement that: "When the conductivity of a solution is unity, a current of 1 amp. passed through it between electrodes 1 cm.^{2} in area and 1 cm. apart will deposit one electrochemical equivalent per second." J. S. CARTER.

Temperature coefficients of electrical conductivity for concentrated solutions of calcium chloride, with precision measurements of conductivity for the higher concentrations. M. CROWE (Trans. Roy. Soc. Canada, 1927, [iii], **21**, III, 145—156).—Tabulated values and curves are given of the conductivity and density of solutions of calcium chloride containing 29—46 g. per 100 g. of solution at 10°, 15°, 17·9°, 20°, 25°, and 30°. The specific conductance at 18° and the temperature coefficient, respectively, are: 29·60%, 0·1661, 0 0216; 37·30%, 0·1202, 0·0241; 38·36%, 0·1124, 0·0249; 40·73%, 0·0934, 0·0284; 41·98%, 0·0868, 0·0286; 45·95%, 0·0576, 0·0330. A. A. ELDRIDGE.

Conductivity and transport numbers of cadmium salts in acetamide. L. BELLADEN (Gazzetta, 1927, **57**, 412—415).—The molecular conductivity of cadmium chloride, bromide, and fluoride has been determined at 90° in molten acetamide at $v=10$—1200. It is found that the iodine transport number for solutions of cadmium iodide increases from 0·68 to 1·41 as the concentration of the salt increases from 1·9 to 15%. These values are slightly greater than those of Hittorf for aqueous solutions, in agreement with the smaller dissociating power of acetamide. R. W. LUNT.

Conductivity of electrolytes in fused acetamide. L. BELLADEN (Gazzetta, 1927, **57**, 407—411).—Acetamide was purified by careful drying and repeated fractionation at 220 mm.; the substance so produced had a specific conductance of $1·5 \times 10^{-5}$ mho at 90°. Data are given for the molecular conductivity of sodium chloride, bromide, and iodide in molten acetamide at 90° for $v=10$—720; the values observed are of the same order of magnitude, although only the bromide and iodide are known to form complexes with the solvent. Data are also given for calcium and barium chlorides and for potassium iodide for $v=10$—960. The conductivity of the barium salt is slightly greater than that of the calcium salt, which forms a complex with six molecules of the solvent. The author's data for potassium iodide are compared with Walker's, which show a maximum at $v=54900$, whilst the former increase regularly to infinite dilution. The discrepancy is attributed to inadequate purification of Walker's solvent. R. W. LUNT.

Moving-boundary method for determining transference numbers. VI. Further developments in experimental technique. D. A. MAC-

INNES, I. A. COWPERTHWAITE, and T. C. HUANG (J. Amer. Chem. Soc., 1927, 49, 1710—1717).—The form of the cell and the method of measuring the time intervals have been improved. The effects of vibration are eliminated by suspending the thermostat with springs. Boundaries must always descend, *i.e.*, the solution of lower conductivity must always be uppermost; otherwise, heat effects and mixing occur. An improved method of viewing the boundary is described and some factors governing "adjustment" (*i.e.*, of the indicator concentration) are discussed. With these improvements, the transport number of silver in 0·05*N*-silver nitrate is 0·4664 at 25°.

S. K. TWEEDY.

Space charge in electrolytes. D. ROLLER (Proc. Oklahoma Acad. Sci., 1927, 6, 290—293).—Measurements of the potential differences between two platinum points, 1 cm. apart, placed between two electrodes (*E.M.F.* between 5·3 and 26 volts) in 0·005—0·3*N*-hydrochloric acid indicated that the field in the electrolyte was unidirectional and normal to the electrodes. Appreciable non-uniform electrical distributions could be explained on the basis of space-charges in the electrolyte. CHEMICAL ABSTRACTS.

Effect of the concentration gradient on the electric field in a conducting electrolyte. D. ROLLER (Proc. Oklahoma Acad. Sci., 1927, 6, 294).—In hydrochloric acid solutions the electric field has a maximum value near the cathode. Effects due to concentration polarisation are important in such measurements. CHEMICAL ABSTRACTS.

Electrochemical properties of bromine–ether mixtures. B. P. BRUNS (Z. anorg. Chem., 1927, 163, 120—136).—A simple method is described for varying to a known extent the concentration of a solution contained in a closed system. The conductivities have been determined of bromine solutions of methyl, ethyl, propyl, *iso*amyl, and dichloroethyl ethers, and methylal. In the methyl ether series the specific conductance decreases with increase of mol. wt., methyl ether, however, having an abnormally low value. Methylal has a conductivity similar to that of ethyl ether, and is a more convenient substance with which to work since it reacts more slowly with bromine.

The curves showing the relationship between molecular conductivity and concentration are of the type normally given by solvents possessing a low dielectric constant. With the exception of dichloroethyl ether, all the solutions exhibit a large increase of conductivity with rise of temperature. Dichloroethyl ether, in which the positive character of the oxygen atom is weakened, has a conductivity of only about 0·01 of that of ethyl ether, probably owing to the reduced tendency to complex formation; this is also the probable cause of the negative temperature coefficient of the conductivity. In all cases the current passed by the solution is directly proportional to the applied voltage. Electrolysis yields bromine at the anode quantitatively, whilst no change occurs at the cathode.

Comparison of the molecular conductivity of the hydrogen halides in ether and of ether in the hydrogen halides with that of the ethers in bromine indicates that the ionisation is most probably due to the dissociation of a complex formed between the ether and bromine. H. F. GILLBE.

Electrochemistry of solutions of aluminium bromide in nitrobenzene. V. A. PLOTNIKOV and M. A. BENDETZKY (Z. physikal. Chem., 1927, 127, 225—232).—Measurements have been made of the conductivity of solutions of aluminium bromide in nitrobenzene at concentrations between 0·27 and 58·6% over the range 0—80°. The specific conductance-concentration curves, at all temperatures, rise to a maximum and then fall to very low values. At 10° and 50° the maxima correspond with 16 and 24%, respectively. For a solution containing 28·3% of aluminium bromide the specific conductance at 50° is 252×10^{-5} mho. The conductivity at constant concentration increases at first with rising temperature, reaches a maximum, and then falls; the temperature coefficient increases with the concentration. Electrolysis of the solution yields bromine at the anode in quantitative agreement with Faraday's law. H. F. GILLBE.

Volta effect. E. DUBOIS (Compt. rend., 1927, 185, 110—111).—A metal electrode heated in air and cooled becomes electronegative in relation to its initial state. Silver, gold, copper, and platinum become slightly electropositive after heating at 500°, but change to electronegative after heating at 1000°. The effect is independent of the oxidisability of the metal, and the action of the vapour of an alkali chloride is to change an electronegative electrode back to an electropositive state, which is characterised by a greater degree of stability than the original.

J. GRANT.

Becquerel effect with copper oxide electrodes. W. J. D. VAN DYCK (Z. physikal. Chem., 1927, 127, 249—301).—The method of Goldmann and Brodsky has been modified to permit of more rapid measurements of the photoelectric effects and the electrode has been improved by depositing a layer of cupric oxide or of a mixture of cuprous and cupric oxides on platinum. The dependence of the photo-electric characteristic on the wave-length of the incident light indicates that the Becquerel effect for cupric oxide cannot be explained as a simple Hallwachs effec . The photoelectric sensitivities of the two oxides per unit of incident light energy have been measured, and a thermopile is described by means of which t e quantum yield by the Becquerel effect has been determined. With no current flow no decomposition is caused by the action of light. The capacity o e surface layer of the oxide has been measured, an i influence on the form of the photo-electric curves i discussed.

The theoretical significance of the effect is considered. According to this it appears that peculiarities of the crystal structure play a gr part, and the varying stability of the lattice varying external oxygen concentration is emphasis . Thermodynamic considerations suggest the exis e of a *P.D.*, above which no effect is to be expec e . H. F. GILLBE.

Influence of gelatin on the potential and dis charge potential of zinc in zinc sulphate so u N. ISGARISCHEV and P. TITOV (Z. Elektrochem.,

33, 211—212).—Results obtained by Rabald (A., 1926, 804) are regarded as extending but not contradicting the authors' previous observations (A., 1921, ii, 620).

H. J. T. ELLINGHAM.

Passivity of metals from the point of view of the activation process. I. Activation process and steady anodic gas evolution. D. REICHINSTEIN and W. VON REYTER (Z. Elektrochem., 1927, 33, 237—244).—Measurements have been made at various constant current densities of the potential of smooth platinum electrodes acting as anodes in dilute sulphuric acid solutions. At a given current density the anode potential eventually reaches a steady value which is independent of the acid concentration (between 0·1 and 1·8N) and of the previous history of the electrode, but the time required for the attainment of this steady value is greatly dependent on the previous history, previous cathodic treatment making it very long and previous anodic treatment at a higher current density making it very short. In the latter case, on lowering the current density the potential falls rapidly and actually reaches as much as 30 millivolts below the steady value corresponding with the new current density; it then rises again to this steady value. This phenomenon is discussed in connexion with other anomalous activation processes observed by one of the authors (A., 1915, ii, 678; 1922, ii, 736) and an explanation is suggested on the basis of his displacement theory (cf. this vol., 515). The steady values of the anode potential at various current densities from 10^{-7} to $4{\cdot}4\times10^{-4}$ amp./cm.^{2} are recorded.

H. J. T. ELLINGHAM.

Application of electrometric methods to the study of the oxidisability of organic substances. II. G. LEJEUNE (J. Chim. phys., 1927, **24**, 482—495).—The difference of potential between two alkaline solutions of permanganate of different concentrations has been shown to be represented by the formula $\varepsilon_1-\varepsilon_2=2/3\times0{\cdot}0002T\log c_1/c_2$. The rate of change of potential in the presence of readily oxidisable organic compounds has thus been determined. The rate of change of potential does not represent the rate of oxidation of the organic compound, but there is evidently some relation between them since the phenomena observed are strictly reproducible and the qualitative classification of the different compounds studied is exactly the same as that obtained by purely chemical methods. A method for determining the potential of mixtures of cerous and ceric salts has been described. In accordance with the Nernst formula $\varepsilon=\varepsilon_0+0{\cdot}0002T\log \mathrm{Ce^{III}}/\mathrm{Ce^{IV}}$, where $\varepsilon_0=0{\cdot}059$ volt. The rate of oxidation of various sugars has been followed by the rate of change of potential of a cerous–ceric mixture in the presence the sugar. There is a proportionality between these oxidation velocities and the maximum oxidation-reduction potentials as found by Goard and Rideal (A., 1924, ii, 161) for the aldehydic sugars dextrose, galactose, arabinose, and lactose, but the ketonic sugar lævulose oxidises much more rapidly than is to be expected from its oxidation potential.

M. S. BURR.

Electrolysis of insoluble alkaline-earth compounds, and especially of barium carbonate. DONY and F. MEUNIER (Bull. Acad. roy. Belg., 1927, [v], **13**, 9—27).—Electrolysis of barium carbonate in suspension in solutions of barium chlorate and perchlorate with a mercury cathode gives better yields than the Siemens and Halske method, in which a diaphragm is employed between two inert electrodes.

H. F. GILLBE.

Theories of unimolecular gas reactions at low pressures. O. K. RICE and H. C. RAMSPERGER (J. Amer. Chem. Soc., 1927, **49**, 1617—1629).—Collision theories capable of explaining why a gas reaction which is unimolecular at high pressures can deviate from unimolecularity at low pressures are considered. In particular, using the methods of classical statistical mechanics and assuming that molecular interchange of energy occurs only at collisions, expressions are developed for the reaction rate at low pressures both on the basis of Hinshelwood's theory (A., 1926, 804) and also on the assumption that a molecule is activated when its total non-translational energy is at least ε_0, the minimum amount of energy which some particular degree of freedom must possess for reaction to occur, and it may redistribute itself between collisions. The data for the decomposition of propaldehyde (Hinshelwood and Thompson, this vol., 26) fit the theoretical curves of both the above theories equally well, and more accurate and extensive data are required for deciding between the theories.

S. K. TWEEDY.

Striated photographic records of explosion waves. C. CAMPBELL and D. W. WOODHEAD (J.C.S., 1927, 1572—1578).—An undulatory form of explosion wave, which in a tube of 15 mm. internal diameter has a wave-length of 45 mm., is characteristic of the mixture $2CO+O_2$, and of certain dilute mixtures of carbon monoxide and other gases with oxygen or with oxygen and nitrogen. The mixture $2CO+O_2$, when saturated with water vapour at ordinary temperatures, exhibits no undulations in the presence of about 6% of hydrogen. Increase of the initial pressure up to 3 atm. does not influence the length of the undulation, which is, however, directly proportional to the internal diameter of the explosion tube.

H. F. GILLBE.

Inflammability of hydrogen. IV. Influence of hydrogen selenide on the limits of inflammability of hydrogen–air mixtures. Y. TANAKA and Y. NAGAI (Rept. Aeronaut. Res. Inst., Tokyo Imp. Univ., 1927, **2**, 275—282; cf. *ibid.*, 265; this vol., 212).—Hydrogen selenide lowers the upper limit of inflammability of hydrogen–air mixtures, and it is shown that the temperature necessary for the activation of hydrogen selenide is 1750°, a value equal to that obtained for diethyl selenide; this temperature is, however, dependent on the negative part of the molecule, being 1040° for hydrogen sulphide. 2% of hydrogen selenide as compared with 1% of diethyl selenide is required to raise the theoretical flame propagation temperature of hydrogen from the initial value, 1090°, to 1750°. Both hydrogen and hydrogen selenide then behave as if they have the same flame propagation temperature, and they obey Le Chatelier's rule. Unlike diethyl selenide, hydrogen selenide also raises the lower limit of inflammability of hydrogen–air mixtures; this difference is attributed to the

smaller heat of combustion of hydrogen selenide. The addition of 4% of hydrogen selenide raised the lower limit to 12% of hydrogen, but further addition reduced it slightly. G. A. ELLIOTT.

Lower limit of inflammability of ethyl alcohol, ethyl ether, methyl*cyclo*hexane, and their mixtures. Y. TANAKA, Y. NAGAI, and K. AKIYAMA (Rept. Aeronaut. Res. Inst., Tokyo Imp. Univ., 1927, 2, 235—246).—The minimum percentage of the combustible substance when mixed with air which was necessary for inflammability (tested by a simple spark-ignition method) was measured for each of these substances and also for their mixtures. The flame propagation temperature calculated, assuming that the combustion was complete, from the results of experiments in which the compounds were used singly, was in each case about 1450°. This value is in good agreement with those of White (A., 1925, ii, 48) for some lower members of the paraffin series; the presence of the naphthene ring had therefore no appreciable influence. The compositions of the lower-limit mixtures containing two or more combustibles were in agreement (within 0·5 mol.-%) with Le Chatelier's rule. Such agreement is to be expected for substances having the same flame propagation temperature. G. A. ELLIOTT.

Effect of pressure on the limits of inflammability and the average life-period of activated molecules in combustion. Y. NAGAI (J. Fac. Eng. Tokyo, 1927, **17**, 89—105).—The effect of pressure on the limits of inflammability is explained by a consideration of the limited life-periods of the activated molecules of the combustible gas or vapour. The average life-periods of the activated molecules of methane and ethyl ether are deduced to be of the order of 10^{-8} sec., and that of carbon monoxide of the order of 10^{-9} sec. When measured in a tube of too small diameter, the effect of pressure on the limits of inflammability deviates considerably from the theoretical value, but the lack of agreement is only apparent, resulting from the difficulty in igniting the gaseous mixture at low pressure in a tube of small diameter. When the mixture is ignited in a large tube and the flame then travels through the tube of small diameter, anticipated results are obtained. Two kinds of activated carbon monoxide molecules are assumed in order to explain the inflammability of compressed carbon monoxide in the absence of water vapour. Those of the first kind either are formed by collision with molecules of water vapour, or they burn only in presence of water vapour, and they are the cause of the " steam line " in the flame spectrum. They have an average life-period of the order of 10^{-9} sec. Those of the second kind, which burn independently of the presence of water vapour, have a very short average life-period (about 10^{-10} sec.). At high pressures, the activated carbon monoxide molecules of the second kind encounter oxygen molecules, and burn, whilst at low pressures the probability of their encountering oxygen molecules while still activated decreases, owing to the lengthened free path of the molecules; consequently, carbon monoxide becomes non-inflammable.

E. S. HEDGES.

Explosibility of methane and natural gas. H. F. COWARD, G. W. JONES, C. G. DUNKLE, and B. E. HESS (Carnegie Inst. Tech. and U.S. Bur. Mines Min. Met. Invest. Bull., 1926, **30**, 1—42).—The ignition temperature of Pittsburgh natural gas is almost constant over the whole range of inflammable mixtures with air; that of methane increases, and of ethane decreases with the concentration. The time lag, and lower and upper limits of inflammability, are less than for methane. The limits can be calculated from those of the constituent hydrocarbons and the composition; the lower limit can also be obtained from the ratio between the contraction on explosion and the volume of carbon dioxide produced. The limits for upward inflammability for pure hydrocarbons are, under quasi-industrial conditions, methane 5·24—14·02, ethane 3·22—12·45, propane 2·37—9·5, butane 1·86—8·41. The speeds of uniform movement of flame in tubes of diameter 2·5 cm. in any natural gas–air mixture can be calculated from the composition of the gas and the known flame speeds in mixtures of the individual hydrocarbons and air. The behaviour of flame during the vibratory phase is similar for natural gas and methane. Pittsburgh natural gas is slightly more inflammable than methane.

CHEMICAL ABSTRACTS.

Combustion limits under high pressure of mixtures of air with inflammable gases and vapours. E. BERL and G. WERNER.—See B., 1927, 546.

Kinetics of ozonisation under the influence of α-particles. W. MUND and J. D'OLIESLAGER (Bull. Soc. chim. Belg., 1927, **36**, 339—412).—When radon is mixed with pure dry oxygen the equilibrium $3O_2 \rightleftharpoons 2O_3$ is set up. Experiments are described proving that, for a given radiation, ozone is formed at a constant rate and decomposes at a rate proportional to its concentration. The rates of both reactions are proportional to the intensity of the radiation. One molecule of ozone is produced for each pair of ions formed. S. K. TWEEDY.

Thermal decomposition of ozone. III. Temperature coefficient of reaction rate. O. R. WULF and R. C. TOLMAN (J. Amer. Chem. Soc., 1927, **49**, 1650—1664; cf. this vol., 631).—The rate of decomposition of ozone at 452·2°, 441·7°, 431·3°, 426·1°, and 420·9° Abs. was determined by a dynamic method in a new type of decomposition vessel. The activation energy is calculated, on the basis of four different reaction hypotheses, to be approx. 30,000 g.-cal. in each case. Assuming the temperature coefficient to be determined by some unimolecular process with an activation energy of 30,900 g.-cal., and neglecting the inhibiting effect of oxygen (or else assuming the inhibiting effect to be determined solely by the total pressure), the specific second-order rate of decomposition of dilute ozonised oxygen at approximately 1 atm. pressure is given by $2·04 \times 10^{20} e^{-30,900/RT}$, or, if Jahn's mechanism is assumed (A., 1906, ii, 225), by $(5·89 \times 10^{13}/C_{O_2}) T^{0·5} e^{-29,600/RT}$, an expression which holds approximately for total pressures other than 1 atm. Calculation shows that the Jahn mechanism requires more collisions between ozone molecules and oxygen atoms than could actually

occur, so that, in its original form, the theory is untenable. S. K. TWEEDY.

Unimolecular decomposition of azomethane; the adequacy of activation by collision. B. LEWIS (Proc. Nat. Acad. Sci., 1927, **13**, 546—549).—The method given by Fowler and Rideal (this vol., 114) for calculating the number of collisions with available energy for redistribution, has been applied to the homogeneous unimolecular decomposition of azomethane (Ramsperger, *ibid.*, 425). On this basis, a very conservative estimate of the number of effective internal degrees of freedom still leaves it possible to account adequately for the rate of decomposition on the basis of activation by collision. R. A. MORTON.

Velocity of decomposition of nitroacetic acid in aqueous solution. K. J. PEDERSEN (Trans. Faraday Soc., 1927, **23**, 316—328).—Nitroacetic acid decomposes in acid solution according to the equation $NO_2{\cdot}CH_2{\cdot}CO_2H \longrightarrow CH_3{\cdot}NO_2+CO_2$, and the reaction has been followed by measuring the increase in pressure of carbon dioxide. In hydrochloric acid solution the velocity coefficient decreases as the concentration of acid increases. A greater velocity coefficient is found in acetate–acetic acid buffer solutions than in hydrochloric acid, and this coefficient, 0·0316 (min.$^{-1}$ dekad. logs), is independent of changes in the hydrogen-ion concentration within the range of the acetate buffer mixtures. Thus the undissociated acid is stable in aqueous solution, and one of the three possible isomeric univalent ions is decomposed unimolecularly. From the experiments in hydrochloric acid the concentration dissociation coefficient has been determined. Its variation with the concentration of hydrochloric acid, and the effect of the addition of sodium chloride, are in agreement with the theory of complete dissociation and interionic forces. The dissociation constant in 0·1*N*-hydrochloric acid is 0·0340. The effect of a number of salts on the velocity of decomposition of the nitroacetate ion has been studied. Sodium salts and ammonium chloride produce no effect, whilst potassium salts, cæsium bromide, and hexamminecobaltic chloride cause acceleration. Most salts, however, retard the reaction, and the effect is especially marked in the case of copper salts. The curves representing these effects appear to exhibit discontinuities. No explanation can be offered of the individual salt effects.

M. S. BURR.

Does the hydrolysis of sucrose by dilute acids belong to the unimolecular group of reactions? H. COLIN and A. CHAUDUN (J. Chim. phys., 1927, 507—511).—Determinations of the rate of inversion of sucrose by 0·1*N*-solutions of sulphuric, hydrochloric, oxalic, and nitric acids shows that $(1/t) \log a/$ is a function of the time t. Hence this cannot be regarded as a simple unimolecular reaction, nor even as the resultant of n reactions of which $n-1$ are instantaneous. The result is, however, consistent with the view that the reaction is catalysed by both the hydrogen ion and the anion of the acid.

M. S. BURR.

Effect of alkali hydroxide on the oxidation of stannous chloride with air. S. MIYAMOTO (Bull. Soc. Japan, 1927, **2**, 155—160).—The rate of oxidation of alkaline solutions of stannous chloride when air is passed through is independent of the salt concentration. The influence of temperature and of rate of passage of air is small. The rate of oxidation initially increases with the concentration of free alkali, is maximal at 0·2*N*-alkali, and then slowly decreases. For alkali concentrations greater than 0·2*N* the oxidation velocity is the same as that of alkaline solutions of sodium sulphite under corresponding conditions (this vol., 525) and the same explanation holds. J. S. CARTER.

Hydrolysis of aromatic acid chlorides and the theory of induced alternate polarities. G. BERGER and S. C. J. OLIVIER (Rec. trav. chim., 1927, **46**, 516—527; cf. A., 1926, 1239).—A study of the relative rates of hydrolysis of substituted benzoyl chlorides and benzenesulphonyl chlorides indicates that the hydrolysis proceeds more readily when, according to the theory of induced alternate polarities, the negative character of the chlorine or the oxygen atom is diminished by the substituent. In the case of the substituted benzoyl chlorides, this requires for the nitrobenzoyl chlorides $p>A$, for the chlorobenzoyl chlorides $m>A$ and $m>p$, for the bromobenzoyl chlorides $m>A$ and $m>p$, and for the toluoyl chlorides $A>p$, where A, m, p are the rates of hydrolysis of benzoyl chloride itself and the appropriate m- and p-derivatives. The rates of hydrolysis at 0° in 50% acetone of the substituted benzoyl chlorides are in accordance with these requirements, with the exception that p-toluoyl chloride has a higher rate than benzoyl chloride. It is suggested that the hydrolysis takes place in two stages, viz., the combination of water with the acid chloride, and the elimination of hydrochloric acid from the additive product formed. The first stage, which determines the rate of hydrolysis, is accelerated when the negative character of the oxygen atom is decreased by the presence of a substituent, whilst the second stage, which takes place at a much greater velocity, is retarded under the same conditions.

W. J. POWELL.

Kinetic laws of homogeneous catalysis. Inner mechanism of a homogeneous catalytic reaction. E. SPITALSKY and N. KOBOSEV (Z. physikal. Chem., 1927, **127**, 129—177).—The change with time in the condition of a catalyst which is to be expected from the theory of the reversible formation of an intermediate compound between the catalyst and a reactant forms the basis for a method of testing experimentally the theory of homogeneous catalysis. It follows also from the theory that this time change will be apparent only in those reactions in which the affinity constant of the intermediate compound is large. For these reasons the catalytic decomposition of hydrogen peroxide by chromic acid has been investigated by measuring the conductivity changes during the reaction in a special type of apparatus designed for the purpose.

During the catalysis of hydrogen peroxide by chromic acid or by acidified solutions of potassium dichromate the conductivity at first decreases sharply to a value which remains approximately constant during the major part of the reaction and then returns

to its initial value as the reaction approaches completion. These changes are due to the formation and decomposition of catalytic intermediate compounds, and are, as is the catalysis itself, completely reversible, so that for each initial concentration of the substrate a definite value is obtained for the conductivity decrease and for the minimum conductivity. That the conductivity changes afford a parallel with the complicated kinetics of the reaction in dilute acid solutions is indicated by the coincidence of the maxima of the velocity of catalysis and of the velocity of the conductivity change. From the decrease of the conductivity the extent to which the hydrogen ions are used up in the formation of intermediate compounds may be calculated: the flat portion of the velocity curves represents the complete removal of the hydrogen ions, whilst the velocity maximum expresses their liberation near the end of the reaction.

The relationships have been determined at constant substrate concentration of the reaction velocity and of the conductivity decrease with (1) variation of the dichromate concentration at constant acid concentration; (2) variation of the acid concentration at constant dichromate concentration; and (3) variation in constant ratio of both the acid and dichromate concentrations. In the third case only are the reaction velocity and the conductivity decrease influenced in the same manner by the concentration changes. The nature of the curves obtained leads to the hypothesis that during the course of the reaction two intermediate compounds M_1 and M_2 are formed reversibly, which require no hydrogen ions for their formation and possess relatively small affinity constants, together with a third compound M_3 which is much more stable and requires hydrogen ions for its formation. From the initial acid and dichromate concentrations and the decrease of hydrogen-ion concentration during the catalysis the most probable nature of the more stable compound M_3 is given by the equation: $2Cr_2O_7'' + 2H_2O_2 + K^{\cdot} + H^{\cdot} = KH_5Cr_4O_{18}''$, the affinity constant of the reaction being 1×10^{13}. The courses of the conductivity curves have been calculated from this value, and agree closely with the observed curves.

The complicated kinetics of the chromic acid catalysis have been investigated mathematically in the light of the experimental data; on the flat portion of the velocity curve, where, at high concentrations of hydrogen peroxide, the more stable additive compound M_3 is but little dissociated, the catalysis is effected simultaneously by two intermediate compounds, viz., M_3 and the compound M_1, which is the active agent in the catalysis in neutral solution. Calculation of the lability constants k_1 and k_3 from a number of independent observations give the values $k_1=42$ and $k_3=5{\cdot}6$. Towards the end of the reaction, as the hydrogen peroxide concentration becomes very small, M_3 decomposes and releases the hydrogen ions; very active but short-lived intermediate compounds are then formed, and account for the sharp maximum in the reaction velocity.

From the affinity constants of M_1 and M_3, bearing in mind the possible existence of another substance M_2, the reaction velocity curves have been calculated, and agree fairly well in part with the experimental curves. H. F. GILLBE.

Increase in ionisation of weak electrolytes by complex-formation and its importance for catalytic processes. H. MEERWEIN (Annalen, 1927, **455**, 227—253).—Many organic reactions are probably ionic even in cases ("crypto-ionic" reactions) where ionisation cannot be directly measured. The theory that such reactions are accelerated by circumstances which increase ionisation (this vol., 568), and particularly by the addition of substances capable of forming large complex ions (cf. Kossel, A., 1916, ii, 243), is shown to throw light on the mechanism of many catalytic processes. In extension of Werner's term "anhydro-acids," neutral molecules which combine with a solvent increasing its acidity by forming complex anions are named "ansolvo-acids." Alkoxides of many metals give acid solutions in alcohols. Aluminium alkoxides are monobasic to sodium ethoxide and form well-defined salts, $[Al(OR)_4]M$ and $[Al(OR)_6]M_3$. Similarly salts of the acids $[B(OR)_4]H$ and $[Sb(OR)_4]H$ are obtained, whilst $[Sn(OR)_6]H_2$ gives salts $[Sn(OR)_6]HM$ and $[Sn(OR)_6]_2H_3M$, and $[Ti(OR)_6]H_2$ gives $[Ti(OR)_6]HM$ and $[Ti(OR)_6]_2H_3M$. Alkoxides of calcium, beryllium, magnesium, silicon, phosphorus, arsenic, and bismuth do not form complex acids with alcohols, although salts $[Be(OR)_4]K_2$ and $[Mg(OR)_4]K_2$ are known. Zinc benzyloxide gives an acid (?)$[Zn(OCH_2Ph)_3]H$. Glycerolboric acid and the alkali salts of aluminium hydroxide are compounds of the same type. Alcohols, being neutral, cannot be methylated by diazomethane, but in presence of one of the above ansolvo-acids they are readily attacked.

Dilute aqueous solutions of zinc chloride or bromide are neutral; in more concentrated solutions complex acids of the type $[(ZnCl_2)_m(OH)_n]H_n$ are formed. Sucrose-inversion experiments show that the hydrogen-ion concentrations of 11·2*M*-zinc chloride and of *N*-hydrochloric acid are equal. The similarity between the catalytic action of zinc chloride and that of the strong mineral acids is thus explained. For instance, the zinc chloride compound of *iso*borneol, $C_{10}H_{18}O,2ZnCl_2$, is transformed in the same way as the *iso*bornyl esters of strong acids (cf. A., 1924, i, 186), the reaction velocity depending, as usual, on the dielectric constant of the solvent. The halochromy of the zinc chloride compounds of triarylcarbinols indicates that these also are salts of strong complex acids. The catalytic effect of zinc chloride on the addition of organic acids to olefines and terpenes is explained analogously by the formation of acids of the type $[RCO_2\cdot(ZnCl_2)_x]H$. Liquid zinc chloride–acetic acids give crystalline *etherates*, $2[ZnCl_2\cdot OAc]H,C_4H_{10}O$ and $[(ZnCl_2)_2\cdot OAc]H,C_4H_{10}O$. They combine readily with camphene, giving equilibrium mixtures containing the zinc chloride compound of *iso*bornyl acetate. Comparison of the velocity of addition to camphene of the acids $[(ZnCl_2)_2\cdot OH]H$ and $[(ZnCl_2)_x\cdot OAc]H$, where x is 2, 4, and 6, indicates that, in agreement with Kossel's theory, they increase in strength in the order named. When more than 1 mol. of zinc chloride is present in a complex acid, the anion (*e.g.*, OH or OAc) is

regarded as the co-ordination centre. Many other compounds, such as magnesium chloride, zinc chlorate, sulphur dioxide, boron trioxide, and pyroboric acetate, increase the ionisation of organic acids. The most strongly acting ansolvo-acid is, however, boron trifluoride. *Boron trifluoride-acetic acid*, b. p. 59°/13 mm. (undecomp.), is as strong as sulphuric acid and gives the same halochromic colours with triarylcarbinols. It combines vigorously with pinene and camphene. It is shown by simple experiments that the strength of the halogen acids may be similarly increased (*a*) by adding metallic halides such as stannic chloride, (*b*) by forming bimolecular acids such as $[HCl_2]H$, and (*c*) by adding organic acids, the halogen acid then behaving as an ansolvo-acid, $[RCO_2 \cdot HCl]H$. H. E. F. NOTTON.

Mechanism of the catalytic decomposition of hydrogen peroxide by metallic ions. A. VON KISS and (MISS) E. LEDERER (Rec. trav. chim., 1927, 46, 453—462).—The catalytic decomposition of acidified hydrogen peroxide solutions in presence of various metallic ions has been investigated. Ions of constant valency, such as those of the alkaline-earth metals, have no catalytic influence, whilst the small acceleration of the reaction produced by cobalt, manganese, and nickel ions is ascribed to the presence of small quantities of copper or iron. The mechanism of the reaction in presence of the copper ion has been explained. The catalytic decomposition produced by the ferrous ion cannot be an ionic reaction. H. F. GILLBE.

Promoter action in homogeneous catalysis. IV. Decomposition of hydrogen peroxide by potassium dichromate accelerated by manganese salts. A. C. ROBERTSON (J. Amer. Chem. Soc., 1927, **49**, 1630—1642).—The catalytic decomposition of hydrogen peroxide by potassium dichromate, promoted by small quantities of manganous chloride, is made up of two superimposed unimolecular reactions (cf. A., 1926, 917); the reaction in presence of manganous chloride alone is autocatalytic unless all traces of alkali are removed, when it becomes unimolecular. The primary reaction is not changed in rate by the promoting reaction. An intermediate compound containing tervalent manganese is produced in an amount proportional to the amount of hydrogen peroxide used. The normal reaction: $2KCrO_4+H_2O_2=K_2Cr_2O_7+H_2O+O_2$, is probably supplanted by the rapid reaction: $2HMnO_2+4HCl+H_2O_2=2MnCl_2+4H_2O+O_2$, which occurs because of the instantaneous reaction: $2KCrO_4+2MnCl_2+3H_2O=K_2Cr_2O_7+2HMnO_2+4HCl$. Spectrographic investigations indicate that when the manganese concentration is higher (0·09*N*) the reaction involves formation and decomposition of a permanganate. The results serve to confirm earlier work. S. K. TWEEDY.

Catalytic decomposition of hydrogen peroxide by hæmin. H. VON EULER and K. JOSEPHSON (Annalen, 1927, **456**, 111—126).—In spite of the great difference in activity between catalase (*C.F.*>43,000; cf. this vol., 376) and hæmin (*C.F.* about 5) their behaviour towards hydrogen peroxide appears to be similar. Although (cf. Kuhn and Brann, A., 1926, 1215) the activity of hæmin is gradually destroyed by hydrogen peroxide, the reaction velocity in the initial stages is exactly proportional to the concentration of hæmin. In 0·02*N*- or stronger hydrogen peroxide the activity of hæmin is independent of the hydrogen peroxide concentration. In weaker solutions the activity-[*S*]-curve has been calculated using hæmin concentrations of $7-26\times10^{-6}M$. The results are in accordance with the law of mass action and yield a value for the affinity-constant (130) of the hæmin–hydrogen peroxide complex of the same order as that (40) previously obtained in the same way for catalase–hydrogen peroxide (this vol., 793). The latter complex must therefore have a very much greater velocity of decomposition. H. E. F. NOTTON.

Rate of transformation of acetylchloroaminobenzene into *o*- and *p*-chloroanilides as a measure of the catalytic power of hydrochloric acid. F. G. SOPER (J. Physical Chem., 1927, **31**, 1192—1196; cf. Åkerlof, A., 1926, 125).—The measurement of the rate of transformation of the chloroamine using potassium iodide gives too high a value for the catalytic activity of the hydrochloric acid for concentrated solutions. The true catalytic activity of the acid should be measured in the presence of substances such as acetanilide, phenol, or *p*-cresol which remove the chlorine formed in the first stage of the transformation. The catalytic activity of the hydrochloric acid given by the rate of formation of chlorine is then not proportional to the velocity coefficient of the transformation as ordinarily measured. L. S. THEOBALD.

Displacements of equilibria by substances which simultaneously act as catalytic accelerators. II. N. SCHLESINGER [with R. MALKINA-OKUN] (Ber., 1927, **60**, [*B*], 1479—1483; cf. A., 1926, 1109).—The interaction of ethyl alcohol, acetic acid, ethyl acetate, and water in the presence of hydrogen chloride, hydrogen bromide, and sulphuric acid at 100° and, in some cases, at 13° has been investigated. Mineral acids depress the equilibrium constant, the effect being proportional to the concentration of the mineral acid; hydrogen bromide is most and sulphuric acid least active. In the case of hydrogen bromide, the effect appears less noticeable as the temperature is lowered. H. WREN.

Fifth report of the committee on contact catalysis. E. E. REID (J. Physical Chem., 1927, **31**, 1121—1149; cf. Taylor, A., 1926, 365).—The literature of the subject for the years 1925 and 1926 is reviewed, prominence being given to papers on the theories of catalysis. L. S. THEOBALD.

Catalytic reactions of ethylene. H. W. WALKER (J. Physical Chem., 1927, **31**, 961—996).—The products obtained when ethylene is passed over various solid catalysts have been investigated. Ethylene is stable towards heat at 600°; at 615°, decomposition commences in a Jena glass tube. Polymerisation to a colourless and to a brown oil occurs accompanied by decomposition into acetylene, hydrogen, methane, and carbon, and by hydrogenation to ethane. Acetylene is less stable than ethylene, decomposing above 400°. Mixtures of equal quantities of acetylene

and ethylene at 600° in contact with Jena glass yield a mixture of the polymerised initial constituents. Silica gel, silica gel and borax, silica gel and calcium hydroxide, borax, calcium silicate, and zinc oxide are all inert towards ethylene up to 600°. Complete reduction by ethylene of ferric oxide, zinc oxide, and lead monoxide occurs at 500°, 800—900°, and 600°, respectively. Over the range 100—500°, ethylene is polymerised by sodium to a colourless oil and is decomposed to carbon, hydrogen, and methane. Ethane, carbides, and hydrides are also formed. With nickel at 400°, no polymerisation occurs but the ethylene is decomposed into hydrogen and acetylene. Rapid carbonisation at 400° and complete decomposition at 545° take place in presence of cobalt. No liquid polymerides are formed. Iron polymerises ethylene at 360° to a colourless oil and decomposes it slowly into carbon and hydrogen. At 425°, decomposition is practically complete. A small percentage of potassium hydroxide does not increase the polymerisation brought about by the iron. Chromium oxide does not promote activity of the iron. Increased pressure does not permit the continuous formation of liquid polymerides owing to carbon deposition. Pressure studies show that methane is produced from ethylene by fission of the two carbon atoms to yield two CH_2 groups which are subsequently hydrogenated. L. S. THEOBALD.

Oxidation of ammonia to nitrate at alkaline surfaces. K. A. HOFMANN [with K. LESCHEWSKI, W. LEMME, H. GALOTTI, K. MAYEN, and W. GUNDELACH].—See B., 1927, 600.

Decomposition of hydrogen sulphide. H. A. TAYLOR and C. F. PICKETT (J. Physical Chem., 1927, **31**, 1212—1219).—The decomposition of hydrogen sulphide on a heated platinum filament has been studied by a dynamic method at 948°, 1041°, 1138°, and 1269°. The curves obtained by plotting the amount of gas decomposed against the rate of flow show a general increase in decomposition with increased flow. The middle portions of the curves for the three lower temperatures, however, are parallel to the flow axis, showing decomposition to be independent of the rate of flow over a range which shortens with a rise in temperature. The temperature coefficient for these portions of the curves is 1·035 per 10°, and the heat of activation calculated from the Arrhenius equation is 11,750 g.-cal., which value, at these temperatures, is equivalent to the heat of evaporation of sulphur from the platinum surface.

The suggested mechanism of the reaction consists of the primary adsorption of hydrogen sulphide oriented with the sulphur atom to the platinum, a fission of the adsorbed molecule, the liberation of hydrogen and the subsequent evaporation of sulphur from the heated filament. L. S. THEOBALD.

Catalytic synthesis of hydrocyanic acid from nitric oxide and hydrocarbons. E. ELOD and H. NEDELMANN (Z. Elektrochem., 1927, **33**, 217—236).—Preliminary experiments showed that the reaction between nitric oxide and ethylene yields hydrocyanic acid in amounts which increase with rising reaction temperature. At 1000°, however, ethylene decomposes very rapidly, depositing much carbon in the reaction tube, and polymerisation products (mainly aromatic hydrocarbons) are also produced. Below 900° there is considerable production of formaldehyde. Acetylene and nitric oxide give a slightly higher yield of hydrocyanic acid than do ethylene and nitric oxide under the same conditions, but there is a greater production of polymerisation products and of formaldehyde. With methane and nitric oxide much higher temperatures were necessary to give comparable yields of hydrocyanic acid. The reaction between nitric oxide and ethylene has been investigated in detail. It was shown to be a surface reaction and various catalysts were examined, a mixture of equal parts of alumina and quartz proving most effective, and by its use the production of formaldehyde was eliminated. Mixtures of nitric oxide and ethylene with hydrogen and sometimes nitrogen were passed through a pear-shaped tube containing the catalyst heated at 900° and the amounts of hydrocyanic acid, ammonia, carbon monoxide, carbon dioxide, methane, water, hydrogen, nitrogen, and carbon produced were determined under various conditions. Increasing the proportion of ethylene in the mixture increases the yields of hydrocyanic acid, methane, hydrogen, and carbon, decreases the amounts of carbon monoxide and nitrogen, whilst the yield of ammonia increases to a maximum and then falls off. Increasing the proportion of hydrogen in the mixture increases the yield of hydrocyanic acid, and decreases the decomposition of the ethylene. With nitrogen added instead of hydrogen the formation of hydrocyanic acid is always less, and the ethylene decomposition greater. Decreasing the period of contact with the catalyst (from 1·3 to 0·7 seconds) lowers the yield of hydrocyanic acid but increases that of ammonia considerably. The decomposition of the ethylene and the yield of carbon monoxide fall with decreasing period of contact, whilst the production of water increases and that of methane is practically constant. Raising the temperature over the range 700—1000° causes a rapid increase in the yield of hydrocyanic acid, but the production of ammonia reaches a maximum at about 800° and then falls sharply to a very low value. Rise of temperature also increases the decomposition of ethylene and the production of hydrogen and carbon, but the yields of methane and carbon monoxide are practically independent of temperature above 700°. With nitric oxide, ethylene, and hydrogen in the proportions 1 : 2 : 2 at 950° with a period of contact of 1·2 seconds, the yield of hydrocyanic acid is 64·8% and that of ammonia 2·4% (calculated on the nitric oxide used).

From a detailed examination of these results it is concluded that the first stage in the reaction is the reduction of nitric oxide to ammonia, part of which reacts to form hydrocyanic acid, whilst part dissociates into hydrogen and nitrogen. Ethylene decomposes gradually giving methane, hydrogen, and carbon, but acetylene and highly unsaturate hydrocarbon residues ($CH_2{=}$ and $CH{=}$) are proba y intermediate products. The formation of hydrocyanic acid is then completed by the action of ie ammonia either on ethylene or on one of these in ermediate products. Methane and solid carbon nee

scarcely be considered in this connexion. Carbon monoxide is probably produced by the interaction of ethylene with the water vapour formed in the reduction of nitric oxide. H. J. T. ELLINGHAM.

Sintering of active copper catalysts. F. H. CONSTABLE (J.C.S., 1927, 1578—1584).—By measurements of conductivity and of surface area a study has been made of the reduction of catalytic activity and of the surface area which occurs when an active copper catalyst is allowed to oxidise in air at 210°. The reduction of surface area on sintering at 440° has also been calculated. These results, together with the influence of the decrease of surface area on the catalytic dehydrogenation of alcohol, indicate that there is a simultaneous collapse both of the centres of activity of the surface and of the coarse structure. The conclusions are reached that the theories of Taylor and of Armstrong and Hilditch attribute to the centres of activity a store of latent energy in excess of that which they actually possess, and that Pease and Constable's theories are more in accordance with the experimental facts. H. F. GILLBE.

Temperature and activity of nickel catalysts. I. F. THOREN (Z. anorg. Chem., 1927, **163**, 367—395).—The relation between the temperature and the activity of nickel in catalysing the reduction by hydrogen of ethylene to ethane, benzene to *cyclo*hexane, and oxygen to water has been studied by following the pressure within a closed vessel containing the reactants and the catalyst when the temperature is gradually raised. It is found that with rising temperature there is a series of small temperature intervals in which there are sudden rapid increases in the reaction velocity, one of which is much the greatest and can be regarded as the transition from slow catalysis to rapid catalysis. The temperatures at which these effects commence are approximately the same, independent of the nature of the reaction and of the way in which the catalyst is prepared. In some cases, the reaction velocity passes through a series of minima. If the same catalyst is used for a consecutive series of reductions of ethylene or benzene not separated by any intervals, the temperature at which rapid catalysis commences gradually falls. Keeping the catalyst in an atmosphere of hydrogen or using it for the water synthesis has the reverse effect. No complete explanation of the observed phenomena can be advanced, but it is suggested that the temperatures at which sudden increases in reaction velocity occur may correspond with some kind of transitions in the catalyst. R. CUTHILL.

Catalytic activity of metallised silica gels. I. Hydrogenation of ethylene. V. N. MORRIS and L. H. REYERSON (J. Physical Chem., 1927, **31**, 1220—1229).—The hydrogenation of ethylene by silica gels metallised with platinum, palladium, or copper has been studied by the streaming method. The first two metallised gels show marked and uniform catalytic activity over the temperature range 0—240°, a slightly diminished activity at the higher temperatures being due probably to diminished adsorption. The copper gel shows a variable activity, which is minimal at 30° and maximal at 240°. Hydride formation is suggested as an explanation of this behaviour. Catalytic efficiency decreases with an increase in the rate of streaming of the mixed gases through the catalysts, the effect being greatest with the copperised gel. The efficiency of the catalysts is inversely proportional to the partial pressure of the ethylene in the gaseous mixture. Silverised gel has no catalytic effect. L. S. THEOBALD.

Law of alternating-current electrolysis and the electrolytic capacity of metallic electrodes. J. W. SHIPLEY and C. F. GOODEVE.—See B., 1927, 633.

Poisoning of hydrogen electrodes. I. A. H. W. ATEN, P. BRUIN, and W. DE LANGE (Rec. trav. chim., 1927, **46**, 417—429).—The poisoning of the hydrogen electrode by arsenious oxide is influenced by the area and surface condition of the electrode, the presence of oxygen, the nature of the electrolyte, and the agitation of the solution. The extent of the poisoning is increased by decreasing the area of the electrode and the thickness of the platinum coating, and by increasing the rate of passage of hydrogen and the concentration of oxygen. Poisoning takes place in two stages, the first being an acute poisoning from which the electrode recovers after a short interval, and the second a permanent poisoning which increases for several days. Hydrogen sulphide and potassium cyanide have but slight poisoning action, whilst mercuric chloride at low concentrations has an influence similar to that of arsenious oxide. In order to reduce errors due to a poison, when present, it is recommended that a large electrode, coated with platinum-black, be used, that the hydrogen be free from oxygen, and that the hydrogen current be stopped immediately before taking a reading.
H. F. GILLBE.

Electro-deposition of chromium from chromic acid solutions. I. STSCHERBAKOV and O. ESSIN (Z. Elektrochem., 1927, **33**, 245—252).—25% chromic acid solutions containing various amounts of sulphuric acid or sulphates have been electrolysed with a current density of 0·15 amp./cm.^{2} and a current concentration of 0·03 amp./cm.^{3}, using a platinum anode and an iron cathode without a diaphragm. During prolonged electrolysis frequent measurements were made of the concentrations of chromic acid, C_{CrO_3}, and hydrogen ions, C_{H^+}, and of the current efficiencies of cathodic reduction, η_R, of anodic oxidation, η_O, and of chromium deposition, η_{Cr}. With pure chromic acid solutions, these efficiencies are zero, all the current being used in producing hydrogen and oxygen, and it is only in the presence of an anion other than the chromate ion that reduction occurs. With solutions containing sulphate ions, η_R is initially 100% but decreases notably during electrolysis, whilst η_O and η_{Cr}, which are initially zero, gradually increase: during this stage C_{CrO_3} and C_{H^+} decrease. Eventually, a condition is reached in which the composition of the solution is practically constant, η_R being also constant and always greater than η_O, which now increases only very slowly. η_{Cr}, which reaches a maximum just before the condition of constant composition is attained, should be equal to $\eta_R - \eta_O$: this is found to be so, if it is assumed the chromium results from the discharge of chromic ions. These effects are quantitatively the same whether the

sulphate ion is added as sulphuric acid, potassium sulphate, or chromic sulphate, but the nature of the cation has some effect on the physical character of the deposited chromium. Increasing the sulphate concentration changes the conditions in the constant composition stage, C_{CrO_3} being lowered and η_R, η_O, and η_{Cr} increased. With 14 g. of sulphuric acid per litre, the steady value of C_{CrO_3} is about 70% of its original value and the maximum η_{Cr} is about 12%. With high concentrations of sulphuric acid, η_{Cr} does not exhibit a maximum but falls gradually throughout the electrolysis. Breaking the circuit for a time produces a notable but only temporary increase in η_{Cr}. A fresh iron cathode substituted for the chromium-coated one acts similarly, but to a smaller extent. Reducing the current density had no effect except to give smoother and brighter deposits. The low values of η_R in the condition of constant composition suggest that an invisible film on the cathode is preventing reduction of chromic acid. In pure chromic acid solutions, the film is probably so continuous that only hydrogen ions can penetrate it, but its density is less when sulphate ions are present. Under such conditions, the film begins to be effective only when a notable concentration of chromic sulphate has been produced; chromium deposition increases as chromic ions accumulate. On continued electrolysis the film becomes so dense that discharge of chromic ions is also hindered, η_{Cr} falls again, and hydrogen evolution increases. The increasing denseness of the film is attributed to colloidal substances in the partly reduced solution being carried to the cathode by cataphoresis. By electrolysis with a diaphragm between the electrodes a visible cathode film is produced. In order to obtain a high current efficiency of chromium deposition, the accumulation of colloid at the cathode must be kept down; this can be achieved by using a low current concentration, by stirring the electrolyte, or by occasional interruption of the current. H. J. T. Ellingham.

Electro-deposition of chromium from chromic acid baths. H. E. Haring and W. P. Barrows.—See B., 1927, 607.

Electrolysis of copper in presence of gelatin. C. Marie and A. Buffat (J. Chim. phys., 1927, 24, 470—481).—When a solution of copper sulphate is electrolysed in the presence of gelatin the weight of copper deposited is apparently greater than corresponds with the current passed. The excess is due to a mixture (2 : 1 approx.) of gelatin with adsorbed copper sulphate. The amount is independent of the current density, but depends on the gelatin concentration of the bath. The relation between the excess weight S and gelatin concentration C may be expressed by the equation $S=KC^{\frac{1}{4}}$, where K is a constant. S appears to be approaching a limiting value in the neighbourhood of 5%. M. S. Burr.

Couple deposition of metals. R. Saxon (Chem. News, 1927, 135, 33; cf. this vol., 322).—When iron and carbon electrodes are placed in copper sulphate solution and connected outside the liquid, copper is deposited principally on the iron, but also to a smaller extent on the carbon. With copper nitrate as electrolyte, considerable quantities of colloidal ferrous and copper hydroxides are produced. Meldrum's acid-resisting metal produces less hydroxide. The effect of attaching a metal spiral to electrodes of this metal in copper sulphate solution is described.

G. A. Elliott.

Electrolytic reduction of acetone and the theory of electrolytic reduction. E. Müller (Z. Elektrochem., 1927, 33, 253—259).—Solutions of acetone in 40% sulphuric acid have been electrolysed in a diaphragm cell under various conditions and using various cathode materials (cf. Tafel, A., 1912, i, 8). The cathode potential was measured and the gaseous reduction products were collected and analysed. The current efficiency for the production of propane was determined as well as the efficiency of total cathodic reduction. Rise of temperature or increase of current density (from 0·1 to 0·25 amp./cm.^{2}) tends to increase both current efficiencies. The total current efficiency of reduction decreases with change of cathode material in the sequence, amalgamated zinc, cadmium, mercury, lead, silver, becoming zero with copper and platinum. The sequence of current efficiencies of propane formation is the same except that silver and lead are interchanged. The cathode potential, however, decreases in the order, lead, mercury, amalgamated zinc, cadmium, copper, platinum, silver, showing that the progress of reduction is determined not only by the cathode potential but also by specific catalytic effects of the different metals. Propane is the principal reduction product except at mercury cathodes. Other products are *iso*propyl alcohol and pinacone, but at mercury and lead cathodes metal alkyls are also produced and at these two metals the cathode potential is actually more negative than in the electrolysis of pure 40% sulphuric acid under similar conditions. With other metals a small depolarising effect is produced by the presence of the acetone. In the chemical reduction of acetone, propane has not been hitherto recorded as a reduction product, but it is obtained by chemical reduction with amalgamated zinc. A heavier hydrocarbon, which seems to be essentially propylene, is also produced, however, whereas electrolytic reduction gave no such product.

In a discussion of the theory of electrolytic reductions, it is suggested that the mechanism in the present case involves the formation of surface compounds according to equations such as $(CH_3)_2C(OH)_2+M+\ominus=(CH_3)_2C(OH)\ldots M+OH'$ and $(CH_3)_2C(OH)_2+2M+2\ominus=(CH_3)_2C\ldots 2M+2OH'$, where M is an atom of the cathode metal. These surface compounds are supposed to have a single electron shared between each metal atom and the acetone residue. The former compound can then react according to the schemes, $(CH_3)_2C(OH)\ldots M+\ominus=M+(CH_3)_2C(OH)'$, or $(CH_3)_2C(OH)\ldots M=M+(CH_3)_2C(OH)'$; similarly the latter gives $(CH_3)_2C$. Reaction of the former ion with a hydrogen ion gives *iso*propyl alcohol or with acetone gives pinacone and a hydroxyl ion, whilst reaction of the latter ion with two hydrogen ions gives propane. Some such mechanism is necessary in order to account for the observed specific effects of the different metals; the formation of metal alkyls can also then be explained.

H. J. T. Ellingham.

Decomposition of some organic substances by the electric spark. N. R. FOWLER and E. W. J. MARDLES (Trans. Faraday Soc., 1927, 23, 301—306).—The decomposition taking place when an electric discharge between carbon electrodes is passed through a number of organic liquids from a 25 cm. induction coil and Wehnelt interrupter, using a primary current of 8 amp., has been studied to determine the possible action of these substances in delaying detonation in the internal-combustion engine. Paraffin oil, *d* 0·82, b. p. 182—300°, benzene, aniline, dimethylaniline, and monomethylaniline all give a deposit of carbon and gases consisting mainly of hydrogen and methane with small quantities of acetylene and other unsaturated hydrocarbons. The residual liquid from the paraffin oil has a distillation range similar to that of the original liquid. In the other cases fractional distillation leaves a thick tar. The anilines give hydrogen cyanide which, after a few minutes, causes the liquid to become electrically conducting without disruption, so that the discharge ceases. No disruptive discharge can be passed through ethyl alcohol, the liquid conducting the current, but sparks pass through the vapour alone. Only a small quantity of carbon is deposited, but the gases contain a considerable quantity of carbon monoxide, and there is a distinct odour of acetaldehyde. When a 1·25 cm. spark, with a primary current of 2 amp., is passed between copper electrodes through acetylene, the spark gap, after the first flash, is bridged by fine carbon threads conducting the current. M. S. BURR.

Chemical method for the standardisation of ultra-violet light. J. E. Moss and A. W. KNAPP.—See B., 1927, 635.

Role of water in the photochemical decomposition of zinc sulphide. H. B. WEISER and A. D. GARRISON (J. Physical Chem., 1927, 31, 1237—1245; cf. Schleede, A., 1923, ii, 813; Maass and Kempf, *ibid.*, 491).—Mainly a theoretical discussion of the role of water in the photochemical decomposition of zinc sulphide. Zinc sulphide is not photochemically decomposed by ultra-violet light in the absence of water, which acts neither as a catalyst nor as a component for the synthesis of formaldehyde which reduces the sulphide (cf. Maass and Kempf, *loc. cit.*). The water plays the part of an ionising solvent for zinc sulphide and adsorbed zinc salts yielding zinc ions which, being adsorbed on the sulphide lattice, render it sensitive to light. Experiments show that soluble zinc salts containing univalent anions increase the sensitivity of the sulphide. Thus, zinc chloride can render even the unignited zinc-blende sensitive to light. Salts containing ions which are more readily adsorbed than the cations inhibit the darkening of zinc sulphide by light. The mechanism of photochemical sensitisation and stabilisation by adsorbed ions is discussed. L. S. THEOBALD.

Decomposition of silver bromide per quantum *X*-radiation. J. EGGERT and W. NODDACK (Z. Di [illegible] 222—229).—From measurements of the energy absorbed by silver bromide films from beam of mean wave-length 0·45 Å., and from the corresponding amount of silver liberated it is concluded that 10^3 silver atoms are liberated per quantum absorbed, and that in a photographic film one silver bromide particle is activated per quantum absorbed. In photographic films sensitised with calcium tungstate the density of blackening due to fluorescent light corresponds with the emission of at least thirty fluorescence quanta per *X*-ray quantum absorbed. R. W. LUNT.

Latent image. J. EGGERT and J. REITSTOTTER.—See B., 1927, 620.

System: sodium oxide–barium oxide–silica–carbon dioxide. I. Reactions in the solid state between sodium carbonate, barium carbonate, and silica. H. F. KRAUSE and W. WEYL (Z. anorg. Chem., 1927, 163, 355—366).—The evolution of carbon dioxide from a mixture of solid barium carbonate and silica when heated in a current of carbon dioxide commences at 700—750°. At a given temperature, the amount of the gas given off is approximately proportional to the logarithm of the length of time for which the mixture is maintained at that temperature. If the ratio of barium oxide to silica in the original mixture lies between 1 and 0·2, the amount of silica entering into reaction increases with increase in the relative amount present, but the amounts of the two components reacting do not approach any stoicheiometric ratio. If, on the other hand, the value of the above ratio exceeds about 2, the ratio of the reactants tends to $2BaO : 1SiO_2$. Addition of sodium carbonate to the system causes the reaction to start at about 400°. Nevertheless, conductivity measurements show that no fused eutectic is present at the beginning of the reaction. The behaviour of the mixtures Na_2CO_3–$BaCO_3$–$2SiO_2$ and Na_2CO_3–$BaCO_3$–$6SiO_2$ has been examined in detail. R. CUTHILL.

Spontaneous ignition of sodium sulphide. A. MEURICE (Ing. Chim., 1925, 9, 81—88).—Spontaneous ignition of crude anhydrous sodium sulphide in oxygen does not take place unless the material is heated locally below red heat, or when it is cooled to 100° and again exposed to a current of oxygen. Powdered, but not molten, sodium sulphide continues to burn after the withdrawal of an impinging flame. Moist oxygen or air causes the temperature of sodium sulphide to rise, but ignition does not occur. Fused sodium sulphide containing about 30% of water does not ignite, even with local heating, unless it is thereby dehydrated. CHEMICAL ABSTRACTS.

Ebullioscopic determination of some complexes. F. BOURION and E. ROUYER (Compt. rend., 1927, 185, 127—130).—The existence of the following complexes has been demonstrated ebullioscopically, and in most cases the corresponding affinity-constants have been determined: in solutions of potassium and cadmium chlorides, $K_n[CdCl_4]$ and $K[CdCl_3]$, when the former and latter salts, respectively, are in excess; in mercuric chloride and potassium bromide solutions $2HgCl_2,3KBr$ (in equimolecular solutions) and $K_2[HgCl_2]$, $[HgCl_2,4KBr]$, and $K_2[HgBr_4]$ (for non-equimolecular solutions), the last resulting from double decomposition; for equimolecular solutions of sodium acetate and mercuric chloride $2CH_3{\cdot}CO_2Na,3HgCl_2$ (probably a mixture of two

salts), and for non-equimolecular solutions a mixture of this salt and one richer in sodium acetate the composition of which was not determined. J. GRANT.

Double sulphates of the alkali and rare-earth metals. IX. Neodymium rubidium sulphates. F. ZAMBONINI and V. CAGLIOTI (Atti R. Accad. Lincei, 1927, [vi], 5, 630—636).—The system $Nd_2(SO_4)_3$–Rb_2SO_4–H_2O has been investigated at 25°. The double sulphate, $Nd_2(SO_4)_3,Rb_2SO_4,8H_2O$, is in equilibrium with solutions containing up to 4·73% of neodymium sulphate and from 1·2 to 45% of rubidium sulphate. The crystals have $a:b:c=0·3015:1:0·921$; $\beta=96°\ 40'$. R. W. LUNT.

Basic beryllium carbonate. F. TABOURY (Compt. rend., 1927, 185, 275—277).—The decomposition product at 100° of beryllium ammonium carbonate prepared by precipitation of pure beryllium sulphate with ammonia in presence of a stream of carbon dioxide has not the composition $CO_2,3BeO,5H_2O$, as is usually supposed, but contains ammonia. This is not easily washed out with a solution of carbon dioxide in water, and after 20 years the ammonia and water contents are lowered only slightly. The removal of water and of ammonia is slightly accelerated by the presence of concentrated sulphuric acid, and by washing under pressure, respectively. J. GRANT.

Action of strontium oxide and lead oxide on aluminosilicates. B. GARRE (Z. anorg. Chem., 1927, 164, 202—206; cf. Tammann and Grevemeyer, A., 1925, ii, 580).—The heating curves for mixtures of barium oxide with nepheline, orthoelase, or leucite show that an evolution of heat commences at about 435°, the effect being more pronounced if hydrated mixtures are examined. Alumina is much more readily attacked by barium oxide than is silica, although the heat of reaction is smaller, so that it seems that the extent of interaction in mixtures of solids depends not on the magnitude of the accompanying heat effects but only on the diffusibility of the reactants through the resultants. Mixtures of lead oxide with quartz, alumina, or the above silicates first evolve heat at about 710°, but with the silicates the electrical resistance of the mixtures falls suddenly above 675°, owing to the formation of fused eutectics. Lead aluminate may be obtained by heating an intimate mixture of finely-powdered lead oxide and alumina at 700° for a long time, the reaction occurring entirely in the solid state. Lead oxide attacks alumina more readily than it attacks silica. R. CUTHILL.

Samarium sulphide. W. KLEMM and J. ROCKSTROH (Z. anorg. Chem., 1927, 163, 253—256).—Heating samarium sulphate in hydrogen sulphide at 500—600° does not give a pure sulphide, some oxide always being formed. At 800—860°, however, the nearly pure sulphide, with d_4^{25} 5·82, is obtained after long heating. There are some signs of the existence of a polysulphide. R. CUTHILL.

Activation of wood charcoal by progressive oxidation in relation to bulk density and iodine adsorption. A. B. P. PAGE (J.C.S., 1927, 1476—1494).—A considerable quantity of wood charcoal of uniform quality was prepared, and portions were oxidised by heating in mixtures of oxygen and nitrogen under rigidly controlled conditions of temperature, time of treatment, and the composition and rate of passage of the oxidising gas. The bulk density of the charcoal is independent of the degree of oxidation when the latter takes place at 500°, but at higher temperatures it decreases regularly with increase of the degree of oxidation. The adsorption isotherms obtained by determining the quantity of iodine removed from benzene solutions of iodine of concentrations between 0·2*N* and 0·01*N* are mostly parabolic, the variations of the two Freundlich constants being reciprocal; with increasing oxidation the exponent at first decreases, then increases rapidly, and finally decreases slowly. The suggestion is made that the rapid variations correspond with a change in the number of attracting centres per unit surface area of the charcoal, and that the slow change is due to increase of surface area per unit weight. These views are supported by the nature of the bulk density curves. H. F. GILLBE.

Azido mixed salts. A. C. VOURNAZOS (Z. anorg. Chem., 1927, 164, 263—273).—The following white or colourless *compounds* have been obtained by the reaction in methyl alcohol or acetone solution of sodium azide and a salt: with arsenious chloride, $Na_3[AsBr_3(N_3)_3]$; with arsenious iodide, $Na_3[AsI_3,(N_3)_3]$; with zinc chloride, $[ZnCl_2,N_3]Na$; with zinc bromide, $[ZnBr_2,N_3]Na$; with zinc iodide, $[ZnI_2,N_3]Na$; with zinc cyanide, $[Zn(CN)_2,(N_3)_6]Na_6$; with zinc formate, $[Zn(HCO_2)_2,N_3]Na$; with zinc acetate, $[Zn(CH_3·CO_2)_2,N_3]Na$. In general, all the soluble azides form similar *compounds* with a great variety of zinc salts. The triple *compounds* $[Zn(NO_3)_2,4ZnCl_2,N_3]Na_4,6H_2O$, $2ZnI_2,2NaN_3,AgI$, and $PbI_2,4(ZnI_2,NaN_3)$ have been obtained. R. CUTHILL.

Hyposulphurous acid. M. BAZLEN (Ber., 1927, 60, [*B*], 1470—1479).—The following evidence is adduced in favour of the view that the compounds of aldehydes with sulphurous and sulphoxylic acids are hydroxysulphonic and hydroxysulphinic acids (cf. Raschig, A., 1926, 598) and that hyposulphurous acid is disulphinic acid, $H·SO_2·SO_2H$. The formation of the latter compound by reduction of sulphurous acid is thus readily explained and the formulation, as contrasted with that of a mixed anhydride, is in harmony with the stability of the sodium salt only in presence of an excess of alkali hydroxide. Powerful oxidising agents, such as iodine, cause rupture of the S·S linking with production of sulphate in place of the expected dithionate. Under certain conditions, manganese dioxide, potassium permanganate, or nickel oxide cause the formation of dithionic acid, which is also obtained from sulphurous acid, in alkaline solution, however, dithionate is either not obtained or produced only in subordinate amount from sulphite. Formaldehyde and sodium sulphite yield sodium hydroxymethane-sulphonate and -sulphinate, the salt thus suffering fission with addition of water in the same manner as the dithionate. Sodium hydroxymethanesulphinate and sodium hydrogen sulphite give sodium hyposulphite and

formaldehyde. The free hydroxysulphonic acids are extremely unstable, whereas the hydroxysulphinic acids are stable.

Hydroxymethanesulphonic acid is monobasic, whereas the corresponding sulphinic acid gives salts of the types, $OH\cdot CH_2\cdot SO_2X$ and $OX\cdot CH_2\cdot SO_2X$. The di-zinc salt is prepared as the trihydrate and *monohydrate* which when heated at 160—165°/vacuum afford the anhydrous *compound*; the composition of the latter compound and its stability towards heat are considered to establish that the secondary salts are formed from the primary compounds by an alkoxide reaction. This conclusion is confirmed by the observations that secondary salts do not give amino-compounds and only primary salts can be obtained from the amino-derivatives of mono-salts. Attempts to prepare secondary salts by the action of zinc oxide or calcium hydroxide on the zinc or calcium salts of the amino-compounds from aldehydesulphinic acids were unsuccessful and the preparation of anhydrous *zinc anilinomethanesulphinate* shows that the sulphoxylic acids cannot be ortho-acids. The production of a dibarium salt from the condensation product of sodium hydroxymethanesulphinate and monomethylaniline (cf. Forke, Diss., Berlin, 1923) could not be confirmed. The diformaldehydesulphoxylic acid described by Binz (A., 1918, i, 4) must be regarded as dihydroxymethylsulphone; the ready loss of one formaldehyde molecule from this compound is exactly analogous to the instability of *phenyl-α-hydroxyethylsulphone*, m. p. 52°, prepared from benzenesulphinic acid and acetaldehyde in ether.

Methanesulphinic acid is oxidised by iodine to methanesulphonic acid as final product. Hydroxymethanesulphonic acid is however converted into sulphuric acid and formaldehyde. With permanganate at 0° and in presence of magnesium chloride it gives hydroxymethanesulphonic acid. H. Wren.

Compound intermediate between vanadium sulphate, V_2O_5,nSO_3 and vanadyl sulphate, $VOSO_4$. V. Auger and C. Eichner (Compt. rend., 1927, **185**, 208—210).—The slow reduction by sulphur dioxide of a solution of a vanadic salt in sulphuric acid by sulphur dioxide gives rise to an indigo-coloured solution intermediate in composition between the vanadic and vanadyl states. It is also produced on mixing solutions containing equal proportions of the sulphates of the oxides V_2O_5 and V_2O_4. It has not been possible to isolate this vanadic vanadyl sulphate in a crystalline state, but the conditions of stability of its solution, and its absorption spectrum, have been determined. The colour is readily dispersed by acid, but is regenerated on the addition of water. he formula $HSO_4\cdot VO(OH)\cdot SO_4\cdot V(OH)_2\cdot HSO_4$ is suggested. J Grant.

Inter-relationships of the sulphur acids. H. Bassett and R. G. Durrant (J.C.S., 1927, 1401—1468).—When sulphoxylic acid is liberated by ydrolysis from sodium formaldehydesulphoxylate 1 readily decomposes into hydrogen sulphide and u pnurous acid; from this and other evidence it concluded that the hydrolysis of sulphur takes cc ding to the reaction $S_2+2H_2O\rightleftharpoons H_2S+$ S The mechanism of the decomposition of sulphoxylic acid and its bearing on the initial stage in the Wackenroder reaction are discussed. On decomposition, hyposulphurous acid yields hydrogen sulphide as well as sulphur dioxide. The colour of this compound, or an isomeride, and of other sulphur compounds, is attributed to the presence of a sulphur atom with a 10-electron sheath.

The decomposition of thiosulphuric acid may occur in three ways, expressed by the equations: $H_2S_2O_3\rightleftharpoons H_2SO_3+S$, $2H_2S_2O_3\rightleftharpoons H_2S+H_2S_3O_6$, and $2H_2S_2O_3\rightleftharpoons H_2O+H_2S_4O_5$. The decomposition of thiosulphuric acid as expressed by the first of these equations is probably bimolecular, involving a diatomic sulphur molecule. The second method of decomposition is an essential step in the Wackenroder reaction, trithionic acid being the primary thionic acid formed both in the decomposition of thiosulphates and in the Wackenroder reaction. Thiosulphates probably never decompose with the direct formation of sulphate, which is produced from trithionate. Decomposition of thiosulphates into the new *anhydroacid*, $H_2S_4O_5$, and the oxidation of the latter by methylene-blue to tetrathionic acid are described. The modes of hydrolysis and structural formulæ of the thionic acids are discussed. H. F. Gillbe.

Reaction of sulphur with aluminium and magnesium. H. Danneel and K. W. Frohlich (Z. angew. Chem., 1927, **40**, 809).—Rapid ignition of an aluminium–sulphur mixture by means of a mixture of magnesium and barium peroxide resulted in an explosive reaction. A 5 g. mixture of sulphur and magnesium, ignited by a little potassium chlorate and sulphur, shattered the jaws of a strong iron stand. A. Cousen.

Reaction between manganese salts and sodium hypochlorite in presence of certain other salts. B. E. Dixon and J. L. White (J.C.S., 1927, 1469—1476).—Sodium hypochlorite precipitates manganese almost quantitatively from a solution of a manganous salt as hydrated manganese dioxide. The presence of certain other salts, notably those of copper, cobalt, nickel, and molybdenum, causes permanganate to be the main product. A study has been made of the relationships between the time of heating, the volume of oxygen evolved, and the quantity of permanganate produced: permanganate formation practically ceases after boiling for about 3 min., by which time about one third of the total oxygen evolution has taken place. The catalytic influence of cobalt differs fundamentally from that of copper in that it is scarcely affected by hydroxyl-ion concentration, that the quantity of permanganate formed decreases as the proportion of manganous salt is increased, and that a different type of precipitate is formed, the cobalt being incompletely precipitated even on prolonged boiling. The necessary condition for the quantitative oxidation of a manganous salt to permanganate in presence of cupric salts is the neutrality of the solution, which may be maintained by a sodium carbonate–sodium hydrogen carbonate buffer solution. H. F. Gillbe.

Active iron. A. Simon and K. Kotschau [with W. Gutmann and G. Buss] (Z. anorg. Chem., 1927, **164**, 101—126).—Using 5—10 c.c. of a 0·5%

alcoholic solution of guaiacum resin per 250 c.c. of water, a blue colour is produced by $5{\cdot}6\times10^{-6}$ g. of ferrous iron in presence of hydrogen peroxide in 1 litre of neutral solution, and $6{\cdot}8\times10^{-5}$ g. in a slightly acid solution. The best results are obtained by adding the hydrogen peroxide to the mixture of ferrous salt and guaiacum solution. Light should be excluded, and appreciable amounts of acetic or hydrochloric acid interfere, whereas alkaline solutions do not give the test at all. If "ferrum redactum" is ground up in a mortar, it commences to give the benzidine and guaiacum resin reactions, ferrous hydrogen carbonate being formed by atmospheric moisture and carbon dioxide. By filtration of a suspension of the activated preparation through a membrane filter, an active liquid is obtained, but this gradually loses its activity, the activity towards benzidine and guaiacum resin being a function of the ferrous-ion concentration. The activity of the liquor in respect of the catalysed decomposition of hydrogen peroxide is scarcely different from that of the liquor obtained from untreated ferrum redactum, so that it is uncertain whether the therapeutic efficacy is improved by the grinding. By filtering a suspension of ferrum redactum in oxygen-free water saturated with carbon dioxide through a membrane-filter, a liquid results which is active, and retains its activity for weeks, even if light is not excluded, provided that it is kept out of contact with air. The effect of ultra-violet radiation is very slight so long as air is carefully excluded. It is concluded that the activity of natural waters containing iron depends on the presence of ferrous iron, and when this is oxidised the activity disappears. Cobaltous, nickelous, manganous, mercurous, and cuprous salts or the ground-up metals give, in presence of hydrogen peroxide, the benzidine and guaiacum resin reactions, whilst cadmium and zinc do not do so.

R. CUTHILL.

Precipitation of iridium from its solutions by hydrogen under pressure. V. IPATIEV and J. ANDREEVSKI (Compt. rend., 1927, **185**, 357—359).—The authors' method (A., 1926, 1219) has been extended to chloroiridate solutions at 100° and 103°. As in the case of platinum the production of metal is greatest at low concentrations, and increases with pressure, temperature, and time. Under the same conditions iridium is deposited more completely than platinum at 100°. In cases of incomplete precipitation a blue, unstable solution of colloidal iridium is produced.

J. GRANT.

[Decomposition of iron carbide by acids.] T. MILLNER (Z. anorg. Chem., 1927, **164**, 186—188).—Extrapolation of Eucken and Fried's data for the equilibrium $C+2H_2\rightleftharpoons CH_4$ (A., 1925, ii, 97) shows that the separation of solid carbon when iron carbide is treated with acids such as acetic acid is due to the inertness of the carbon rather than to the hydrogen tension on the carbide being too small for complete reduction of the carbon, as Schenck and Stenkhoff have suggested (this vol., 532). It is further probable that of the two reactions $Fe_3C+6H^{\cdot}=3Fe^{\cdot\cdot}+CH_4+H_2$ and $Fe_3C+6H^{\cdot}=3Fe^{\cdot\cdot}+C+3H_2$ the latter occurs to the greater extent with both strong acids and moderately strong acids because it involves the greater heat effect.

R. CUTHILL.

Weakening of the oxidising properties of ferric chloride on warming. M. J. GRAMENITZKI (Biochem. Z., 1927, **185**, 430—432).—The oxidation of guaiacum, and the liberation of iodine from potassium iodide, by ferric chloride are much delayed if the ferric chloride solution has been recently boiled; when kept, the cooled solution gradually regains its original oxidising activity. The effect may be due to diminution of the dissociated ferric chloride molecules on boiling; an analogy is drawn between this phenomenon and the behaviour of certain enzymes towards heat.

C. R. HARINGTON.

Production of fluorite in the electric furnace. D. C. STOCKBARGER.—See B., 1927, 600.

Preparation of boron. L. ANDRIEUX (Compt. rend., 1927, **185**, 119—120; cf. this vol., 216).—Boron may be prepared continuously by the electrolysis at 1100° of the mixture $(2B_2O_3+MgO+MgF_2)$ in a charcoal crucible which acts as anode, the cathode being an iron rod. The cathode deposit consists of boron agglomerated by the solidified electrolyte. It is ground and extracted with hydrochloric acid, and a residue of amorphous boron obtained of 92% purity. The yield is 95%.

J. GRANT.

Preparation and properties of pure silicon. R. HOLBLING (Z. angew. Chem., 1927, **40**, 655—659).—A current of hydrogen, prepared from pure zinc and pure hydrochloric acid, and exhaustively freed from all suspended matter and moisture, is passed through pure silicon tetrachloride, and the mixture of gas and vapour passed over a glowing carbon filament 0·3 mm. thick, maintained at 1000° by an electric current. The resistance of the filament increases as the temperature falls by deposition of silicon; it is not possible to prepare rods of thickness more than 4 mm. in this way, since the current necessary to give a temperature at the surface of the rod sufficient to ensure decomposition of the tetrachloride raises the internal temperature to the point at which the unchanged carbon filament unites with the silicon to form the carbide. The product has a metallic appearance, is very stable in the air, and appears to become more brittle as the temperature rises. The coefficient of linear expansion is $3{\cdot}55\times10^{-6}$/18—950°; the electrical conductivity increases with rise in temperature. Tables and curves are given for the conductivities at different temperatures.

S. I. LEVY.

Purification of cerium. L. IMRE (Z. anorg. Chem., 1927, **164**, 214—218).—If nitric acid solutions of cerium nitrate are shaken with ethyl ether, part of the cerium passes into the ether, but the accompanying impurities or cerous salts do not do so. The distribution ratio varies in a complex manner with the concentrations and with the relative proportions of the phases, but the best results are obtained if the acid concentration is about 10·0N.

R. CUTHILL.

Decomposition of phosphate rock by sulphuric acid. W. STOLLENWERK.—See B., 1927, 554.

Application of spectrum analysis to the detection of metallic impurities. E. BAYLE and L. AMY (Compt. rend., 1927, **185**, 268—270).—Small quantities of metallic impurities may be separated from large quantities of salts by electrolytic deposition from a boiling solution on the tip of an electrode which is subsequently used to obtain the spectrum of the metal. The deposition may be performed in presence of large quantities of alkali, alkaline-earth, or ammoniacal salts, and it has been possible to recover 10^{-4} mg. of copper from 0·5 g. of zinc. The sensitiveness of the method varies from 10^{-6} to 10^{-10} g. for the metals gold, silver, lead, copper, iron, cobalt, nickel, chromium, manganese, and zinc. J. GRANT.

An absolute method of quantitative analysis by emission spectra. II. E. SCHWEITZER (Z. anorg. Chem., 1927, **164**, 127—144).—The "ultimate-ray" method of determining small amounts of impurities in a substance is unsatisfactory because the intensities of the ultimate rays are largely dependent on the experimental conditions. Gerlach's method of analysis by comparing the intensity of a line in the spectrum of the impurity with that of a neighbouring line in the spectrum of the main substance both in the substance under examination and in a series of standards (A., 1925, ii, 711) has therefore been developed. It is in some cases possible to select a number of pairs of lines, one in the spectrum of the main substance and the other in that of the impurity, the relative intensities of which are comparatively insensitive to variations in the conditions of the discharge producing the spectra. If for each pair there is determined the composition of the mixture in the spectrum of which both lines are equally intense, the test-sample is analysed by ascertaining for which pair the two lines are of the same intensity. In this way it is possible to determine lead, bismuth, or cadmium in tin, and tin in lead. Where a suitable number of pairs of lines cannot be found, the spectrum of a second substance is photographed on top of the spectrum of the substance for analysis. If this auxiliary spectrum is related in a fixed manner to that of the main substance by adjusting the time of exposure so that a selected line in one spectrum has the same intensity as a selected line in the other, both spectra can be used to find suitable pairs of lines. Bismuth can be determined in lead, using as the auxiliary spectrum that of tin. R. CUTHILL.

Apparatus for gas analysis. J. N. J. PERQUIN.—See B., 1927, 591.

Hempel gas analysis apparatus without absorption bulbs. R. C. FREDERICK.—See B., 1927, 601.

Modification of the Haldane general air apparatus. R. C. FREDERICK.—See B., 1927, 600.

Gas analysis instrument based on sound-measurement. E. GRIFFITHS.—See B., 1927, 591.

Measurement of gases dissolved in water. L. DUNOYER (Compt. rend., 1927, **185**, 271—273).—An apparatus and technique for the determination of gases dissolved in water by evaporating 1—2 c.c. of it, absorbing the vapour, and measuring the pressure of a known volume of the residual gas, are described. Complete removal of the vapour is essential and absorption in phosphorus pentoxide gives more constant pressure values than condensation using carbon dioxide–acetone snow. If the water is introduced into a high vacuum, it solidifies at once, evolving most of the dissolved gas, and then evaporates slowly. The method ensures a more complete separation of the gas than that usually employed, a value of 34 c.c. of air per litre of distilled water being obtained. J. GRANT.

Evolution of mineral substances and its analytical applications. A. JOUNIAUX (Bull. Soc. chim., 1927, [iv], **41**, 905—920).—A lecture delivered before the Lille section of the Société chimique de France on May 2, 1927.

Use of yellow mercuric oxide and of metallic mercury as standards in volumetric analysis. I. M. KOLTHOFF and L. H. VAN BERK (Z. anal. Chem., 1927, **71**, 339—348).—For the standardisation of hydrochloric acid with yellow mercuric oxide 1 g. of the oxide is dissolved in a warm solution of 20 g. of neutral potassium bromide in 25 c.c. of water and the liquid is titrated with the acid using dimethyl-yellow or methyl-orange as indicator. The results are within 0·1% of those obtained with borax. As mercury can be prepared in an exceedingly pure condition by distillation in a vacuum it forms a useful standard for thiocyanate solutions instead of silver. Provided the temperature of the solution during titration is kept below 15° the error is less than 0·02%, but is increased by working at higher temperatures. This may be allowed for by working with solutions saturated with mercuric thiocyanate at the temperature of titration. A. R. POWELL.

Precise volumetric analysis. III. Standards for alkaline solutions. K. O. SCHMITT (Z. anal. Chem., 1927, 71, 273—290; cf. this vol., 329).—For the standardisation of alkali hydroxide solutions pure oxalic acid dihydrate or potassium tetroxalate give equally accurate results. Both compounds should be recrystallised from water in small crystals and dried at the ordinary temperature. The tetroxalate is made by mixing potassium oxalate (1 mol.) and oxalic acid (3 mol.) solutions at 100° and cooling rapidly. Phenolphthalein must be used as indicator in both cases. Neutral calcium oxalate free from acid or basic salts is obtained by treating oxalic acid solution with neutral calcium chloride solution. The hydrochloric acid liberated by the oxalic acid can then be used for standardising an alkali hydroxide solution using methyl-orange or dimethyl-yellow as indicator. A. R. POWELL.

Determination of moisture by the volatile solvent method. J. M. JONES and T. MCLACHLAN.—See B., 1927, 591.

Detection of chlorides in mercury oxide. C. J. W. FERREY.—See B., 1927, 600.

Colorimetric determination of perchlorate in saltpetre. O. S. FEDOROVA.—See B., 1927, 600.

Volumetric determination of iodides. A. J. JONES.—See B., 1927, 554.

Apparatus for the [collection of ammonia in the] determination of nitrogen. R. KATTWINKEL (Chem.-Ztg., 1927, **51**, 568).—The bulb trap used above the distillation flask to catch any spray is sealed directly to the condenser so that the vapours pass upwards from the distillation flask through the trap, then downwards through a three-bulb condenser the lower end of which passes through the outer wall and downwards to the collecting flask. The top of the condenser tube is provided with a glass stopper to allow the inside to be rinsed out after the distillation is finished. A. R. POWELL.

Rapid determination of gaseous hydrogen phosphide in a mixture. M. WILMET (Compt. rend., 1927, **185**, 206—208).—The colour, weight, and composition of the precipitate obtained according to Lemoult's equation $PH_3+3HgCl_2=P(HgCl)_3+3HCl$, are variable. The ratio of the volume of the gaseous hydrogen chloride, however, to that of the reacting phosphine is constant, whatever the nature of the precipitate. Consequently, an excess of mercuric chloride is shaken with distilled water and the sample of gas (100 c.c.), and the acid produced is titrated with 0·1*N*-sodium hydroxide solution (*n* c.c.), with methyl-orange as indicator, after removal of the precipitate by filtration. The corresponding volume of phosphine at 15° and 760 mm. pressure is 0·784*n* c.c. For less than 0·5% of phosphine by volume the determination is made by comparison with standard solutions, and 1 part in 70,000 parts may be determined. The standards are stable in the dark for 2—3 days. J. GRANT.

Determination of sulphur [in coal]. H. TER MEULEN.—See B., 1927, 545.

Determination of sulphate by the palmitate method. J. ZINK and F. HOLLANDT (Z. anal. Chem., 1927, **71**, 386—388; cf. A., 1914, ii, 670, and Bahrdt, B., 1927, 238).—The palmitate method for the determination of sulphate in water gives sufficiently accurate results for most purposes without previously removing the lime and magnesia as advocated by Bahrdt. A combined hardness and sulphate test is carried out as follows. Two separate 100 c.c. portions of the water are neutralised with 0·1*N*-hydrochloric acid using methyl-red as indicator, a small excess of acid is added to both and 5 c.c. of 0·1*N*-barium chloride solution to one portion only, and, after boiling, cooling, and neutralising with sodium hydroxide, both are titrated with the palmitate solution. If *a* c.c. of the latter are consumed by the portion without barium chloride, *b* c.c. by the portion with barium chloride, and *c* c.c. by 5 c.c. of barium chloride, then $a+c-b$ c.c. of palmitate solution correspond with the sulphate content of the water and *a* c.c. with the hardness. A. R. POWELL.

Thiocarbamide as an impurity in thiocyanates. T. S. PRICE and J. W. GLASSETT.—See B., 1927, 600.

Absence of stratification and rapidity of mixing of carbon dioxide in air samples. T. M. CARPENTER and E. L. FOX (J. Biol. Chem., 1927, **73**, 379—381).—A mixture of carbon dioxide and air was kept in a long sampling tube in a vertical position. Samples withdrawn from the same end of the tube on successive days were of constant composition; no stratification had therefore taken place. After introduction of carbon dioxide into the bottom of such a tube, with avoidance of mechanical disturbance, diffusion was complete within 1·5 hrs.

C. R. HARINGTON.

Quantitative microscopic analysis [of rocks]. H. L. ALLING and W. G. VALENTINE (Amer. J. Sci., 1927, **14**, 50—65).—To determine the actual percentages of the various minerals in a rock the areas of the fields occupied by them in a microscopic section are traced by means of a camera lucida on a circular area of 50 sq. in. The sum of the areas of every constituent is then measured by means of a planimeter and from a knowledge of the chemical composition of the various minerals and of the complete analysis of the rock the proportion of every mineral present can be calculated. The possible sources of error are discussed and various typical results are given and compared with those obtained by other authors on similar rocks. A. R. POWELL.

Determination of alkalis in ores, clays, and refractory materials. J. CIOCHINA.—See B., 1927, 605.

Determination of sodium nitrite. F. A. HOEG.—See B., 1927. 600.

Extension of the use of borax in acidimetry. T. MILOBEDSKI and H. KAMINSKA (*Bull.* Soc. chim., 1927, [iv], **41**, 957—960).—The compound $Na_2B_4O_7,10H_2O$ is obtained in the pure state and protected against efflorescence and carbon dioxide. It can then be used as a substitute for anhydrous sodium carbonate when standardising acids, methyl-red being used as an indicator. F. S. HAWKINS.

Volumetric determination of calcium and ferrocyanide ions. T. GASPAR Y ARNAL (Diss., Madrid, 1923).—Calcium can be completely and rapidly precipitated in the presence of strontium and barium from a dilute solution containing 50 vol.-% of alcohol by the addition of standard potassium ferrocyanide solution; a dilute solution of ammonium molybdate, acidified with acetic acid, is used as an external indicator.

CHEMICAL ABSTRACTS.

Analysis of fluorspar. BRAUER and RUTHSATZ (Chem.-Ztg., 1927, **51**, 618—619).—Drawe's method (*ibid.*, 1925, **50**, 497, 623) is satisfactory. When the mineral contains barium sulphate, this may be decomposed on boiling with soda, and account must be taken of the barium thus brought into solution.

S. I. LEVY.

Analysis of calcium nitrate. J. M. MCCANDLESS.—See B., 1927, 637.

Determination and separation of rare metals from other metals. IX. Quantitative separation of beryllium and aluminium. L. MOSER and M. NIESSER (Monatsh., 1927, **48**, 113—121). Previous unsatisfactory methods for separating beryllium and aluminium are reviewed, and the principles of a possible separation are discussed. The reagent now employed is an ammonium acetate solution,

saturated in the cold and containing 3% of pure tannin. This gives with an aluminium sulphate solution a brown precipitate of aluminium hydroxide and adsorbed tannin, which, unlike aluminium hydroxide alone, is easily soluble in dilute acids; the reagent may be used for the detection of aluminium, having a sensitivity of 1 : 5000. With beryllium sulphate solutions the reagent gives no precipitate, even on prolonged boiling; since solutions of the chloride or the nitrate give slight precipitates, it is necessary to convert the metals into sulphates before separation. As freshly-precipitated and washed beryllium hydroxide dissolves rapidly in the reagent, the beryllium is considered to react chemically to form a soluble complex salt. For the separation of beryllium and aluminium, a solution of the sulphates is diluted with hot water and the ammonium acetate and tannin solution, heated at 80°, is added. On boiling, the aluminium is quantitatively removed in the precipitate, which contains no beryllium. The tannin is removed by oxidation with nitric acid; residual traces of organic substances have no influence on the determination of either metal.

E. W. WIGNALL.

Colorimetric determination of traces of magnesium. I. M. KOLTHOFF (Biochem. Z., 1927, **185**, 344—348).—Addition of titan-yellow to an alkaline solution containing small amounts of magnesium produces a red colour, the reaction being specific for this metal. By this means 0·2 mg. per litre of magnesium can be detected, and 0·4—4·0 mg. per litre determined colorimetrically. The reaction cannot be used in presence of aluminium and zinc salts.

C. R. HARINGTON.

Colour reaction of magnesium. W. J. PETRASCHENJ (Z. anal. Chem., 1927, **71**, 291—297).—When a neutral solution of a magnesium salt is treated with a 0·1*N*-solution of iodine which has been almost decolorised by addition of a 0·2*N*-solution of sodium hydroxide a deep red adsorption complex of magnesium hydroxide is precipitated. The reaction is perceptible in magnesium salt solutions as dilute as 0·0005*N* and the presence of the alkaline earths has no disturbing action. Ammonium, cobalt, and manganese salts interfere. A. R. POWELL.

Determination of small quantities of zinc in aluminium. W. BOHM.—See B., 1927, 605.

Separation and determination of metals by means of 8-hydroxyquinoline. IV. Cadmium. R. BERG (Z. anal. Chem., 1927, **71**, 321—331; cf. following abstract).—The cadmium compound with 8-hydroxyquinoline is precipitated in solutions containing sodium acetate or tartrate under conditions similar to those described already for the zinc compound. The precipitate contains $2H_2O$, but, after drying at 100°, it consists of $Cd(C_9H_6ON)_2,1{\cdot}5H_2O$ which becomes anhydrous at 130°. As the cadmium compound is readily soluble in hot 10% acetic acid, whereas copper compound is insoluble in this [illegible] copper may be separated from cadmium in 10% acetic acid and the cadmium recovered from the [illegible] by neutralising with sodium carbonate [illegible] more of the reagent. For the separation of cadmium from mercury the latter is converted into cyanide by addition of potassium cyanide and the cadmium precipitated from the feebly acid acetate solution by means of 8-hydroxyquinoline. From the heavy metals cadmium is separated by double precipitation in alkaline tartrate solution. A. R. POWELL.

Salts of the halogen acids of bismuth and cadmium with organic bases and their analytical application. I. R. BERG and O. WURM (Ber., 1927, **60**, [*B*], 1664—1671).—Cadmium may be determined by treating a solution of the metal in dilute sulphuric acid with sodium tartrate followed by a solution of β-naphthaquinoline in 0·5*N*-sulphuric acid, a few drops of dilute sulphurous acid, and finally potassium iodide solution, whereby the salt $(C_{13}H_9N)_2H_2[CdI_4]$ is precipitated. The precipitate is washed with a solution of β-naphthaquinoline sulphate and potassium iodide in water, and decomposed by ammonia or sodium hydroxide; the solution is acidified with hydrochloric or sulphuric acid and titrated with 0·1*N*-potassium iodate solution. The determination of cadmium may be effected in the same manner in presence of relatively large amounts of zinc; the latter metal is determined by precipitation from the filtrate with 8-hydroxyquinoline. Its separation from cobalt, nickel, manganese, ferrous iron, chromium, aluminium, and magnesium is similarly effected. In the separation of cadmium from tin and antimony a larger proportion of sodium tartrate (or ammonium oxalate) is necessary.

In the determination of bismuth, the solution, slightly acidified with nitric or sulphuric acid, is treated with an excess of 8-hydroxyquinoline dissolved in 0·2*N*-sulphuric acid followed by potassium iodide until the precipitated salt, $(C_9H_7ON),H[BiI_4]$, collects together. The precipitate is washed with an acid solution containing 8-hydroxyquinoline, potassium iodide, and a little hydrazine sulphate, dissolved in acid, and titrated with potassium iodate solution. The method is suitable for the separation of bismuth from the other metals except mercury, silver, lead, and thallium. Hydrochloric acid in considerable concentration is harmful. In the presence of cupric and ferric salts pyridine must be added. A large excess of tartaric acid is required if antimony or tin is present. H. WREN.

Determination of lead and ferrocyanide ions by Fajans' method. R. BURSTEIN (Z. anorg. Chem., 1927, **164**, 219—222; cf. Fajans and Wolff, A., 1924, ii, 776).—Potassium ferrocyanide can be titrated with lead nitrate, using a 0·4% solution of sodium alizarinsulphonate as indicator, the colour change at the end-point being from yellow to red. The most suitable concentration of the nitrate solution is 0·03—0·015*N*. Lead may be determined by adding excess of ferrocyanide and titrating back the excess. Fajans' adsorption method of titration can be used successfully only if the anion of the salt to be determined forms a sparingly soluble salt with the heavy metal cation, which is less soluble than the salt of the heavy metal cation and the dye anion, this also being sparingly soluble and different in colour from the original solution. R. CUTHILL.

Quantitative analysis of a mixture of rare earths. E. DELAUNEY (Compt. rend., 1927, **185**,

354—357).—The variation in size of the absorption-bands of solutions of neodymium, praseodymium, and a mixture of these elements, in neutral and in nitric acid solutions, has been plotted against the thickness of liquid used. Since Beer's law is obeyed, the strength of an unknown solution (X) may be determined from the thickness (e) of a solution of known concentration (C) required to produce an effect equivalent to the thickness E of the former. Thus, $X=CE/e$. The error is less than 0·05%. By means of the X-ray examination of dysprosium rare-earth fractions (A., 1925, 822) the high magnetic susceptibility of this element has been confirmed.

J. GRANT.

Separation and determination of metals by means of 8-hydroxyquinoline. V. Aluminium. R. BERG (Z. anal. Chem., 1927, 71, 361—380).—The slightly acid solution of aluminium salt is treated with 3—5 g. of sodium acetate and a slight excess of a 2% alcoholic solution of 8-hydroxyquinoline. After heating at 60—70° the greenish-yellow, crystalline precipitate of $Al(C_9H_6ON)_3$ is collected on a porous glass filter crucible, washed with hot water, and either dried at 110° and weighed (5·87% Al) or dissolved in dilute hydrochloric acid and the 8-hydroxyquinoline content determined bromometrically. This procedure serves to separate aluminium from magnesium and the alkaline earths. Aluminium is also precipitated by the reagent from ammoniacal (but not from caustic alkaline) tartrate solutions as follows: Sufficient tartaric acid to keep the aluminium in solution is added followed by 5—10 g. of ammonium chloride, ammonia until neutral, and a 2% alcoholic solution of the reagent until the supernatant liquid is coloured orange. Copper, cadmium, and zinc are separated from aluminium by precipitation with the same reagent in tartrate solutions containing sodium hydroxide the filtrate is acidified and the aluminium precipitated as above after addition of ammonia.

A. R. POWELL.

Potassium permanganate as an acidimetric standard. T. HECZKO (Z. anal. Chem., 1927, 71, 332—338; cf. Tananaev, A., 1925, ii, 440).—Tananaev's method is subject to error due to the large amount of ammonium salt used and to the danger of a small quantity of the liberated ammonia being oxidised to nitric acid. The following procedure is recommended: A measured amount of permanganate solution previously standardised against oxalic acid is treated with a slight excess of sulphuric acid and with 3—4 times as much hydrogen peroxide as is demanded by the equation: $2KMnO_4+3H_2SO_4+5H_2O_2=K_2SO_4+2MnSO_4+8H_2O+5O_2$. After complete decolorisation has occurred, 0·5 g. of ammonium sulphate is added and the solution titrated with potassium hydroxide slightly beyond the end-point with methyl-red; the titration is then finished with a few drops of the sulphuric acid solution and a correction applied for the acidity of the peroxide used. The results are within 0·2% of those obtained with sodium carbonate.

A. R. POWELL.

Detection of traces of iron in combustible volatile substances. E. KAHANE (Ann. Chim. anal., 1927, [ii], 9, 196—198).—The ammonium thiocyanate reaction for iron is most sensitive and at the same time specific if the material to be examined is first incinerated or evaporated, then calcined in a porcelain crucible, the residue cooled, moistened with 1 drop of a 50% solution of ammonium thiocyanate, and 1 drop of 10% sulphuric acid added. The liquid becomes rose-coloured, but the reaction is specific for iron only if the ash particles themselves are coloured. In such a delicate reaction it may be necessary to take precautions against dust. 0·01 μg. of iron was thus detected.

D. G. HEWER.

Determination of ferrous iron in silicates. L. A. SARVER.—See B., 1927, 557.

Determination of tin by "cupferron." Separation from antimony, arsenic, lead, and zinc. A. PINKUS and (MLLE.) J. CLAESSENS (Bull. Soc. chim. Belg., 1927, 36, 413—433).—An improved method of determining stannous and stannic tin by precipitation with cupferron is outlined (cf. Pinkus and Belche, this vol., 639). The method enables this metal to be quantitatively precipitated in presence of quinquevalent antimony, arsenic, lead, and zinc, which may be determined in the filtrate by the usual methods. The method may also be applied in presence of certain other metals.

S. K. TWEEDY.

Liquid amalgams in volumetric analysis. VIII. Oxidimetric determination of tin and copper by bismuth amalgam. K. SOMEYA (Sci. Rep. Tohoku Imp. Univ., 1927, 16, 515—520).—Quadrivalent tin salts can be determined accurately by reducing to the bivalent salt with bismuth amalgam and hydrochloric acid, and titrating with permanganate. The acidity must be between 5N and 12N and the mixture must be shaken for ten minutes at 45°. Phosphates, some sulphates, and chlorides with the exception of sodium or ammonium chlorides have no influence on the accuracy of the method. Cupric salts can be determined in the same way, provided the acidity is between 7N and 10N.

F. S. HAWKINS.

Reduction of stannic chloride by metals. J. W. APPLING and J. H. REEDY (J. Chem. Education, 1927, 4, 527—531).—The solution is concentrated to 10 c.c., 5 c.c. of 6M-hydrochloric acid are added, and the solution is heated just below the b. p. for 3—4 min. with 10 mg. of aluminium wire; any metallic tin is dissolved in concentrated hydrochloric acid and filtered into mercuric chloride solution, which detects 0·01 mg. in 10 c.c.

CHEMICAL ABSTRACTS.

Determination of titanic acid in refractory earths. L. LEMAL.—See B., 1927, 602.

Determination of vanadium in iron minerals and rocks. V. A. SILBERMITZ and L. V. ROZHKOVA.—See B., 1927, 559.

Liquid amalgams in volumetric analysis. IX. New determinations of vanadium and tungsten. K. SOMEYA (Sci. Rep. Tohoku Imp. Univ., 1927, 16, 521—529).—Vanadium, present as vanadic acid, is determined by reducing it to the bivalent state by zinc amalgam and mineral acid of concentration 0·5—4N, adding excesses of iodine, sodium hydrogen carbonate, and sodium arsenite, and titrating

back with standard iodine solution. Another method of determination is by reducing the vanadate to the bivalent state with lead amalgam and hydrochloric acid stronger than 9·5*N*, oxidising to the quadrivalent state with copper sulphate, and titrating with dichromate. Sexavalent tungsten is determined by reducing to the tervalent state with lead amalgam and titrating with copper sulphate. F. S. HAWKINS.

Determination of tantalum by *X*-ray spectroscopy. G. VON HEVESY and J. BÖHM (Z. anorg. Chem., 1927, **164**, 69—80).—The tantalum oxide content of various minerals has been determined by adding erbium oxide until a certain line in the *X*-ray spectrum of one element is of the same intensity as another line in the spectrum of the other element, and then finding the ratio in which the pure oxides must be mixed to give the same result. In general, the minerals need not be opened up. The most suitable comparison lines for most of the elements between sodium and uranium are given.

R. CUTHILL.

Determination of the precious metals in ores. G. LUNDE.—See B., 1927, 605.

Thermostat and observation tubes for polarimetric work. T. S. PATTERSON (J.C.S., 1927, 1717—1720).—A polarimeter tube having a vertical side tube is placed in position in a thermostat, in the sides of which two pieces of brass tubing are fixed in such a manner that their ends may be cemented to the ends of the polarimeter tube, with glass discs in between. In order to prevent the condensation of moisture on the end plates when the apparatus is used at a low temperature, a current of dry air is allowed to flow through the brass tubes.

H. F. GILLBE.

Thermoregulator. S. C. COLLINS (J. Physical Chem., 1927, **31**, 1097—1098).—The thermoregulator is operated directly by an alternating current of 110 volts, the heating effect being produced by the passage of the current through the dilute salt solution of the bath itself. The differential expansion of ether vapour and air forms the basis of the sensitive member, and the maximum temperature variation at low temperatures is not greater than 0·02°. The regulator can be used up to 68°.

L. S. THEOBALD.

Simple colorimeter. R. C. FREDERICK (Analyst, 1927, **52**, 469).—Two colourless glass tubes, 3 mm. apart, to which glass discs have been attached, are connected by side tubes at their lower ends to two adjustable glass reservoirs which can be moved up and down by sliding cradles on metal rods, with fine adjustments by screws. An adjustable mirror reflects light through the cylinders and the colour images are thrown on an upper mirror. The standard and sample solutions are poured into the respective reservoirs which are moved up and down until an exact match is obtained, and the ratio is determined y reading the scale on the back of the instrument, e capacity of each cylinder being such that 100 c.c. o solution reaches the 100 mark on the scale.

D. G. HEWER.

Evolution of gases from hot quartz vessels. W. BILTZ and H. MÜLLER (Z. anorg. Chem., 1927, **163**, 297—301).—Heating certain quartz bulbs in which the pressure had been reduced to a few thousandths of a mm. at temperatures above about 600° caused an appreciable and continuous increase in the internal pressure, in spite of the fact that the vessels had previously been heated in a vacuum in the usual way, and that steps were taken to prevent diffusion. The magnitude of the effect depended to some extent on the nature of the gas used for heating in the blowing of the bulbs. Where a mixture of hydrogen and acetylene had been used for this purpose, a dark sublimate appeared on the inner wall of the bulb, probably originating in some dissolved carbon-containing gas. By keeping such a bulb for a long time at 1000° alternately evacuated and filled with oxygen, it could temporarily be improved. It therefore seems that quartz is able to take up gases and retain them very tenaciously.

R. CUTHILL.

Simple automatic mercury still. H. L. BRONSON (J. Opt. Soc. Amer., 1927, **14**, 517—518).—A simple still is described that will distil at the rate of 110 g. of mercury per hr. for three days without attention. The power consumption is 25 watts.

R. W. LUNT.

Apparatus for the semi-micro-determination of mol. wts. by the ebullioscopic method. E. SUCHARDA and B. BOBRANSKI (Chem.-Ztg., 1927, **51**, 568).—The apparatus consists of a small bulb to which is sealed at its upper end a horizontal undulating tube connected with a funnel in which is sealed a small test-tube of mercury into which the thermometer dips. The vapour from the liquid heats the mercury to a constant temperature and then passes back along another tube, connected with a reflux condenser, into the boiling bulb again. To carry out a determination the solvent (4—5 c.c.) is boiled gently in the bulb and the mercury tube is heated gently until the vapours just cease to condense on the outside; in a further 5—7 min. the whole apparatus is at equilibrium and the temperature of the mercury is read. Heating of the boiling bulb is continued and a weighed quantity of the substance the mol. wt. of which is required is dropped down the reflux tube into the liquid. After a further 5 min. the rise in temperature of the mercury is read to 0·001° and the mol. wt. calculated as usual.

A. R. POWELL.

Apparatus for physical or chemical experiments at various temperatures under liquid pressures of 15,000 kg./cm.^{2} J. BASSET (Compt. rend., 1927, **185**, 343—345).—The apparatus consists essentially of a high-power piston-pump connected by a narrow tube with a reaction chamber furnished with a support for a crucible, and also with insulated electrodes for the measurement of conductivity, or for heating or electrolysis of the reaction mixture, under pressure. An air-tight system of jointing is employed, and the apparatus has been used safely over a range of pressures up to 15,000 kg./cm.^{2}, the pressure being variable to within a few hundred kg.

J. GRANT.

Sonic interferometer for liquids. J. C. HUBBARD and A. L. LOOMIS (Nature, 1927, **120**, 189).—An interferometer, which is in many respects the

sonic analogue of the Perot–Fabry interferometer, is described. The instrument is capable of measuring the velocity of compressional waves in small quantities of liquids with an accuracy of 1 in 10^3; corrections for the elasticity of the vessel are eliminated. Values of the velocity of sound waves at various temperatures in water, sodium chloride solutions, mercury, carbon disulphide, and chloroform are tabulated. The results lead to a method for calculating the number of degrees of freedom, and consequently the association of molecules in the liquid state. A. A. ELDRIDGE.

Apparatus for determining high m. p. R. ANSCHUTZ (J. pr. Chem., 1927, [ii], **116**, 291—292).—A tall cylindrical copper air-bath with mica windows is figured. The bottom is protected by a copper flame spreader. The thermometer and a stout asbestos inner jacket depend from the cover, which is removable. H. E. F. NOTTON.

Perforated extraction apparatus for heavy and light liquids. M. WAGENAAR (Chem.-Ztg., 1927, **51**, 528).—For the extraction of a solid with a light liquid such as ether or benzene the vapours pass up the central tube of the extraction column and condense at its upper end, the drops of liquid falling into a funnel at the top of a narrow tube which enters the outer mantle of the apparatus at the lower end. The solid to be extracted is placed on a perforated plate in the upper part of this mantle so that the hot liquid passes upwards through it and overflows at the top back into the distilling flask. For extractions with heavy liquids the tube through which the vapour enters the extraction column is bent at right angles at the top, so that the condensed vapours fall down the sides of the outer mantle and percolate downwards through the mass to be extracted, which is placed on a perforated plate halfway down the column. The liquid below the plate overflows back into the flask through a tube leading from the bottom of the mantle up through the centre tube to a point just below the level of the solid on the plate.
A. R. POWELL.

All-glass gas circulating apparatus. W. S. FUNNELL and G. I. HOOVER (J. Physical Chem., 1927, **31**, 1099—1100).—A pump capable of circulating dry gases in a closed system over a wide range of pressures is described. The essential feature is a glass piston filled with soft iron wire actuated in a length of glass tubing by means of two solenoids.
L. S. THEOBALD.

Relationship between Chinese and Arabic alchemy. J. R. PARTINGTON (Nature, 1927, **120**, 158).—Although Stapleton, Azo, and Husain (Mem. Asiatic Soc. Bengal, 1927, **8**, 405) regard Chinese alchemy of 200 B.C. as well established, the author considers this unproved. A. A. ELDRIDGE.

Mineralogical Chemistry.

Atmospheric ozone and solar variability. H. H. CLAYTON (Nature, 1927, **120**, 153—154).—The monthly means of the values obtained by Dobson, Harrison, and Lawrence (this vol., 439) for the amount of ozone in the earth's atmosphere at Oxford show an inverse relation to the monthly means of solar radiation, as measured by the Smithsonian Institution, and to Wolfer's sunspot numbers. The correlation coefficient are, respectively, $r=-0{\cdot}54\pm0{\cdot}11$ and $r=-0{\cdot}62\pm0{\cdot}09$. A. A. ELDRIDGE.

Helium in Canada. R. T. ELWORTHY.—See B., 1927, 554.

Occurrence of helium in oil-well gases. D. BUTESCU and V. ATANASIU.—See B., 1927, 580.

Seasonal variation in inorganic nitrogen compounds in the water of Lake Castelgandolfo. S. CAMPANILE (Atti R. Accad. Lincei, 1927, [vi], **5**, 705—711).—The inorganic nitrogen content (almost entirely nitrates) in the water of Lake Castelgandolfo reaches a maximum in January and a minimum in August. This variation can be accounted for by the use made of the nitrates by the plankton population (the growth of which is very abundant during the early summer months), which gradually consumes the nitrates produced by animal and vegetable decay during the winter. In the deep central waters of the lake the plankton growth is smaller and hence the amplitude of the variation in the inorganic nitrogen content is smaller than the corresponding amplitude of the variation for the shore water. E. A. LUNT.

Quantitative microscopic analysis [of rocks]. H. L. ALLING and W. G. VALENTINE.—See this vol., 846.

Composition and structure of meteoric iron from Tamentit. Oxidation of meteoric iron at a high temperature. A. LACROIX (Compt. rend., 1927, **185**, 313—317).—The structure of the meteoric iron previously described (*ibid.*, 1927, **184**, 1217) has been determined. In particular, regions of colour due to parallel bands of thin taenite, in bands of camacite, or formed from grains of camacite surrounding small round grains of taenite, have been noted. Grains of schreibersite surrounded by large grains of pyrrhotite were also observed in the camacite. Analysis showed the presence of iron (91%), nickel (8·4%), and traces of cobalt, manganese, phosphorus, sulphur, carbon, and silicon. Oxidation in the oxygen–acetylene flame at 1580°, and examination of the nickel content of the magnetic oxide, supports the author's theory that the chondrites are derived from the same magma in which the proportion of the metals is fairly constant, the elements being partly or totally oxidised. The nickel concentrates in the last portions of iron remaining in the metallic state. J. GRANT.

Amphibole grunerite of the Lake Superior region. S. RICHARZ (Amer. J. Sci., 1927, [v], **14**, 150—154).—Analysis of fresh grunerite, from Mt. Humboldt, Michigan, after separation of small amounts of calcite and magnetite, gave: SiO_2 48·00,

Al_2O_3 1·02, Fe_2O_3 1·14, FeO 39·20, MnO 0·66, CaO 1·31, MgO 4·06, K_2O 0·19, Na_2O 1·06, H_2O (over 110°) 1·71, total 98·88; d 3·44. The material is light-grey with a yellowish tingo and forms small laths. Extinction-angle 14—15°, 2V large, negative, α 1·666, β 1·684, γ 1·700. Compared with the original grünerite from France, this shows less FeO and more MgO, with correspondingly lower values for the refractive indices. L. J. SPENCER.

Orthite from Arendal (Norway). R. LLORD Y GAMBOA (Anal. Fis. Quím., 1927, **25**, 216—229).—The composition of orthite, especially as regards the occurrence of rare elements, appears to vary considerably with the locality. Analysis of a dark brown mineral (d 3·22) from Arendal (Norway) gave the following results: SiO_2 36·92, Fe_2O_3 10·70, FeO 6·33, MnO 1·04, Al_2O_3 17·96, CaO 15·93, MgO 0·42, Ce_2O_3 3·47, $(La, Nd, Pr, Sm, Y, Eu)_2O_3$ 5·73, combined water 2·22, moisture 0·08, total 100·80%. The general formula appears to be $H_2M''_4(M'''_2)_3Si_6O_{26}$. Details of the analytical method and a possible structural formula are given. J. S. CARTER.

Palladium mineral from Potgietersrust platinum fields. H. R. ADAM (J. Chem. Met. Soc. S. Afr., 1927, **27**, 249—250).—A silvery-white mineral obtained from pannings in the Potgietersrust district of the Transvaal contained 70·4% Pd, 26·0% Sb, and 3·3% "gangue." The palladium and antimony correspond with the formula Pd_3Sb. The mineral has d 9·5 and is insoluble in hydrochloric acid, slowly attacked by nitric or by sulphuric acid, and readily soluble in dilute aqua regia. A. R. POWELL.

Organic Chemistry.

Anomalies in the properties of long-chain compounds. W. B. LEE (Nature, 1927, **120**, 48).—Cumulative evidence can now be adduced indicating that anomalies or turning points exist in many of the properties of certain long-chain compounds at or near the fifth, tenth, and fifteenth carbon atoms, the abnormality being most pronounced at C_{15}. A. A. ELDRIDGE.

Low-temperature oxidation of hydrocarbons. J. S. LEWIS (J.C.S., 1927, 1555—1572).—When paraffins are slowly heated in a bulb at constant volume a sudden rise in the pressure occurs at the "critical inflexion temperature" (C.I.T.), indicating rapid chemical action at this point involving an increase in the number of molecules. An oxidising catalyst such as platinum promotes pressures higher than normal below the C.I.T., whereas lead tetraethyl usually inhibits the initial oxidation; the activity of this negative catalyst, however, decreases slowly. It is suggested that oxygen combines with loosely-attached hydrogen atoms of the paraffins, the products being water and unsaturated hydrocarbons, this explaining the increase in the number of molecules, the high percentage of water, and the presence of unsaturated hydrocarbons immediately above the Secondary reactions, with formation of aldehydes, peroxides, etc., occur later, causing a slight fall in the temperature–pressure curves just above the C.I.T. The exothermic nature of the initial reaction, together with the increase in pressure due to the larger number of molecules present, promotes detonation, and the action of anti-knocks is due to their prevention of this primary dehydrogenation. B ANDERSON.

Catalytic reactions of ethylene. H. W. WALKER —See this vol., 837.

New class of tautomeric compounds. Ionic theory of tautomerism. C. PRÉVOST (Compt. rend., 1927, **185**, 132—134).—The ionised forms of the allyl compounds are represented by the scheme $(X^-),(R^1{\cdot}CH^+{\cdot}CH^-{\cdot}CH^+{\cdot}R^2)$, this being common to $CHXR^1{\cdot}CH{:}CHR_2$ and $CHR^1{:}CH{\cdot}CHXR^2$, and, in general, tautomerism is regarded as a consequence of the existence of an ion common to two isomeric forms. Such ion must be multipolar and of equal global charge and contrary sign to that of mobile substitution. This phenomenon, termed synionism, is always realised when a mobile group is attached to an atom linked to another doubly-linked atom. Thus the compound $A{:}B{\cdot}CX$ ionises in the form $A^{\pm}{\cdot}B^{\mp}{\cdot}C^{\pm},X^{\mp}$, which is also the activated form of $XA{\cdot}B{:}C$. The consequences of synionism are as follows: (1) X is only slightly mobile: $AX{\cdot}B{:}C$ and $A{:}B{\cdot}CX$ may exist separately and are isomerides. All reactions not involving the common ion are normal for both forms, but when this ion comes into play one at least of the isomerides exhibits an abnormal reaction. (2) X is highly mobile, but of the two positions it can occupy one confers on it greatly increased mobility. X will then be fixed solely or almost so at the other position, and the compounds are pseudo-isomeric. If X is replaced by the less mobile X′ by a reaction involving the common ion, two isomeric reaction products may often be separated. (3) When X is highly mobile and the positions A and C are similarly influenced, $AX{\cdot}B{:}C$ and $A{:}B{\cdot}CX$ are desmotropic. Examples of these different cases are cited. T. H. POPE.

Preparation and physical properties of *iso*butylene. C. C. COFFIN and O. MAASS (Trans. Roy. Soc. Canada, 1927, [iii], **21**, III, 33—40).—*iso*-Butylene, m. p. 146·8°, b. p. −6·6°, was prepared by the dehydration of *iso*butyl alcohol by alumina at 250—300°, dried by a freezing method, and fractionated in a vacuum. Values are tabulated of the vapour pressure (*e.g.*, 1044 mm. at 1·8°, 2017 mm. at 22·1°), density ($d^{0\cdot1}$ 0·6190, $d^{22\cdot5}$ 0·6444), surface tension (14·84 at 0°) and molecular surface energy (299·3 at 0°) over a considerable range of temperatures. The physical properties of ethylene, propylene, and *iso*butylene are summarised. A. A. ELDRIDGE.

Reactions of nitrosyl chloride. IV. Action of nitrosyl chloride on ketoximes. H. RHEINBOLDT and M. DEWALD (Annalen, 1927, **455**, 300—

314).—The chloronitroso-derivatives formed by the action of nitrosyl chloride on ketoximes are blue, unimolecular liquids or crystalline solids which do not polymerise at the temperature of liquid air. They are more stable than the αα-chloronitroso-compounds (this vol., 229) and do not pass into *iso*-nitroso-compounds. They are oxidised by air and light or, better, by warm nitric acid to chloronitro-derivatives. In this way are prepared ββ-*chloro-nitroso*-derivatives of propane, b. p. 70° (cf. Ponzio, A., 1906, i, 482); butane, b. p. 24—25°/22 mm.; pentane, b. p. 32°/23 mm.; γ-methylbutane, b. p. 31°/26 mm.; hexane, b. p. 47—48°/21 mm.; δ-methyl-pentane, b. p. 41—42°/18 mm.; γγ-dimethylbutane, m. p. 121—122°; *n*-octane, b. p. 41°/4 mm.; *n*-undecane, b. p. 84—85°/3 mm.; α-phenylpropane, b. p. 65°/4 mm., and αγ-diphenylpropane, m. p. 90—91°, decomp. 105°; the ββ-*chloronitro*-derivatives of butane, b. p. 51—52°/16 mm.; pentane, b. p. 72—73°/22 mm.; hexane, b. p. 83—84°/18 mm.; δ-methylpentane, b. p. 79°/17 mm.; γγ-dimethyl-butane, m. p. 169—170°; *n*-octane, b. p. 115°/19 mm.; *n*-undecane, b. p. 119—120°/4 mm.; α-phenyl-propane, b. p. 88°/2 mm.; αγ-diphenylpropane, m. p. 127°; also γγ-*chloronitrosopentane*, b. p. 32°/20 mm.; γγ-*chloronitropentane*, b. p. 73°/24 mm.; *ethyl propyl ketoxime*, b. p. 86°/17 mm.; γγ-*chloronitrosohexane*, b. p. 46—47°/17 mm.; γγ-*chloronitrohexane*, b. p. 79—80°/17 mm.; δδ-*chloronitrosoheptane*, b. p. 49°/12 mm.; δδ-*chloronitroheptane*, b. p. 94—95°/17 mm.; ωω-*chloronitrosohentriacontane*, m. p. 49—50°; σσ-*chloronitrosopentatriacontane*, m. p. 51—52°; σσ-*chloronitropentatriacontane*, m. p. 52°; 1 : 1-*chloro-nitroso*cyclo*hexane*, b. p. 52°/12 mm.; and 1 : 1-*chloronitro*cyclo*hexane*, b. p. 93—94°/13 mm. Benzo-phenoneoxime, butane-βγ-dione- mono- and -di-oximes, benzilmonoxime, fluorenoneoxime, and phenanthra-quinonemonoxime do not give chloronitroso-deriv-atives with nitrosyl chloride. H. E. F. Notton.

Mechanism of the change of *iso*nitro- to nitro-compounds. G. E. K. Branch and J. Jaxon-Deelman (J. Amer. Chem. Soc., 1927, 49, 1765—1779).—When the sodium salts of *iso*nitromethane, phenyl*iso*nitromethane, and *p-iso*nitrophenol in 0·01*N*-aqueous solution are added to 0·01*N*-aqueous hydrochloric acid at temperatures between −23·8° and +5·2°, the rate of decrease in conductivity falls very rapidly at first, and then becomes and remains proportional to the conductivity of the solutions due to the *iso*nitro-compounds. It is concluded that the first rapid change in conductivity is due to the establishment of an equilibrium according to the scheme $R\cdot CH{:}N\lessdot^{O}_{O^-} + H^+ \rightleftharpoons R\cdot CH(O)\text{–}N\cdot OH$, whilst the subsequent slower change is due to an isomerisation according to the scheme $R\cdot CH{:}N\lessdot_{O^-} \longrightarrow R\cdot CH{:}N\lessdot^{O}_{O}$, which is then followed by the very rapid combination with hydrogen ion to form the true nitro-compound: $R\cdot CH{:}N\lessdot^{O}_{O} + H^+ \longrightarrow R\cdot CH_2\cdot NO_2$. The heats of activation of the above three nitro-compounds, calculated from the changes in rates of isomerisation with temperature, are respectively, 8450±600, 22,000±2000, and 4250±800 g.-cal./mol. F. G. Willson.

Polyvinyl alcohol. W. O. Herrmann and W. Haehnel (Ber., 1927, 60, [*B*], 1658—1663).—Polyvinyl alcohol is prepared by the hydrolysis of polyvinyl esters by alkali or acid. Since the substance has marked adsorptive power for inorganic salts, it has a high ash content when prepared by means of alkali, whereas acid hydrolysis gives a purer product from which acid can be removed by dialysis. The properties vary greatly with the mode of preparation both in respect of colour and density. Most of the forms are soluble in water but a black, insoluble modification may be prepared by heating an aqueous solution of polyvinyl alcohol with hydrochloric acid followed by dialysis of the product. As judged by determinations of mol. wt. by osmotic methods it has the composition $(CH_2{:}CH\cdot OH)_{20}$. When heated at 250°/1000 atm. it forms a hard, elastic material, *d* 1·5810. It behaves generally as a reversible colloid similar to gum arabic or albumin. It is well adapted as a protective colloid for metals, hydroxides, oxides, sulphides, etc. When heated at 200—220°/30 atm. polyvinyl alcohol appears to undergo transformation. It adds chlorine or bromine, forming compounds which have not been investigated fully; they are transformed by boiling water into black *polyvinyl* alcohol. Iodine and potassium carbonate convert it into iodoform. The action of oxidising agents is described. With sodium hydroxide it gives sodium polyvinyl oxide trihydrate. Acids or their anhydrides convert it into polyvinyl esters. Its relationship to the carbohydrates is shown by the production of substances resembling amyloform with formaldehyde. Like crude rubber, it can be vulcanised with sulphur in the presence or absence of accelerators.
H. Wren.

Stereochemistry of the tetrahedral carbon atom. VI. Configuration of the glycols obtained by reduction of aldehydes by zinc-copper couple. R. Kuhn and O. Rebel (Ber., 1927, 60, [*B*], 1565—1572).—The reduction of glyoxylic acid, benzaldehyde, acraldehyde, crotonaldehyde, and cinnamaldehyde has been examined. The configuration of the glycols formed from the first two substances is established by their known resolvability. In the cases of the unsaturated glycols obtained from the last three aldehydes the structure is established by ozonisation in glacial acetic acid solution (gelatinous, highly polymerised ozonides are produced in chloroform or carbon tetrachloride) followed by decomposition of the ozonides and oxidation of the products by bromine to *r*- or *meso*-tartaric acid. In all cases either the *r*- or the glycol appears to be produced exclusively. It is not possible to establish a simple relationship between the electrochemical nature or valency demand of the substituent and the configuration of the resulting glycol. The influence of groups remote from the aldehydic group is, however, remarkable. The necessary thermo-chemical data are not available for consideration of conditions with regard to energy.

Δ$^{\alpha\epsilon}$-Hexadiene-γδ-diol, b. p. 98°/12 mm.,

mm., d_4^{20} 1·006, n_D^{20} 1·4700, prepared by reduction of acraldehyde, is oxidised by permanganate to oxalic acid and converted through the ozonide into *meso*-tartaric acid. It is hydrogenated in the presence of spongy platinum to meso*hexane-γδ-diol*, b. p. 91°/20 mm., m. p. 88°.

$\Delta^{\beta\delta}$-Octadiene-δε-diol, b. p. 122°/9 mm., obtained from crotonaldehyde after ozonisation (preferably of the corresponding diacetate), affords *r*-tartaric acid. Hydrocinnamoin, as the diacetate, similarly gives *meso*tartaric acid in 46% yield; meso-*αζ-diphenylhexane-γδ-diol*, m. p. 132°, and its *diacetate*, m. p. 70°, are described. Benzaldehyde yields exclusively *meso*hydrobenzoin. H. WREN.

Alkylation with *p*-toluenesulphonic esters. L. BLANCHARD (Bull. Soc. chim., 1927, [iv], **41**, 824—833).—Methyl *p*-toluenesulphonate reacts at 140—155° with dihalogenohydrins, $CH_2X{\cdot}CH(OH){\cdot}CH_2X$, affording the corresponding methoxy-derivative; below 120° no reaction occurs and at 160° decomposition takes place. The ester employed must be dry and free from *p*-toluenesulphonyl chloride. The following ethers were prepared by this method: *αγ*-dichloro-β-methoxypropane, b. p. 160°/760 mm., d^{19} 1·21, n 1·45262; *α-chloro-γ-bromo-β-methoxypropane*, b. p. 70—72°/15 mm., d^{15} 1·54, n 1·48519; and *α-chloro-βγ-dimethoxypropane*, b. p. 156—157°/760 mm., d^{15} 1·088, n 1·432 (from "epimethyline," γ-methoxypropane-αβ-oxide). α-Chloro-β-iodo-γ-methoxypropane cannot be obtained by this method. α-Bromo-βγ-dimethoxypropane is obtained with difficulty.

With dichlorohydrin in presence of sodium hydroxide, *p*-toluenesulphonyl chloride affords *αγ-dichloropropyl* β-*p-toluenesulphonate*, m. p. 52—53°, b. p. 180—210°/13 mm., d^{15} 1·356, n 1·53572. Chlorobromohydrin behaves similarly. γ-Methoxypropane-αβ-oxide, b. p. 113—114°/770 mm., d^{6} 1·002, n 1·41158, is obtained by the action of cold, concentrated sodium hydroxide on α-chloro-β-hydroxy-γ-methoxypropane (A., 1926, 1123). With 48% hydrobromic acid (b. p. 126°) it affords *α-bromo-β-hydroxy-γ-methoxypropane*, b. p. 79°/12 mm., 190°/760 mm. (decomp.), d^{7} 1·545, n 1·4832, and with aqueous hydriodic acid, b. p. 127°, "iodomethyline," *α-iodo-β-hydroxy-γ-methoxypropane*, b. p. 93—94°/11 mm., d^{5} 1·851, n 1·5363. Epichlorohydrin is best obtained technical dichlorohydrin. Addition of epichlorohydrin to aqueous hydrobromic acid (48%) affords α-chloro-γ-bromohydrin in quantitative yield. R. BRIGHTMAN.

Bromine derivatives of pentoic and hexoic acids. R. MERCHANT, J. N. WICKERT, and C. S. [illegible]EL (J. Amer. Chem. Soc., 1927, **49**, 1828—1831). γ-phenoxypropylmalonate, b. p. 185—[illegible] mm., 1·0858, 1·488, is obtained in [illegible]80% yield by treating ethyl sodiomalonate with [illegible]henyl γ-bromopropyl ether. When treated accord-[illegible] Gabriel's method (A., 1892, 717) the ester [illegible] δ-phenoxyvaleric acid, m. p. 65—66°, b. p. [illegible] mm., in 87—93% yield. Treatment of the [illegible] 48% hydrobromic acid under such con-[illegible]ions phenol and water are continuously boiled [illegible] δ-bromovaleric acid, m. p. 38—39°, b. p. [illegible] mm., in 63—64% yield, which is also obtained by a similar method, in 65—69% yield, directly from ethyl γ-phenoxypropylmalonate. Ethyl δ-bromovalerate has b. p. 94—97°/7 mm., b. p. 106—110°/20 mm., d_{24}^{24} 1·3191, n_D^{24} 1·4580 (cf. Cloves, A., 1902, i, 200). *δ-Bromovaleryl chloride*, b. p. 102—104°/15 mm., d_4^{27} 1·5010, n_D^{20} 1·4879, was prepared. Treatment of δ-bromovaleric acid with bromine and phosphorus tribromide yields *αδ*-dibromovaleric acid, b. p. 150—152°/5 mm., d_4^{25} 1·8629, n_D^{25} 1·5347 (acid chloride, b. p. 138—145°/15 mm.; *ethyl* ester, b. p. 133—135°/14 mm., d_4^{25} 1·6829, n_D^{25} 1·4947) (cf. Fischer and Suzuki, A., 1904, i, 771). ε-Bromohexoic acid, b. p. 160—168°/18 mm., is obtained similarly from ethyl δ-phenoxybutylmalonate, in 62% yield. On bromination as above, it affords *αε-dibromohexoic acid*, b. p. 158—160°/4 mm., d_4^{21} 1·7897, n_D^{21} 1·5245, the product, m. p. 144—146°, obtained by Marvel and others (A., 1925, i, 234) by the action of hydrobromic acid on α-bromo-ε-phenoxyhexoic acid, having been therefore incorrectly described as this acid. F. G. WILSON.

Three-carbon system. XIII. Effect of bulky substituents and of the *cyclo*heptane group on the tautomerism. G. A. R. KON and C. J. MAY (J.C.S., 1927, 1549—1555).—The equilibrium between ββ-dipropyl- and ββ-di*iso*butyl-acrylic acids and their βγ-isomerides is discussed and it is shown that steric factors are largely responsible for the conditions observed.

Dehydration of ββ-dipropylhydracrylic acid with acetic anhydride yields ββ-*dipropylacrylic acid*, m. p. 9° (cf. Albitski, A., 1885, 242), b. p. 144°/17 mm., d_4^{20} 0·93624, n^{20} 1·46350 (*silver* salt; *chloride*, b. p. 128°/25 mm.; *amide*, m. p. 72°; p-*toluidide*, m. p. 82·5°; *ethyl* ester, b. p. 108—109°/14 mm., d_4^{18} 0·89284, [illegible] 1·44923), yielding, on oxidation with potassium permanganate, dipropyl ketone. β-Propyl-Δ^{β}-hexenoic acid has b. p. 138—140°/22 mm. and 126—128°/11 mm. (*ethyl* ester, b. p. 116—118°/25 mm., d_4^{25} 0·89264, n_D^{25} 1·43778; *chloride*, b. p. 107°/30 mm.; *amide*, m. p. 120—121°). Equilibration of the acids by refluxing with potassium hydroxide gives a mean value of 33% of αβ-acid, 67% of βγ-acid.

Ethyl hydrogen iso*heptylmalonate* has b. p. 168°/35 mm. β-*Propylhexoic acid* has b. p. 144°/30 mm. Inseparable mixtures of ββ-di*iso*butylacrylic acid and its βγ-isomeride were obtained in all cases. Equilibration of the acids gives a mean value of 49% of αβ-acid, 51% of βγ-acid.

Investigation of the equilibrium between *cyclo*heptylideneacetic acid and its βγ-isomeride shows that the *cyclo*heptane ring has less tendency to acquire a double linking than either the five- or six-membered rings. The equilibration mixture contains 25·6% of αβ-acid. Pure *cyclo*heptylideneacetic acid has m. p. 54°. *αβ-Dibromocyclo*heptylacetic acid has m p 125°; *βγ-dibromocyclo*heptylacetic acid has m. p. 103—104°. M. CLARK.

Composition of parsley-seed oil. J. VAN LOON (Rec. trav. chim., 1927, **46**, 492—500).—The oil obtained by extraction of Dutch parsley-seed (*Apium petroselinum*, L.; *Petroselinum sativum*, Hoffm.) with light petroleum has d^{20} 0·9663, n_D^{40} 1·4800, acid value 3·2, saponification value 129·7, ester value

126·5, iodine value 171·1, Reichert–Meissl value 1·09. The unsaponifiable portion (30% of the oil) has a setting point below 0°, n_D^{40} 1·5198, iodine value 136·0, and possesses in marked degree the characteristic odour of parsley. On fractional distillation myristicin was identified in the fraction of b. p. 70—100°/18 mm. whilst that of b. p. 163°/18 mm. contained a *substance* $C_{10}H_{18}O_2$ of very agreeable odour. The fatty acids from the oil (65%) were dark green in colour and had m. p. 26° (indef.), n_D^{40} 1·4597, iodine value 96·6, acid value 188·3, and were separated into solid (45%) and liquid acids by fractional recrystallisation of the lead salts from alcohol. The solid acids consist mainly of "petroselic acid," $C_{18}H_{34}O_2$ (cf. Vongerichten and Köhler, A., 1909, i, 454; Hilditch and Jones, this vol., 540), m. p. 29·4°, 1·4534, iodine value 89·9, and acid value 198·7 (cf. Palazzo and Tamburello, A., 1915, i, 862). On ozonisation it yields lauric acid (m. p. 43·6°) and adipic acid, and the liquid *methyl* ester on hydrogenation affords methyl stearate, m. p. 39·2°. These facts are in agreement with the formula $CH_3{\cdot}[CH_2]_{10}{\cdot}CH{:}CH{\cdot}[CH_2]_4{\cdot}CO_2H$ ascribed by Vongerichten and Köhler to petroselic acid. The solid fatty acids also contain a small quantity of palmitic and stearic acids. The liquid fatty acids, the lead salts of which were soluble in alcohol, were distilled in a vacuum and yielded, on treatment with bromine in ethereal solution, linoleic tetrabromide, m. p. 114·2°, but no linolenic hexabromide, and therefore contained 33% of linoleic acid, the remaining acids being of the oleic series. Δ^9-Oleic acid was proved to be present by the formation of Δ^9-elaidic acid, m. p. 43°, on treatment of the liquid fatty acid with nitrogen peroxide, and confirmed by the production of *n*-nonoic and azelaic acids on ozonisation.

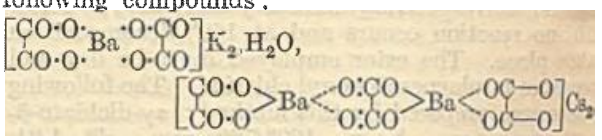
W. J. POWELL.

Preparation of myristic acid from nutmeg butter and ucuhuba fat. P. E. VERKADE and J. COOPS (Rec. trav. chim., 1927, **46**, 528—533).—Nutmeg butter is the most convenient source of myristic acid since it contains in appreciable quantities only triolein and trimyristin, and the latter, the chief constituent, is readily obtained in a pure state by recrystallisation from a mixture of 4 vols. of 96% alcohol and 1 vol. of ether. Myristic acid, setting point 53·6°, is obtained in nearly theoretical yield by saponification and recrystallisation of the product from 80% acetic acid. The fatty acids from a sample of ucuhuba fat contained myristic acid (58%), *n*-decoic acid, and lauric acid (8%), which were separated by fractional distillation of the methyl esters. Since many previous investigators (cf. Reimer and Will, A., 1885, 1197; Nördlinger, A., 1886, 139; Valenta, B., 1889, 202) have found ucuhuba fat to contain no higher saturated acids other than myristic acid, it is concluded that the ucuhuba fat of commerce may be of varied botanical origin. W. J. POWELL.

Metallic hydroxy-acid derivatives. IV. Complexes formed by copper with the monobasic monohydroxy-acids. I. W. WARK (J.C.S., 1927, 1753—1758; cf. *ibid.*, 1923, **123**, 1816).—*Sodium cuprimandelate*, $Na_2[Cu(C_8H_6O_3)_2]$, is best prepared by dissolving cupric mandelate in alcoholic sodium ethoxide; in a similar manner *sodium cupriglycollate*, $Na_2[Cu(C_2H_2O_3)_2]$,2·5MeOH, and *cuprisalicylate*, $Na_2[Cu(C_7H_4O_3)_2]$, may be obtained. As shown by hydrogen-ion concentration measurements in solution cupric salicylate is more acidic than the glycollate or lactate, and, as expected, the complex salicylates and mandelates are found to be more stable than the corresponding glycollates and lactates. The following salts have been isolated from aqueous solutions: *sodium hydrogen cuprimandelate*, $NaH[Cu(C_8H_6O_3)_2]$; *silver cuprimandelate*, $Ag_2[Cu(C_8H_6O_3)_2]$; *mercurous cuprimandelate*, $Hg_2[Cu(C_8H_6O_3)_2],5H_2O$; *ferric cuprimandelate*, $Fe_2[Cu(C_8H_6O_3)_2]_3,14H_2O$; *cupric cuprimandelate*, $Cu[Cu(C_8H_6O_3)_2]$.

B. W. ANDERSON.

Oxalato-derivatives of the alkaline-earth metals and lead. R. SCHOLDER, E. GADENNE, and H. NIEMANN (Ber., 1927, **60**, [*B*], 1488—1498).—The complex oxalates of the alkaline-earth metals and lead exist in three types exemplified by the following compounds:



and $[Sr_5(C_2O_4)_6]K_2,12H_2O$. The salts are prepared from their components under highly individual conditions. They are colourless, microcrystalline powders, insoluble in water, by which those belonging to the first two types are immediately decomposed. *Salts* of the following formulæ are described:

$K_2C_2O_4,BaC_2O_4,2H_2O$; $Rb_2C_2O_4,BaC_2O_4,2H_2O$; $Tl_2C_2O_4,BaC_2O_4,2H_2O$; $(NH_4)_2C_2O_4,2BaC_2O_4$; $Cs_2C_2O_4,2BaC_2O_4$; $K_2C_2O_4,5BaC_2O_4,4H_2O$; $K_2C_2O_4,2PbC_2O_4,4H_2O$; $Rb_2C_2O_4,2PbC_2O_4,4H_2O$ (or $2H_2O$); $Cs_2C_2O_4,PbC_2O_4,2H_2O$; $H_2C_2O_4,2SrC_2O_4,2H_2O$; $H_2C_2O_4,2SrC_2O_4$; $H_2C_2O_4,2SrC_2O_4,2{\cdot}5H_2O$; $(NH_4)_2C_2O_4,2SrC_2O_4$; $K_2C_2O_4,2SrC_2O_4$; $Rb_2C_2O_4,2SrC_2O_4$; $Cs_2C_2O_4,2SrC_2O_4$; $K_2C_2O_4,5SrC_2O_4,12H_2O$; $Na_2C_2O_4,5SrC_2O_4,12H_2O$; $K_2C_2O_4,CaC_2O_4,H_2O$; $Rb_2C_2O_4,CaC_2O_4,H_2O$; $Cs_2C_2O_4,CaC_2O_4,H_2O$.

H. WREN.

Partial replacement of the oxalate residue in oxalato-anions of bivalent metals. R. SCHOLDER [with E. GADENNE and H. NIEMANN] (Ber., 1927, 60, [*B*], 1499—1509; cf. preceding abstract).—The behaviour of strontium oxalate towards concentrated solutions of a number of alkali salts is described. Typical results are obtained with sodium thiosulphate solution, which deposits crystals of strontium oxalate or the more stable sodium strontium oxalate, $Na_2C_2O_4,5SrC_2O_4,12H_2O$. Sodium nitrite and potassium acetate are exceptional since they yield the *compounds* $Na_2C_2O_4,SrC_2O_4,NaNO_2,H_2O$ and $K_2C_2O_4,3SrC_2O_4,2CH_3{\cdot}CO_2K,4{\cdot}5H_2O$. The oxalates of the alkaline earths exhibit enhanced solubility in solutions of alkali formates and hypophosphites but in the majority of cases either double decomposition ensues or the corresponding double oxalate crystallises; the *salts* $SrC_2O_4,H{\cdot}CO_2K,2H_2O$, $SrC_2O_4,H{\cdot}CO_2Rb,2H_2O$, $SrC_2O_4,KH_2PO_2,2H_2O$, and $CaC_2O_4,2H{\cdot}CO_2K,H_2O$, have been isolated. Oxalates of bivalent heavy metals are more freely soluble than those of the alkaline earths in alkali formate

and hypophosphite solutions and yield double oxalates or mixed *compounds*, of which the following individuals are described: $ZnC_2O_4,2H{\cdot}CO_2K$; $CdC_2O_4,2H{\cdot}CO_2K,(H_2O$ and $3H_2O)$; $CoC_2O_4,2H{\cdot}CO_2K$; $CoC_2O_4,3H{\cdot}CO_2Na$; $CoC_2O_4,H{\cdot}CO_2NH_4$; $2CdC_2O_4,K_2C_2O_4,2H{\cdot}CO_2K,2H_2O$; $2ZnC_2O_4,3KH_2PO_2,2H_2O$; $5NiC_2O_4,16H{\cdot}CO_2Na,5H_2O$; $3CdC_2O_4,(NH_4)_2C_2O_4,7H_2O$. On the supposition that the oxalates of the alkaline-earth metals are themselves complex compounds, *e.g.*, $[Ba(C_2O_4)_2]Ba$, the behaviour of these compounds in solutions of the alkaline-earth formates has been investigated. When the same basic ion is present in each salt the oxalate is insoluble. With dissimilar cations enhanced solubility is observed. The systems thus produced are exceedingly labile and the extent to which double decomposition occurs depends greatly on the temperature; the *compound*, $[BaC_2O_4,(H{\cdot}CO_2)_2]Ba,6H_2O$, is the only member of the class which could be isolated. H. WREN.

Auto-complex formation with oxalates of bivalent metals. II. Determinations of conductivity and solubility. R. SCHOLDER [with E. GADENNE and H. NIEMANN] (Ber., 1927, **60**, [*B*], 1510—1525; cf. preceding abstracts).—The conductivities of saturated aqueous solutions of the oxalates of barium ($+0{\cdot}5$, 2, and $3{\cdot}5H_2O$), strontium ($+1H_2O$), calcium ($+1H_2O$), magnesium ($+2H_2O$), zinc ($+2H_2O$), cadmium ($+3H_2O$), ferrous iron ($+2H_2O$), cobalt ($+2H_2O$), nickel ($+2H_2O$), and silver have been determined and their solubility has been found by direct measurement (treatment of the solution with sulphuric acid followed by concentration and titration with 0·01*N*-permanganate). The production of an auto-complex is regarded as established if the ratio, conductivity/solubility is considerably less than the conductivity at infinite dilution as deduced from the sum of the mobilities of the ions. This is not the case with the oxalates of barium, strontium, calcium, and silver, whereas with those of magnesium, zinc, cadmium, iron, cobalt, and nickel complex compounds appear to exist in solution. Unless, therefore, the possibility of auto-complex formation is excluded, the applicability of Kohlrausch's method for the determination of the solubility of sparingly soluble substances appears doubtful.

H. WREN.

Auto-complex formation with oxalates of bivalent metals. II. Dilution curves. R. SCHOLDER (Ber., 1927, **60**, [*B*], 1525—1532; cf. preceding abstract).—Since it is possible that the abnormally low values of the equivalent conductivity of the oxalates of zinc, cadmium, ferrous iron, nickel, and cobalt may be due to the slight dissociation of these salts, the effect of dilution on the value of Λ and also on the degree of dissociation $\alpha=\Lambda/\Lambda_\infty$ has been examined and compared with the similar values for barium oxalate. A linear relationship between specific conductivity and concentration exists only in the case of barium oxalate. With the other salts, the specific conductivity increases with dilution in a highly individual manner. The results are most fully explained by the assumption of auto-complex formation. In the so-called degree of dissociation, α, two phenomena are superimposed. With increasing dilution, the complex dissociates more completely into the ions of the simple oxalate and, simultaneously, the degree of dissociation of the complex and the simple oxalate increases. With the zinc, cadmium, and cobalt compounds the decomposition of the complex is so pronounced that, in comparison, the increase of α with increasing dilution is almost without moment. With the more stable ferrous oxalate complex, the increase in the actual degree of dissociation is more important. The very individual behaviour of the oxalates of the heavy metals, which are otherwise very similar in their properties, is a further argument in favour of auto-complex formation. It is probable that the constitution of the auto-complex oxalates cannot be expressed by the simple formula, $[X''(C_2O_4)_2]X''$. H. WREN.

Oxalochlorides of cerium. L. DEDE and W. FABER (Ber., 1927, **60**, [*B*], 1654—1658).—Addition of concentrated oxalic acid solution to a boiling, well-stirred solution of cerium chloride in water as long as the initial precipitate immediately dissolves causes the compound, $CeCl(C_2O_4),3H_2O$, to crystallise from the cold solution. The salt is stable to cold but not to boiling water; it may be crystallised from fuming hydrochloric acid. Evaporation of the mother-liquors in a vacuum leads to the isolation of the *salt*, $Ce_2Cl_4(C_2O_4),8H_2O$, which is more readily prepared from cerium chloride, and the compound $CeCl(C_2O_4)$; it is decomposed by excess of cold water. H. WREN.

Therapeutic action of some bismuthyl derivatives of organic hydroxy-acids. C. H. BROWNING, J. B. COHEN, R. GULBRANSEN, E. PHILLIS, and W. R. SNODGRASS (Proc. Roy. Soc., 1927, **B**, **102**, 1—9).—*Bismuthyl* compounds of *saccharic acid*, *disodium saccharate*, *potassium mucate*, *gluconic acid*, *disodium gluconate*, *mannonic acid*, *galactonic acid*, *lactobionic acid*, *maltobionic acid*, *tartaric acid* ($C_8H_{10}O_{12},BiO,2H_2O$), *disodium tartrate*, *ethyl hydrogen tartrate*, *ethyl tartrate*, *glyceric acid*, *ethyl glycerate*, *sodium gallate*, *malic acid*, *citric acid*, *glycollic acid*, *dihydroxymalonic acid*, *ethyl dihydroxymalonate*, *tartronic acid*, and *thiobenzoic acid*, are prepared by treatment of the acid, ester, or salt with bismuth nitrate in acetic acid. Excepting the citric acid and citric ester compounds, all are soluble in aqueous alkali, the saccharic acid compound being stable even in boiling concentrated alkali. In the case of tartaric acid several bismuthyl compounds are obtained: $C_4H_4O_6NO_3{\cdot}BiO$, from a warm solution of bismuth nitrate in dilute acetic acid and aqueous tartaric acid; $C_4H_4O_6{\cdot}BiO$, from equimolecular amounts of bismuth nitrate and tartaric acid in hot acetic acid; and $C_4H_4O_6Bi{\cdot}NO_3,5H_2O$, from excess of tartaric acid in boiling acetic acid. Glycollic acid readily gives a bismuthyl compound, but its phenyl, diphenyl, and dimethyl derivatives fail to react, whilst lactic acid gives an indefinite product. Structures similar to Maschmann's (A., 1925, i, 527) are suggested.

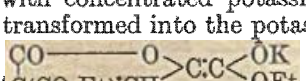
All the products are therapeutically active, but only the saccharic, mannonic, lactobionic, tartaric, and citric derivatives cure mice infected with *Spirochæta laverani*, Breinl and Kinghorn. Bismuthyl-saccharic acid and -gluconic acid, injected intramuscularly, have

a definite antisyphilitic action in man, but are not curative and present no advantage over the known bismuth preparations. C. HOLLINS.

Polarimetric and electrometric study of the alkali aluminotartrates. A double mutarotation phenomenon. PARISELLE (Compt. rend., 1927, 185, 130—132).—The curves obtained from determinations of the specific rotatory powers of mixtures containing one aluminium ion to one molecule of tartaric acid with increasing proportions of sodium hydroxide indicate the existence of a neutral sodium aluminotartrate, $CO_2Na{\cdot}CH(AlO){\cdot}CH(OH){\cdot}CO_2Na$, which is decomposed by an excess of alkali into sodium tartrate and meta-aluminate. Mutarotation phenomena varying in sign and rate of change, and depending on the p_H value, were observed for solutions other than those containing less than 1 mol. or more than 5 mols. of sodium hydroxide to 1 mol. of aluminium. They indicate molecular transformations. Analogous results were obtained for potassium and ammonium hydroxides. J. GRANT.

Allenetetracarboxylic ester. F. FALTIS and J. PIRSCH (Ber., 1927, 60, [*B*], 1621—1632; cf. A., 1922, i, 624).—Ethyl sodiodicarbethoxyglutaconate is obtained in good yield from ethyl malonate, chloroform, and sodium ethoxide in ethyl alcohol if undue rise of temperature is avoided, thus excluding the production of the sodium derivative of *iso*butanehexacarboxylic ester. It is converted by bromine in chloroform or ether into ethyl γ-bromo-$\alpha\gamma$-dicarbethoxyglutaconate, which when treated with moist silver oxide in boiling alcohol affords *ethyl allenetetracarboxylate*, $C(CO_2Et)_2{:}C{:}C(CO_2Et)_2$, m. p. 84°, in 30% yield. The ester immediately decolorises cold, neutral permanganate solution but does not add bromine or hydrogen in the presence of palladised barium sulphate.

The action of potassium ethoxide (1 mol.) on ethyl γ-bromo-$\alpha\gamma$-dicarbethoxyglutaconate leads unexpectedly to the conversion of one half of the ester into ethyl potassio-$\alpha\gamma$-dicarbethoxyglutaconate (the corresponding *copper* and *calcium* salts are described), whereas the other half appears to be transformed into ethyl γ-bromo-$\alpha\beta$-diethoxy-$\alpha\gamma$-dicarbethoxyglutarate; the latter compound could not be isolated and its formation is deduced from its conversion when distilled into ethyl carbonate, polymerised ethyl α-bromoacrylate, ethyl mesoxalate, and (?) ethylene. If the proportion of potassium ethoxide is increased to 2 mols., the potassio-derivative is obtained in 63·4% yield.

Conversion of the bromo-ester into the γ-lactone, $C_{13}H_{16}O_8$ (cf. Faltis, *loc. cit.*), is conveniently effected by distillation under 14 mm. pressure. By treatment with concentrated potassium ethoxide solution it is transformed into the potassium salt,  in 83% yield; the corresponding copper salt has 2EtOH instead of $5H_2O$ as described. Attempts to open the lactone ring by using an excess of potassium ethoxide were not successful. The corresponding *sodium* salt is described. Treatment of the potassium salt with aqueous ethyl alcohol and concentrated sulphuric acid leads to the production of an *ester*, $C_{23}H_{32}O_{14}$, which could not be completely purified; hydrolysis with potassium ethoxide converts it into the *potassium* salt, $C_{23}H_{30}O_{14}K_2$, from which the corresponding *copper* salt, m. p. 169—170° (decomp.) after softening at 160°, is obtained. H. WREN.

Sulphosuccinic acid. H. J. BACKER and J. M. VAN DER ZANDEN (Rec. trav. chim., 1927, 46, 473—491).—The neutralisation of the sulphonic group in *d*-sulphosuccinic acid, obtained by recrystallisation of the neutral strychnine salt, has little effect on the rotatory power, but there is a marked reduction if in addition one or both carboxyl groups are neutralised; thus the free acid, the mono-, di-, tri-sodium, and the tri-ammonium salts have $[M]_D$=53, 52, 39, 33, and 34, respectively. This behaviour is analogous to that of α-sulphopropionic, α- and β-sulphobutyric, and α-sulphovaleric acids. *d*-Sulphosuccinic acid, which, like its salts, is readily racemised at 100°, is moderately stable at ordinary temperatures and may be prepared by the action of sodium sulphite on *l*-bromosuccinic acid in weakly alkaline solution. Sulphosuccinic acid is best prepared by the action of sodium hydrogen sulphite on maleic or fumaric acid. The reaction takes place in the cold, and the sulphonated acid is isolated as the barium salt (yield 90%). The free acid is obtained by decomposing the silver salt with hydrogen sulphide and evaporating the filtered solution; it forms hygroscopic crystals of the monohydrate, which, when heated in a closed tube, decompose at 60°, and become coloured at 80° but do not melt. A colorimetric determination of the tertiary dissociation constant gave $k_3=1\times10^{-5}$, whilst by an electrometric method Mook has obtained $k_2=1{\cdot}6\times10^{-4}$ and $k_3=0{\cdot}5\times10^{-5}$ (private communication). The silver, barium, lead ($+4H_2O$), potassium (anhydrous, decomp. 227°), and *thallium* (anhydrous, decomp. 116—120°) salts are described. The primary *strychnine* salt was not obtained in a crystalline form, but the neutral *tristrychnine* salt and an *acid* salt, $3C_4H_6O_7S,8C_{21}H_{22}O_2N_2$, decomp. 245°, were isolated. Sulphosuccinic acid may also be prepared by the action of sodium sulphite on bromosuccinic acid, but secondary reactions cause the yield to be low (40%). The method involving the direct sulphonation of succinic acid described by Fehling is unsatisfactory since the interaction of sulphur trioxide and succinic acid in equimolecular quantities results in the formation of succinic anhydride, whilst with excess of the former at 50° the product contains unchanged succinic acid, sulphosuccinic acid, and *disulphosuccinic acid*, of which the *lead* and *thallium* (decomp. 145°) salts are described. W. J. POWELL.

Exchange of functional groups between two molecules. A. VERLEY (Bull. Soc. chim., 1927, [iv], 41, 788—804).—The carbonyl group in ketones, aldehydes, or esters possesses the general property of combining with 1 mol. of metallic alkoxides, with evolution of heat, affording compounds of the type, $CRR'(OM){\cdot}OR''$, for which the name metallic "hemiacetal" is proposed. Both the metallic and the free hemiacetal are largely dissociated in solution and have not been obtained pure. Benzaldehyde and aluminium ethoxide in absolute alcohol afford 67% of a crystalline powder, apparently a mixture o

$CHPh[O\cdot Al(OEt)_2]\cdot OEt$, $CH_2Ph\cdot O\cdot Al(OEt)_2$, and $CPh(O\cdot CH_2Ph)[O\cdot Al(OEt)_2]\cdot OEt$, since on treatment with dilute sulphuric acid it yields benzyl alcohol, benzaldehyde, and ethyl and benzyl benzoates. With aluminium ethoxide and acetone the yield of hemiacetal varies from 40% to 80%. The sodium hemiacetal obtained from sodium ethoxide and methyl nonyl ketone on treatment with ethyl bromide affords a small amount of the methyl acetal of methyl nonyl ketone, a reaction supporting the structure advanced above. With esters, aluminium ethoxide affords the hemiacetal in 30—80% yield. The formation from these hemiacetals of products in which the functional groups of the original compounds have been interchanged is attributed to intramolecular change in the hemiacetal, *e.g.*, $CH_2R\cdot O\cdot CHR'\cdot OH \longrightarrow CH_2R'\cdot O\cdot CHR\cdot OM$ (combination of aldehyde with primary alkoxide) or $CHRR'\cdot O\cdot CR''R'''\cdot OM \longrightarrow CHR''R'''\cdot O\cdot CRR'\cdot OM$ (ketone and secondary alkoxide). In the cases where the hemiacetal has the structure $CHRR'\cdot O\cdot CHR''\cdot OM$ (aldehyde and secondary alkoxide) or $CH_2R\cdot O\cdot CR'R''\cdot OM$ (ketone and primary alkoxide) such exchange does not occur. In the third stage the new hemiacetal dissociates in solution into alkoxide and carbonyl compound, the metal being finally distributed between the two alcohols in proportion to their mol. wt. The above theory of exchanges is developed to explain the Claisen–Titschenko reaction, the formation of a hemiacetal, $CHR(OAlk)\cdot OM$, being regarded as the first stage, from which 1 mol. of metallic alkoxide is eliminated, giving $CHR(OM)\cdot O\cdot CHR\cdot OAlk$, from which, by migration of the OM group, the product $CH_2R\cdot O\cdot CR(OM)\cdot OAlk$ is formed. Cannizzaro's reaction is given a similar interpretation, $R\cdot CHO + NaOH = CHR(ONa)\cdot OH \longrightarrow CHR(OH)\cdot O\cdot CHR\cdot ONa \longrightarrow CR(OH)(ONa)\cdot O\cdot CH_2R \longrightarrow R\cdot CO\cdot ONa + CH_2R\cdot OH$. Aldolisation is similarly explained; only those aldehydes aldolising which are capable of yielding an enolic form.

The reaction between alkoxides and ketones, aldehydes, and esters affords a means of preparing otherwise inaccessible esters of secondary or tertiary alcohols. Thus 1 mol. of methyl anthranilate and 1 mol. of geraniol, when heated at 100—120° in presence of 0·05*M* of sodium, aluminium, or magnesium ethoxide, after distillation of the methyl alcohol and removal of unchanged methyl anthranilate, affords *geranyl anthranilate*, b. p. 188°/4 mm. Esters of tertiary alcohols are readily obtained by leaving the alcohol for several days in contact with excess of acetic–formic anhydride. The formate thus obtained is mixed with 1 mol. of the methyl ester of the desired acid and treated with 0·025*M* of the sodium derivative of the tertiary alcohol at 100—120°, affording methyl formate and the required ester.

These exchanges suggest that organic compounds containing metals are capable of ionising, affording ions containing the metal which give reactions strictly parallel to those between metallic salts and bases but differing in order of velocity. R. BRIGHTMAN.

Glyceraldehyde and glycollaldehyde. H. O. L. FISCHER and C. TAUBE [in part with L. Feldmann] (Ber., 1927, 60, [*B*], 1704—1709; cf. this vol., 340).—Diacetylglyceraldehyde is converted by glacial acetic and hydrobromic acids into dimeric *acetobromoglyceraldehyde*, $\left[\begin{matrix}O\text{—}\\ CHBr\end{matrix}\!\!>CH\cdot CH_2\cdot OAc\right]_2$, m. p. 168—169° (decomp.), which is converted by methyl alcohol and silver carbonate into *acetylglyceraldehyde methylcycloacetal*, m. p. 101·5—102·5°, and thence by methylalcoholic ammonia into *glyceraldehyde methylcycloacetal*, $\left|\begin{matrix}O\text{—}\\ CH(OMe)\end{matrix}\!\!>CH\cdot CH_2\cdot OH\right|$, m. p. 158·5—159·5° Crude acetobromoglyceraldehyde is hydrolysed by silver carbonate and aqueous acetone to dimeric *acetylglyceraldehyde*, m. p. 118·5°, the m. p. of which is depressed by crystallisation probably by reason of migration of the acyl groups. The successive action of hydrogen chloride and methyl alcohol and silver carbonate on dihydroxyacetone affords the corresponding methyl*cyclo*acetal, $\begin{matrix}O\\ CH_2\end{matrix}\!\!>C(OMe)\cdot CH_2\cdot OH$, m. p. (anhydrous) 131—132°, m. (+H_2O) 91° (corresponding *acetate*, m. p. 138°).

Glycollaldehyde is conveniently prepared by heating dihydroxymaleic acid in pyridine at 50—55°, removal of the latter under diminished pressure, and subsequent distillation of the residue. It may also be prepared by ozonisation of allyl or cinnamyl alcohol and treatment of the ozonides with zinc dust and glacial acetic acid. The refractive index of the freshly-distilled substance undergoes rapid increase to a constant value, possibly indicating intramolecular transformation. The aldehyde is converted by acetic anhydride and pyridine into dimeric *acetylglycollaldehyde*, $\left[\begin{matrix}O\\ CH_2\end{matrix}\!\!>CH\cdot OAc\right]_2$, m. p. 157—158°, which is transformed by hydrogen bromide in glacial acetic acid into dimeric *bromoglycollaldehyde* (*bromoethylene oxide*), m. p. about 136° (decomp.), and thence into *glycollaldehyde methylcycloacetal*, m. p. 72°; glycollaldehyde ethyl*cyclo*acetal, m. p. 59·5°, is similarly prepared.

H. WREN.

Isolation of ketones by means of their oxonium compounds. W. TSCHELINCEV and (MLLE.) L. NASAROV (Bull. Soc. chim., 1927, [iv], 41, 805—808).—Addition of an ethereal solution of magnesium bromide to a solution of a ketone or ether oxide in benzene or light petroleum affords a crystalline precipitate consisting of magnesium bromide combined with 2 or 3 mols. of ketone (cf. A., 1924, i, 929), which can be utilised for the separation of ketones. Compounds of magnesium bromide with the following are described: acetone (3 mols.); methyl ethyl ketone (3 mols.); γ-methylpentane-ββ-dione (3 mols.); and camphor (2 mols.). The *dietherate*, $2Et_2O,MgBr_2$, is also described. R. BRIGHTMAN.

Electrolytic reduction of acetone. E. MÜLLER. —See this vol., 840.

Reduction of oximes of unsymmetrical ketones and of β-ketonic esters. P. BILLON.—See this vol. 879.

Hydroxymethylenemesityl oxide. H. PAULY and L. STRASSBERGER (Ber., 1927, 60, [*B*], 1679—1680).—*Hydroxymethylenemesityl oxide* [*γ-keto-ε-methyl-*$\Delta^{\alpha\delta}$*-hexadien-α-ol*], b. p. 55—56°/4·5 mm.,

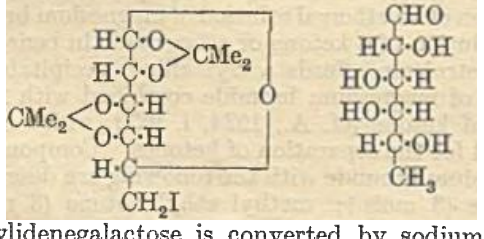
38°/0 mm., $d_4^{23\cdot5}$ 1·0034, $n_\alpha^{23\cdot5}$ 1·50765, $n_D^{23\cdot5}$ 1·51574, 1·53790, is prepared by the addition of a mixture of ethyl formate and mesityl oxide to sodium wire covered by ether. The corresponding *copper* salt, m. p. 130°, *anil*, $C_{13}H_{15}ON$, m. p. 60°, *semicarbazone*, m. p. 178°, and iso*oxazole*, b. p. 193—194°, are described. H. WREN.

Structural relationships in the carbohydrate group. W. N. HAWORTH (J.S.C.I., 1927, **46**, 295—300T).

***l*-Arabinal.** J. MEISENHEIMER and H. JUNG (Ber., 1927, **60**, [*B*], 1462—1465; cf. Gehrke and Aichner, this vol., 544).—*l*(+)-Acetobromoarabinose (cf. Hudson and Dale, A., 1918, i, 335), conveniently prepared by the action of hydrogen bromide and acetic anhydride on *l*-arabinose at 0°, is reduced by zinc dust and acetic acid to *l*-diacetylarabinal which could not be caused to crystallise. It is converted by cold barium hydroxide solution into *l*-arabinal, m. p. 81—83°, $[\alpha]_D$ −202·8° in water, which is not hygroscopic and can be preserved unchanged in presence of air. Cautious treatment of *l*-arabinal with *N*-sulphuric acid affords l-*deoxyarabinose*, $C_5H_{10}O_4$, m. p. about 90° after softening at 80° (*phenylbenzylhydrazone*, m. p. 127—129°). H. WREN.

Dynamic isomerism. XXIII. Mutarotation in aqueous alcohols. E. M. RICHARDS, I. J. FAULKNER, and T. M. LOWRY (J.C.S., 1927, 1733—1739).—In the mutarotation of dextrose and tetramethylglucose in aqueous alcohols, abrupt breaks occur in the velocity coefficient–water concentration curves at 50% and 70% of water in the case of methyl and ethyl alcohols respectively. Curves showing the variation of dielectric constant or the partial vapour pressure of the water in the water–alcohol solutions give no indication of this change. A connexion between the hydrogen-ion concentration of the medium and velocity of mutarotation is highly probable. B. W. ANDERSON.

Acetone sugars. XII. Transformation of *d*-galactose into *d*-fucose [rhodeose]. K. FREUDENBERG and K. RASCHIG (Ber., 1927, **60**, [*B*], 1633—1636).—The *p*-toluenesulphonyl derivative of di*iso*-

(I.)  (II.)

propylidenegalactose is converted by sodium iodide in acetone at 125° into the corresponding *iodohydrin*, (I), m. p. 72°, $[\alpha]_D^{18}$ −50·4° in *s*-tetrachloroethane, which is reduced by sodium and moist ether to crude di*iso*propylidene-*d*-fucose from which *d*-fucose, m. p. 140—145°, $[\alpha]_D$ +75·7° in water (final value), is derived, thus confirming the structure (II) for the methylpentose. Homogeneous *diisopropylidene*-d-*fucose*, prepared from *d*-fucose, acetone, and sulphuric acid, has m. p. 37°, $[\alpha]^{18}$ −52·4°, $[\alpha]_{546}^{19}$ −61·7° in substance. *Di*iso*propylidene*-l-*fucose*, m. p. 37°, $[\alpha]_D^{18}$ +52·2°, $[\alpha]^{19}$ +62·1°, and *diisopropylidene*-dl-*fucose*, m. p. 41°, are described. H. WREN.

Acyl wandering. B. HELFERICH and W. KLEIN (Annalen, 1927, **455**, 173—180).—The isomerisation of β-*d*-glucose 1 : 2 : 3 : 4-tetra-acetate (this vol., 135) also proceeds in the fused substance at 140° in ordinary glass or platinum vessels, but not in Jena glass or quartz, and is conveniently effected by 0·001*N*-sodium hydroxide at the ordinary temperature. Since the same equilibrium product is obtained from either isomeride the change closely resembles the mutarotation of a sugar; the latter is therefore no longer a certain proof of the presence of a 1-hydroxyl group. β-*d*-Glucose 1 : 2 : 3 : 6(?)-tetra-acetate gives with methyl iodide and silver oxide a small yield of β-methylglucoside tetra-acetate; this must be due to further acyl wandering since the starting product is not identical with *d*-glucose 2 : 3 : 4 : 6-tetra-acetate. Pure β-*d*-glucose 1 : 2 : 3 : 6(?)-tetra-acetate 4(?)-toluenesulphonate, m. p. 117—118°, sintering from 112°, $[\alpha]_D^{18}$ −19·3° or −10·1°, is converted by careful hydrolysis (Zemplén, A., 1926, 822) into d-*glucose* 4(?)-*toluenesulphonate*, m. p. 165—167° (decomp.), $[\alpha]_D$ +23° to $[\alpha]_D^{18}$ +41°. On reacetylation the latter gives the initial tetra-acetate, which is not identical with glucose tetra-acetate 3-toluenesulphonate (Freudenberg, A., 1922, i, 523). H. E. F. NOTTON.

Influence of solvent and of concentration on optical rotation of penta-acetylglucose and penta-acetylmannose. P. A. LEVENE and I. BENCOWITZ (J. Biol. Chem., 1927, **73**, 679—694).—Curves and tables are given showing, for the penta-acetyl derivatives of α- and β-glucose and α- and β-mannose, the relationship between the actual and specific rotations and the concentration in various solvents. Most of the curves relating actual rotation to concentration show a break at a certain concentration, and the curves for the different solvents diverge more widely as the concentration increases. Specific rotation changes rapidly with concentration in the strong solutions, and very little in the dilute solutions. The numerical order in which the solvents arrange themselves as regards their effect on rotation is the same for the two dextrose derivatives but different for each of the mannose derivatives, except that all forms show the lowest rotation in pyridine. The possible bearing of these observations on the structure of the penta-acetyl derivatives is discussed. C. R. HARINGTON.

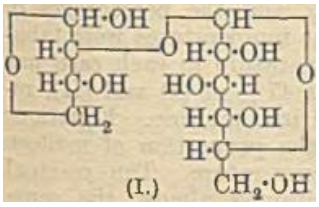
Two new pentabenzoylglucoses. H. H. SCHLUBACH and W. HUNTENBURG (Ber., 1927, **60**, [*b*], 1487—1488).—α-*Pentabenzoyl*-h-*glucose*, m. p. 118—120°, $[\alpha]_D^9$ +58·6° in chloroform, is prepared by the action of benzoyl chloride and pyridine in the presence of chloroform on the additive compound of carbon tetrachloride and tribenzoylglucose derived from *iso*-propylideneglucose (cf. Fischer and Rund, A., 1910, i, 363). If the tribenzoylglucose is treated with benzoyl chloride and 20% sodium hydroxide, *benzoyl*-h-*glucose*, m. p. 149—151°, $[\alpha]_D$ −52·6 in chloroform, is produced. H. WREN.

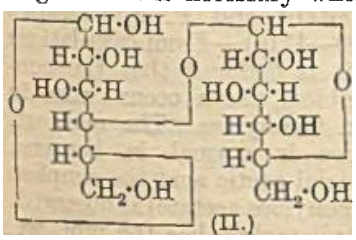
Action of benzylamine on dextrose in acetic acid. III. C. N. CAMERON (J. Amer. Chem. Soc., 1927, **49**, 1759—1765; cf. A., 1926, 1228).—*Glucose-benzylamide*, m. p. 81·5°, $[\alpha]_D^{22}$ −22·66° in methyl alcohol, is obtained by boiling dextrose in 95% alcohol with 3 mols. of benzylamine. The optica

rotation of a solution of dextrose and benzylamine in alcohol at the ordinary temperature first becomes slightly more positive, then less positive, and finally negative (cf. Irvine, J.C.S., 1908, **93**, 1429; 1910, **97**, 1449). If acetic acid (2 mols. per mol. of benzylamine) is also present, the first change to positive rotation is eliminated. The reaction between dextrose and benzylamine in alcohol is also catalysed by acetic acid in amount only sufficient to keep the solution approximately neutral. These acetic acid solutions become coloured, due to reaction between the acetic acid and the glucosebenzylamide, and contain methylglyoxal, identified as the *p*-nitrophenylosazone. In aqueous solution, glucosebenzylamide is hydrolysed to dextrose and benzylamine. In presence of a trace of acetic acid, glucosebenzylamide is formed from its constituents, and a small proportion of brown oil is precipitated. If the acetic acid is present in the proportion of 1 mol. per mol. of benzylamine, no reaction takes place. F. G. Willson.

Sugar syntheses. VII. Synthesis of primeverose. B. Helferich and H. Rauch (Annalen, 1927, **455**, 168—172).—β-*d*-Glucose 1 : 2 : 3 : 4-tetra-acetate (this vol., 135) condenses with acetobromoxylose in chloroform in presence of silver oxide to give 6-β-d-*xylosido*-d-*glucose hepta-acetate*, m. p. 216° (corr.), $[\alpha]_D^0$ −23·5° in chloroform. This is hydrolysed by the method of Zemplen (A., 1926, 822) to 6-β-d-*xylosido*-d-*glucose*, m. p. 208°, sintering from 192°, $[\alpha]_D^{20}$ +23·8° to −3·4° in water, which has been identified with primeverose (Goris, Mascre, and Vischniac, A., 1913, i, 576; 1920, i, 14; Bridel, A., 1925, i, 760) by conversion into its osazone, m. p. 220°, $[\alpha]_D^{19}$ −109·7° or −108° in pyridine. H. E. F. Notton.

Degradation of reducing bioses. VII. Constitution of maltose. G. Zemplén (Ber., 1927, 60, [*B*], 1555—1564).—Maltose, purified by conversion into the β-octa-acetate followed by hydrolysis of the latter compound with barium hydroxide or, preferably, sodium methoxide, is converted into the non-crystalline *oxime*, $[\alpha]_D^{19}$ +85·6° in water, which is transformed by acetic anhydride and sodium acetate into *octa-acetylmaltobiononitrile* mixed with acetylated maltoseoxime. The product is dissolved in chloroform and treated with methyl-alcoholic sodium methoxide; the material thus obtained is re-acetylated and, since further quantities of octa-acetylmaltobiononitrile are thereby produced from the acetylated maltoseoxime, a repetition of the degradation is necessary whereby ultimately a product containing 49·7% of hepta-acetylglucoarabinose is isolated. The free glucoarabinose obtained by hydrolysing the hepta-acetate with barium hydroxide is transformed into the oxime which is acetylated and degraded in the usual manner.


(I.)


(II.)

Treatment of the product with phenylhydrazine affords small amount of the phenylosazones of glucoarabinose and maltose, whereas the *d*-gluco-*d*-erythrose (I) is incapable of yielding an osazone. The structure (II) for maltose is thus confirmed.

β-Octa-acetylmaltose dissolved in chloroform is converted by hydrogen iodide and subsequent treatment with silver oxide into hepta-acetylmaltose, m. p. 176°. The product does not yield furfuraldehyde when subjected to Tollens' reaction and hence has not suffered degradation (cf. Irvine and Dick, J.C.S., 1919, **115**, 593). H. Wren.

Constitution of the disaccharides. XIII. The γ-fructose residue in sucrose. W. N. Haworth, E. L. Hirst, and V. S. Nicholson (J.C.S., 1927, 1513—1526).—In presence of dilute hydrochloric acid tetramethyl-γ-fructose is converted into *ω-methoxy-5-methylfurfuraldehyde*, b. p. about 54°/0·07 mm. (*oxime*, m. p. 103—104°; *semicarbazone*, m. p. 166—167°). On oxidation this gives *ω-methoxy-5-methylfuran-2-carboxylic acid*, m. p. 72—73°, which is also formed by methylation of *ω-hydroxy-5-methylfuran-2-carboxylic acid*, m. p. 165·5—167°, obtainable either by hydrolysis and oxidation of ω-bromo-5-methylfurfuraldehyde or by acetylation and subsequent hydrolysis of chitonic acid. The above inter-relationships confirm the substituted hydrofuran formula previously suggested (cf. A., 1926, 1126) for tetramethyl-γ-fructose. The action of dilute nitric acid converts tetramethyl-γ-fructose into a trimethoxylactol ethyl ester, $C_{11}H_{20}O_7$, which it is difficult to obtain in a pure condition. The corresponding methyl ester on methylation gives a product from which a crystalline amide, m. p. 100—101°, is obtainable. B. W. Anderson.

Constitution of the disaccharides. XIV. Melibiose and its relationship to raffinose. W. Charlton, W. N. Haworth, and W. J. Hickinbottom (J.C.S., 1927, 1527—1536).—Hydrolysis of heptamethyl-methylmelibioside (after repeated recrystallisation, m. p. 106—107°, $[\alpha]_D$ +97·8°) which had been encountered formerly during the isolation of hendecamethylraffinose (J.C.S., 1923, **123**, 3125) was found to yield 2 : 3 : 4 : 6-tetramethylgalactose and a liquid trimethylglucose which on methylation formed 2 : 3 : 4-trimethyl-α- and -β-methylglucosides. This confirms the modified formula for melibiose advanced by Charlton, Haworth, and Peat (A., 1926, 273). B. W. Anderson.

Lactose solubility and lactose crystal formation. II. O. F. Hunziker and B. H. Nissen (J. Dairy Sci., 1927, **10**, 139—154).—Saturated lactose solutions containing milk colloids yield normal crystals; sucrose prevents their full development. Crystals in ordinary sweetened condensed milk are of lactose. Chemical Abstracts.

Melezitose a compound of sucrose with dextrose? M. Bridel and C. Aagaard (Compt. rend., 1927, **185**, 147—148).—The results obtained with enzyme preparations made from *Aspergillus niger* show that a preparation which acts slowly on sucrose may hydrolyse melezitose rapidly, and *vice versa*. The non-identity of the enzymes which attack sucrose and melezitose, thus demonstrated, disproves

Kuhn and von Grundherr's view that melezitose is a compound of sucrose with dextrose (A., 1926, 1127), and the nature of the non-reducing *d*-fructose united with the dextrose remains to be determined.

T. H. POPE.

Lichenin. III. Lichenin, Pringsheim's lichosan, and Bergmann's lichohexosan. K. HESS and H. FRIESE (Annalen, 1927, 455, 180—205).—Attempts to purify lichenin by dissolution in hot water were unsuccessful, but by reprecipitation from alkaline solution by means of carbon dioxide or concentrated sodium hydroxide, and finally from a cuprammonium solution as a copper–alkali compound, a non-reducing product, $[\alpha]_D^{20}$ +8·33° in 2*N*-sodium hydroxide, is obtained. In cuprammonium solution this shows a similar optical behaviour to that of cellulose, the rotation being first increased and then lowered by addition of sodium hydroxide. The formation of a single copper complex containing 9Cu : $10C_6H_{10}O_5$ is indicated, but it is probable that the lichenin still contains inactive impurities and that the actual ratio is 1 : 1. Lichenin triacetate, purified by repeated reprecipitation, has $[\alpha]_D^{20}$ −38° to −39° in chloroform. Previous work (A., 1926, 715) which has been overlooked by Pringsheim (A., 1925, i, 1385; this vol., 136) and by Bergmann and Knehe (A., 1926, 714; cf. this vol., 341) has shown that heating at 235° in naphthalene is not necessary to depolymerise this substance, since this is effected in glacial acetic acid at the ordinary temperature. It is suggested that the changes produced by the former treatment are due to the partial decomposition of the acetate. Lichosan (lichohexosan), $[\alpha]_D^{19}$ ±0° in water, +30·4° in 2*N*-sodium hydroxide, prepared by the glycerol method contains 6% of reducing matter (as dextrose; Allihn's method). In accordance with the results of Pringsheim and of Bergmann it gives a triacetate, $[\alpha]^{19}$ −20° in chloroform. Neither of these substances is, however, pure. The former is separated by one precipitation from aqueous alcohol into fractions of widely-differing rotation, whilst repeated fractional precipitation of the acetate affords a product, $[\alpha]_D$ −35·9° in chloroform, identical with lichenin triacetate and yielding on hydrolysis a non-reducing lichosan (lichenin), $[\alpha]_D^{20}$ +8·42° in 2*N*-sodium hydroxide, which is sparingly soluble in cold water. Lichosan is therefore lichenin which contains sufficient impurity to render it water-soluble. The bearing of these facts on the theoretical considerations of Pringsheim and of Bergmann is fully discussed and it is suggested that further work on lichenin must be preceded by its isolation in a pure state.

H. E. F. NOTTON.

Yeast gum and the purification of compounds with high mol. wt. by adsorption. H. KRAUT and F. EICHHORN (Ber., 1927, 60, [*B*], 1639—1643).—Purification of yeast gum is effected by treating a definite quantity of the product in a constant volume of solution with varying amounts of adsorbent and determination of the optical activity of the residual solution; purification is regarded as complete when the adsorption isotherm follows a normal course. Yeast gum, prepared according to Salkowski's method consists of 14% of reducing sugars readily adsorbed by kaolin (but not by aluminium orthohydroxide) and 86% of the pure gum, $(C_6H_{10}O_5)_n$, $[\alpha]_D^{20}$ +88·8°. The crude and pure materials differ little in chemical composition and in general properties except towards Fehling's solution. Towards chlorine dioxide their behaviour is almost identical.

H. WREN.

Preparation of yeast gum by enzymic degradation and the detection of an enzyme in yeast which hydrolyses yeast gum. H. KRAUT, F. EICHHORN, and H. RUBENBAUER (Ber., 1927, 60, [*B*], 1644—1648; cf. preceding abstract).—The isolation of yeast gum by Salkowski's method involves the use of 3% sodium hydroxide solution and hence the possibility that the gum is to some extent denatured. The product has therefore been isolated by successive treatments of yeast with ethyl acetate, pepsin, and either papain with or without hydrocyanic acid as activator or diastase; it is remarkable that papain is most active in absence of the activator. Products of low mol. wt. are removed by precipitation with alcohol and dialysis and final purification is achieved by adsorption with kaolin and aluminium hydroxide. The substance appears identical with Salkowski's yeast gum, but comparison of the adsorption isotherms of the products suggests that their degree of dispersivity differs. Since the sum of the amounts of yeast gum obtained by the fermentation process and remaining in the unfermentable residue is considerably less than that obtained by Salkowski's method, it must be assumed that an enzyme is present in yeast which hydrolyses yeast gum and retains its activity after treatment of the yeast with ethyl acetate at 37°. The enzyme appears present in the yeast in an unusual manner and separated from the yeast gum. It is liberated by definite processes during autolysis or plasmolysis. Yeast gum is not hydrolysed by taka-diastase, emulsin, or the extracts from *Aspergillus niger* or malt.

H. WREN.

Saccharification of dextrins. P. PETIT and RICHARD (Compt. rend., 1927, 185, 224—225).—Dextrins prepared by the action of amylase on starch paste at 50° (I) and 70° (II) were submitted to the further action of amylase, and the percentages of maltose formed at different temperatures were tabulated. The optimum temperature in each case was about 52°, when 13% and 47% of (I) and (II), respectively, were converted into maltose. Equations are suggested for giving the proportion of maltose formed at any given temperature. The residua dextrins in all cases contained almost the same percentage of dextrose.

B. W. ANDERSON.

Recent advances in our knowledge of starch. A. R. LING (J.S.C.I., 1927, 46, 279—281T).

Starch. XX. Disaggregation of the polyamyloses. H. PRINGSHEIM and P. MEYERSOHN (Ber., 1927, 60, [*B*], 1709—1716).—From calculations of the mol. rotations it is deduced that the configuration of the amylobiose union occurs once in diamylose and twice in triamylose. The mol. w of tetra(triacetyl)amylose is normal in benzene, whereas in phenol or glacial acetic acid the simp es possible value (that of diamylose acetate) is observe . Similarly, α-hexa(triacetyl)amylose has the mo . w . of diamylose acetate in phenol. It has not

found possible to obtain solvents in which the acetates of β-tri- and β-hexa-amylose show differing behaviour. Both acetates give the value for the triacetate in glacial acetic acid or phenol and of the hexa-acetate in benzene. Tetra(triacetyl)amylose and α-hexa-(triacetyl)amylose pass in boiling naphthalene into the acetate of diamylose, from which diamylose is obtained by hydrolysis. H. WREN.

Conditions under which the iodine–starch reaction does not occur normally. M. J. GRAMENITZKI (Biochem. Z., 1927, **185**, 427—428).—In presence of excess of potassium iodide, hydrogen peroxide, and an acid, the blue colour given by iodine and starch is intensified, instead of being abolished, by heat. C. R. HARINGTON.

Inulin. III. L. SCHMID and G. BILOWITZKI (Monatsh., 1927, **48**, 163—165).—Inulin dissolved in dry piperidine does not elevate the b. p. of the latter, and is thus not depolymerised (cf. A., 1925, i, 1386; this vol., 342). E. W. WIGNALL.

Cellulose. XXVI. Crystalline triethylcellulose. K. HESS and A. MÜLLER (Annalen, 1927, **455**, 205—214).—Ethylation of alkali-cellulose with ethyl chloride gives only the diethyl ether (cf. A., 1921, i, 710), but by using ethyl sulphate and alkali as described for cellobiose (A., 1925, i, 1383) *triethylcellulose*, m. p. 255°, sintering from 240°, $[\alpha]_D^{20}$ +26·1° in chloroform, +49·1° in pyridine, is obtained. The products from cellulose-*A* (73%), viscose-cellulose (64%), and cuprammonium-cellulose (84% of theoretical yield) are chemically identical and, unlike trimethylcellulose (this vol., 44), insoluble in water. The pure substance crystallises readily from benzene, but if separation is too rapid an amorphous powder or elastic film is obtained. H. E. F. NOTTON.

Cellulose. XXVII. Oxycellulose. K. HESS and G. KATONA (Annalen, 1927, **455**, 214—226).—Further evidence is adduced in favour of the view that oxycellulose is a mixture of cellulose with products of its oxidative degradation (cf. A., 1925, i, 519). Cellulose has been oxidised by means of bromine water and calcium carbonate (Faber and Tollens, A., 1899, i, 854), permanganate (Nastjukoff, A., 1901, i, 315), nitric acid (Cross and Bevan, J.C.S., 1883, **43**, 22), and chromic acid (Vignon, A., 1898, i, 620). The products cannot be purified by boiling with water, owing to hydrolysis, but complete purification is effected by prolonged extraction with 5% sodium hydrogen carbonate (5—15% loss), and finally with 0·5*N*-sodium hydroxide. No cellulose-like matter is extracted by the sodium hydrogen carbonate, but only simple compounds similar to those which pass into solution during the initial oxidation of the cellulose. The purified oxycellulose shows a diminished solubility in 2*N*-sodium hydroxide from which it is almost quantitatively reprecipitated by acetic acid. Its specific rotation–concentration curve in cuprammonium solution is identical with that of pure cellulose.
H. E. F. NOTTON.

Cellulose. XXVIII. Formation of cellobiose. Acetolysis of cellulose. III. H. FRIESE and K. HESS (Annalen, 1927, **456**, 38—54; cf. this vol., 44, and preceding abstract).—The conversion of cellulose into cellobiose, determined as octa-acetate, during acetolysis with acetic anhydride and sulphuric acid is independent of the origin, pre-treatment, or physical condition of the cellulose. The yield in all cases is about 50% of the theoretical. The polarimetric changes during acetolysis show a similar parallelism for the different celluloses examined (Kahlbaum cotton, linters, ramie, wood cellulose, mercerised cotton; these have already been shown by Hess, Messmer, and Lubitsch, A., 1925, i, 1246, to be chemically identical). Experiments with cellulose triacetate, which in dilute solution in glacial acetic acid has the low mol. wt. of acetylglucosan, show that the formation of cellobiose is also independent of the state of association of the cellulose derivative, a yield of 39·5% being obtained. C. HOLLINS.

Cellulose. XXIX. Preparative separation of cellulose crystals from bast fibres. I. From ramie fibres. K. HESS and G. SCHULTZE (Annalen, 1927, **456**, 55—68).—Selected ramie fibre, repeatedly purified with alkali, chlorine dioxide, and sodium sulphite until ash-free ($\alpha_{435\cdot8}^{t}$ +3·41° in cuprammonium hydroxide solution), is acetylated for 8 hrs. at 70—75° with sulphuric acid, acetic anhydride, and benzene, and the triacetate dissolved out in glacial acetic acid or chloroform. The unacetylated cellulose appears in the form of spindle-shaped crystals, 0·05—0·1 mm. long, suspended in the solution, and may be separated by sedimentation from the detritus with which it is mixed. The crystals are identical chemically with pure cellulose prepared from crystallised diacetate. The "intercrystal substance" which is removed as triacetate, when regenerated from the latter by hydrolysis with 2*N*-methyl-alcoholic sodium hydroxide, shows in cuprammonium solution a slightly smaller optical rotation than the crystals. C. HOLLINS.

Lignin. III. Tautomeric forms in soluble lignin. A. FRIEDRICH (Z. physiol. Chem., 1927, **168**, 50—67).—The preparation of the soluble lignin of pine wood, free from impurities which have similar properties, is described, and it is found that the products can be separated by boiling chloroform into two substances differing only in solubility and colour. These two products are readily interconvertible, and from the colour reactions with ferric chloride and behaviour towards bromine they are regarded as enolic and ketonic forms. The enolic form (chloroform-soluble) has a mol. wt. of about 650, whilst that of the ketonic form is about double this value.
A. WORMALL.

Ultra-violet absorption spectra of lignin and substances with the coniferyl residue. R. O. HERZOG and A. HILLMER (Z. physiol. Chem., 1927, **168**, 117—123; cf. this vol., 342).—The absorption curves of coniferin, coniferyl alcohol, and polymerised coniferyl alcohol have similar shapes but show some differences, especially in the region of the shorter waves. The curve for the polymeride is most like that of ligninsulphonic acid, but the results suggest that the molecule of the latter consists in part only of coniferyl complexes. A. WORMALL.

Humus substances. E. SCHMIDT and M. ATTERER (Ber., 1927, **60**, [*B*], 1671—1679). Furfur-

aldehyde or humus substances of differing origin are allowed to remain in the dark during 9 days in contact with 3% chlorine dioxide solution in the presence of precipitated calcium carbonate and a trace of vanadium chloride. After removal of excess of chlorine dioxide, the calcium oxalate produced is isolated and weighed as calcium oxide or the oxalic acid is isolated from it if the salt is very impure; maleic acid is isolated as such from the filtrate and weighed or converted into calcium maleate and weighed as calcium oxide. In addition to the acids, an ill-defined degradation product of the humus is formed which contains calcium in varying amount. Since the amounts of oxalic acid formed from the same initial material under apparently identical conditions fluctuate considerably it is impossible to attach any well-defined theoretical significance to them. The mean quantities in g. of maleic acid derived from 10 g. of the various products are indicated by figures placed after the names: furfuraldehyde, 8·2; humin from furfuraldehyde, 4·32; humic acid from furfuraldehyde, 2·55; humic acid from sucrose, 1·00; humic acid from dextrose, 1·10; humic acid from sphagnum moss, 0·94; humic acid (Merck), 0·85; humic acid from quinol, 1·00; humic acid from pyrogallol, 0·75. The production of maleic acid appears to depend on the presence of the group C·CH:CH·C or C:CH·CH:C, which may occur in either the benzene or furan ring. Since, however, it may be assumed that maleic acid is formed with equal readiness and therefore in equal amount from substances containing a similar arrangement of the C_4 chain it appears that a structural difference in respect to this group exists between the products derived from furfuraldehyde and the humic acids from the carbohydrates, phenols, and moss.

The relative quantities of maleic acid derived from furfuraldehyde humus and the corresponding humic acid support the view that the action of potassium hydroxide on the former is accompanied by a profound change and does not consist merely in hydration.

H. WREN.

Infra-red absorption spectra of organic derivatives of ammonia. V. Primary, secondary, and tertiary alkylamines. F. K. BELL (J. Amer. Chem. Soc., 1927, **49**, 1837—1845; cf. A., 1926, 453).—The infra-red absorption spectra of mono-, di-, and tri-*n*-propyl-, -*n*-butyl-, and -*iso*amyl-amines have been examined. All show the band at 3·45 μ, characteristic of the methyl group, a less intense band at 6·85 μ probably related harmonically to the former, and bands of uniform intensity throughout the series at 7·2—7·3 μ and about 9·3 μ. The primary amines show a marked band at 3·05 μ. This persists at lower intensity with the secondary amines, but is practically absent with the tertiary derivatives, thereby confirming earlier results on the differentiation between the three classes of amines. The primary amines are differentiated further from the secondary and tertiary amines by a band at about 6·2 μ.

F. G. WILLSON.

Hexamethyleneimine. III. J. VON BRAUN and O. GOLL (Ber., 1927, **60**, [*B*] 1533—1534; cf. A., 1910, i, 821).—By the action of alkali on ζ-bromo-*n*-hexylamine in quantity it has been found possible to isolate *hexamethyleneimine*, b. p. 134—135°/759 mm., d_4^{22} 0·8643, n_D^{23} 1·4570 (*hydrochloride*, m. p. 222°). In addition, *α-amino-ζ-Δ$^{\epsilon'}$-hexenylamino-*n*-hexane*, CH_2:CH·$[CH_2]_4$·NH·$[CH_2]_6$·NH_2, b. p. 137—140°/12 mm., d_4^{22} 0·8990, is produced; the *hydrochloride*, m. p. 188°, *chloroplatinate*, decomp. 215°, *methiodide*, $C_{17}H_{38}N_2I_2$, m. p. 223°, and the non-crystalline *picrate* and *benzoyl* derivative are described.

H. WREN.

Decomposition of quaternary ammonium hydroxides. Methylalkoxymethyldiethylammonium hydroxides. T. D. STEWART and J. G. ASTON (J. Amer. Chem. Soc., 1927, **49**, 1718—1728).—When an aqueous solution of methylethoxymethyldiethylammonium hydroxide is evaporated at the ordinary temperature in a vacuum over phosphoric oxide, it commences to decompose when the composition of the solution approximates to that of a tetrahydrate of the base, yielding methyldiethylamine (18·5 mols.%) and methylethylamine (81·5 mols. %), the latter being accompanied by an equivalent of ethylene. Above 100°, at atmospheric pressure, decomposition takes place with formation of methyldiethylamine almost exclusively. Treatment of dimethylaminomethyl *iso*butyl ether (Robinson, J.C.S., 1923, **123**, 536) with ethereal methyl iodide affords *trimethylisobutoxymethylammonium iodide*, m. p. 103—110°, from which the corresponding *hydroxide* (*chloroplatinate*, decomp. 231—233°) was prepared in aqueous solution. On evaporation of the latter at the ordinary temperature as above, decomposition takes place with the production of trimethylamine as the only amine. Dimethyldiethylammonium hydroxide decomposes similarly in aqueous solution with formation of ethylene and dimethylethylamine. The carbonate decomposes in aqueous solution, a solid *hydrogen carbonate* being precipitated. The latter decomposes when heated, yielding ethylene, dimethylethylamine, carbon dioxide, and water. Fused methylethoxymethyldiethylammonium iodide has d^{110} 1·361o, Λ 2·56 at 110°.

F. G. WILLSON.

So-called carbohydrate group of protein. Preparation of glucosaminomannose. S. KEL and C. JELLINEK (Biochem. Z., 1927, **185**, 39[illegible]—399).—Egg-white was hydrolysed with barium hydroxide; the barium was removed as carbonate and the filtrate treated with lead acetate and ammonia, the precipitate was dissolved in dilute acetic acid, re-precipitated, collected, and decomposed with carbon dioxide; the filtrate from the lead carbonate was treated with mercuric chloride and, after some days, was filtered, concentrated, and treated with alcohol. The aqueous solution of the resulting precipitate was treated with cupric chloride and a[illegible], the precipitated copper compound was dissolved in methyl alcohol and treated with hydrochloric acid and excess of ether; the resulting precipitate the formula $C_{12}H_{23}O_{10}N$; similar preparations were obtained from egg-white and from egg-yolk al[illegible] by tryptic digestion followed by purification described above. In both cases the produc[illegible] optically inactive. On hydrolysis with [illegible] acid, the substance yields glucosamine hydroc[illegible] and mannose; the absence of free amino-n[illegible]

indicates that, in this compound, glucosamine must be combined with mannose through the amino-group. C. R. HARINGTON.

Degradation of amino-acids and aminopurines by methylglyoxal and related substances. C. NEUBERG and M. KOBEL (Biochem. Z., 1927, 185, 477—479).—When heated in aqueous solution, methylglyoxal and alanine react to form carbon dioxide, ammonia, and acetaldehyde. Reactions of similar type occur, in general, between glyoxal derivatives or dihydroxyacetone, and amino-acids or aminopurines. C. R. HARINGTON.

Synthesis of taurine. C. S. MARVEL, C. F. BAILEY, and M. S. SPARBERG (J. Amer. Chem. Soc., 1927, 49, 1833—1837).—Treatment of ethylene dibromide (615 g.) in boiling 95% alcohol (1250 c.c.) and water (450 c.c.) with anhydrous sodium sulphite (125 g.) in water (450 c.c.) affords sodium β-bromoethylsulphonate in 78—90% yield. Treatment of the latter with an equal weight of phosphorus pentachloride yields *β-bromoethylsulphonyl chloride*, b. p. 119—121°, d^{20} 1·921, n_D^{20} 1·5242 (yield 64—71%). When the latter is treated with water until solution is complete, the solution evaporated under reduced pressure, and the residue treated with concentrated aqueous ammonia, taurine is obtained in 16% yield, whilst a 44—51% yield of taurine is obtained by keeping sodium β-bromoethylsulphonate in aqueous ammonia for 5—7 days, and subsequently evaporating to dryness and extracting the residue with alcohol. F. G. WILLSON.

Diacylamides. II. Preparation of dipropionamide and di*iso*butyramide. K. BRUNNER, R. GRUNER, and Z. BENES (Monatsh., 1927, 48, 123—124; cf. A., 1924, i, 1310).—Dipropionamide is obtained by heating potassium cyanate with propionic anhydride at 100°, adding benzene, and re-heating; di*iso*butyramide by using *iso*butyric anhydride and heating at 138—140°. E. W. WIGNALL.

Peralkylated guanidines. IV. H. LECHER [with F. GRAF, F. GNADINGER, K. BOLZ, and K. CHUDOBA] (Annalen, 1927, 455, 139—168).—*NNN′-Triethyl-S-methyl-ψ-thiocarbamide*, b. p. 85°/12 mm. (corr.), is obtained by boiling together diethylamine and ethylthiocarbimide in benzene and methylating the product (cf. A., 1925, i, 1392). With diethylamine and mercuric chloride it gives *pentaethylguanidine*, b. p. 93—94°/13 mm., from which *hexaethylguanidinium iodide* is obtained. *Hexaethylguanidinium picrate*, m. p. 90·5—92°, forms an additive *product*, m. p. 164—166°, with sodium picrate (1 mol.), but it does not separate in combination with hexamethylguanidinium picrate from solution or from a mixed mixture. Pentamethylthiuronium picrate gives an equimolecular additive *product*, m. p. 175·5—°, with sodium picrate. *Hexamethylguanidinium* :4:6-*trinitro*-m-*tolyloxide*, m. p. 100—102°, from e corresponding iodide and *thallous trinitro*-m-*tolyl*e, with sodium trinitro-*m*-tolyloxide but not with sodium picrate, whilst hexamethylguanidinpicrate does not combine with sodium trinitroyl factor influencing combination is probabl ability of both components to unite in one crystal lattice. Determination of the conductivity and f. p. of aqueous solutions of hexamethylguanidinium picrate indicates that it is ionised to about the same extent as sodium picrate, so that the internal complex salt formula previously suggested for this substance (*loc. cit.*) applies, if at all, only to the solid. According to the dynamic formula for guanidinium salts the two forms of guanidinium picrate (von Cordier, A., 1906, i, 486) and of methylguanidinium picrate (Gulewitsch, *ibid.*, 637) cannot be stereoisomerides, but it is suggested that dimorphism may occur according as the ions in the crystal lattice are separate or united by auxiliary valencies. On repeating Gulewitsch's work, methylguanidinium picrate is found to crystallise from alcohol in an orange-yellow monotropic β-form, which is stable at the ordinary temperature but passes when heated at 150° or shaken with a solvent into the stable egg-yellow γ-form. On recrystallising either form from aqueous picric acid, a stable α-form, m. p. 200·5—201·5° after shrinking at 190°, is obtained. Conversion of the α- or γ- into the β-form can be effected only by recrystallisation. The α- and β-forms differ in crystalline form and optical properties. The γ-form is identical with the α- in chemical properties and is probably a pseudomorph of the latter after the β-form.

When *NNN′*-trimethyl-*N″N″*-diethylguanidine, b. p. 75·2°/14·5 mm., purified through the *picrate*, m. p. 126—127°, is converted as previously described into *NNN′*-trimethyl-*N′N″N″*-triethylguanidinium picrate or chloroplatinate, only one product is obtained in each case, the supposed isomerides being actually impurities introduced by using impure trimethyldiethylguanidine. Attempts to obtain isomerides by recrystallising the pure salts were unsuccessful. When pentamethylguanidine is heated with diethylamine, or pentaethylguanidine (*picrate*, m. p. 92·5—94°) with dimethylamine at 100°, both are recovered unchanged. The preparation of penta-alkylguanidines by Lecher and Graf's method (A., 1923, i, 761) is therefore not accompanied by the displacement of one amino-residue by another, and the source of the impurity in the trimethyldiethylguanidine remains unknown. H. E. F. NOTTON.

Carbamide series. Transformations of nitroguanidine. T. L. DAVIS and A. J. J. ABRAMS (Proc. Amer. Acad. Arts Sci., 1926, 61, 437—457).—Nitroguanidine "dearranges" to form nitroamide and cyanamide, or ammonia and nitrocyanamide. In concentrated sulphuric acid, nitrous oxide and later carbon dioxide, with nitrogen, are evolved, as anticipated if nitroamide were present, and the solution, although containing no nitric acid, serves for the nitration of aniline, phenol, and aceto-*p*-toluidide. In aqueous solution, dearrangement in both ways is indicated. When digested with ammonia, nitroguanidine yields guanidine (from the cyanamide) and carbamide (originating from the nitrocyanamide). Guanidine carbonate is readily prepared in 90% of the theoretical yield by digesting nitroguanidine with excess of aqueous ammonium carbonate for 10—12 hrs. With aniline and water, nitroguanidine yields diphenylcarbamide with some phenylguanidine and phenylcarbamide. With aqueous methylamine at

60—70° methylnitroguanidine, m. p. 160·5—161°, is obtained from either α- or β-nitroguanidine. Ethylnitroguanidine, m. p. 147—148°, butylnitroguanidine, m. p. 84—85°, and benzylnitroguamdine, m. p. 183·5°, were also obtained. Nitrosoamide is probably present in an aqueous solution of nitrosoguanidine. A cold, acidified solution converts dimethylaniline and diphenylamine into nitroso-derivatives.

CHEMICAL ABSTRACTS.

Acetoguanaminesulphonic acid and related substances. R. ANDREASCH (Monatsh., 1927, **48**, 145—154).—*Diguanide acetate*, m. p. 175°, is prepared from diguanide sulphate; the action of copper acetate on dicyanodiamide (cyanoguanidine) yields copper diguanide. By-products of the preparation of copper diguanide sulphate from cyanoguanidine are melamine (2 : 4 : 6-triamino-1 : 3 : 5-triazine), from a solution of which nitric acid precipitates a *nitrate*, and guanylcarbamide (*nitrate* prepared). Diguanide hydrochloride, $C_2H_7N_5$,2HCl, sinters from 200°, and has completely melted at 350°; *copper diguanide nitrate*, $(C_2H_6N_5)_2Cu$,2HNO$_3$,H$_2$O, and *hydrochloride*, $2(C_2H_6N_5)_2Cu$,4HCl,5H$_2$O, are described.

Diguanide acetate when heated with acetic anhydride yields acetoguanamine (2 : 4-diamino-6-methyl-1 : 3 : 5-triazine) which with chlorosulphonic acid gives the *ω-sulphonic acid* (*barium* salt).

Cyanoguanidine when heated with acetic anhydride reacts vigorously to give acetoguanide (4-amino-2-hydroxy-6-methylhexahydro-1 : 3 : 5-triazine) (*picrate*, m. p. 240—260°), of which the *ω-sulphonic acid* (*barium* salt) is prepared.

Acetoguanide, when heated with concentrated sulphuric acid, yields acetoguanamide [2 : 4-dihydroxy-6-methyl-1 : 3 : 5-triazine] (*picrate*, m. p. 270—280°, decomp.), of which the *ω-sulphonic acid* (*barium* salt) is prepared. The *α-sulphonic acids* of the 6-propyl and 6-*iso*propyl homologues (cf. Nencki, A., 1876, ii, 187) are also prepared. E. W. WIGNALL.

Catalytic synthesis of hydrocyanic acid from nitric oxide and hydrocarbons. E. ELOD and H. NEDELMANN.—See this vol., 838.

Action of molecular and combined oxygen on potassium cyanide at 300—500°. E. BIESALSKI and H. VON LEPP (Ber., 1927, **60**, [*B*], 1459—1462; cf. Hofmann and others, A., 1926, 370).—Potassium cyanide mixed with soda-lime and porous clay gives 23·2% of its nitrogen as nitrate and 2·6% as nitrite when heated in air at 270°. Addition of silver powder or nickel carbonate increases the yield of nitrate to 65·2% and 71·5%, respectively. Oxidising agents such as copper, manganese, or arsenic oxides, potassium dichromate, or the oxides of tungsten or molybdenum do not effect the conversion of potassium cyanide into nitrate but, in the absence of air, give free nitrogen. H. WREN.

Alkylation of hydroferrocyanic acid. F. HOLZL [with W. HAUSER and M. ECKMANN] (Monatsh., 1927, **48**, 71—86).—When silver ferrocyanide is treated with methyl iodide (Hartley, J.C.S., 1912, **101**, 705), the substance $Me_6Fe(CN)_6I_2$,4AgI is obtained, and thence $Me_6Fe(CN)_6(NO_3)_2$ and $Me_4Fe(CN)_6$. In absolute methyl alcohol, methyl ferrocyanide is produced directly. As a by-product, a yellow liquid is obtained, which on concentration turns blue and deposits a dark blue substance which develops an odour of carbylamine on treatment with alkali; this is probably identical with the substance described by Hofmann (Annalen, 1904, **337**, 33). Similarly when methyl sulphate reacts with potassium ferrocyanide in presence of absolute methyl alcohol, a colourless *substance*,(?) $[Fe(CN)]_6H_5Me_3,Me_2SO_4$, is obtained; this turns blue when preserved, gives with alkali the carbylamine odour, and forms *silver* and *zinc* salts which also turn blue rapidly.

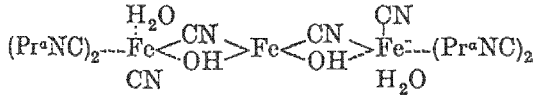
The product of methylation by methyl sulphate in the absence of alcohol, hexamethyl ferrocyanide methyl sulphate (cf. Hartley, J.C.S., 1910, **97**, 1066, 1725), is converted directly into the chloride by heating with hydrochloric acid and barium chloride. Reactions of this type, together with the development of the carbylamine odour, suggest the existence of a stable hexa(methylcarbylamine)ferrous ion, $[Fe(CNMe)_6]^{"}$, of which the above is the chloride. On heating this chloride and extracting with chloroform, a solution of α-tetramethyl ferrocyanide (Hartley, J.C.S., 1913, **103**, 1196) is obtained, which on evaporation gives the β-form, insoluble in chloroform. It is now found that the α-form, rapidly separated, dissolves in water much more slowly than the β-form; whereas the latter gives an immediate precipitate with silver nitrate, the former reacts very slowly; the conductivity in solution is much greater for the β-form than for the α-form. The β-form yields a proportion of cyanide ion indicating the formula $[Fe(CNMe)_4](CN)_2$; it gives no coloration with ferric chloride. When, however, the crude chloride is treated with methyl alcohol and heated, the above α-form remains in the chloroform extract, but the substance which crystallises, and is thereafter insoluble in chloroform, has the electrolytic conductivity of a uni-bivalent salt, and composition and behaviour consistent with the formula $[(MeNC)_2Fe(MeOH)_2](CN)_2(H_2O)_4$; the co-ordination number is again 6.

On evaporating the chloroform containing the α-tetramethyl ferrocyanide, a product is obtained which rapidly turns red; treatment with water gives a red solution from which chloroform extracts the α-form. This gives yellow crystals, which no longer turn red, but dissolve in water slowly to a colourless solution. The properties agree with the non-ionic formula $[(MeNC)_4Fe(CN)_2]$: the substance gives a violet colour with ferric chloride. The red, aqueous solution yields on evaporation a red resinous *substance*, $Fe(Me)_3(CN)_3(H_2O)_2$, which at 100° loses 1 mol. of water to give $[(MeNC)_3Fe(H_2O)(CN)_2]$. This behaves towards silver nitrate similarly to the above α-form, with potassium ferricyanide it gives slowly a blue coloration, and ultimately ferric ferrocyanide separates; with potassium ferrocyanide a blue-green coloration is obtained. On heating alone or with sodium hydroxide solution, a carbylamine odour is observed.

It is thus established that the isomerism of Hartley's α- and β-tetramethyl ferrocyanides is not due to *cis-* and *trans*-nature, but is due to a change of co-ordination number. The crude α-form, however, may be a *cis–trans* isomeric mixture.

Ethylation of silver ferrocyanide by ethyl iodide gives tetraethyl ferrocyanide of which no β-form or aquo-derivative exists. There is no reaction with potassium ferro- or ferri-cyanide; the reaction with silver nitrate is very slow; the conductivity in solution is very small, indicating that the non-electrolyte complex is only slightly dissociated. The substance is therefore regarded as $[(EtNC)_4Fe(CN)_2]$.

Propylation by propyl iodide yields similarly the *compound*, $[(Pr^{\alpha}NC)_4Fe(CN)_2]$, m. p. 107—111°, which is apparently a mixture of isomerides, since addition of water causes partial decomposition, with the separation of a white substance; evaporation of the aqueous solution gives a substance of the same m. p. and composition, which gives no white substance with water. A by-product of the propylation is a *substance*, $C_{20}H_{32}O_4N_8Fe_3$, obtained by extracting the original product with slightly aqueous alcohol. On account of its colourless nature, development of a carbylamine odour under the action of alkali, partial transformation into potassium ferrocyanide by heating with potassium cyanide, and gradual dissolution in pyridine, the formula



is suggested.

The capacity for forming additive compounds decreases, as does the stability towards water, from the methylated to the propylated derivatives; the propyl compound reacts the least slowly with silver nitrate, and further has a rather higher conductivity.

E. W. WIGNALL.

***iso*Butylphosphinic acid bromide.** T. MILOBEDZKI and S. KRAKOVIECKI (Bull. Soc. chim., 1927, [iv], **41**, 932—933).—Phosphorus tribromide (1 mol.) reacts with *iso*butyl alcohol (1 mol.) yielding the *compound* $P(OC_4H_9)Br_2$, b. p. 85—87°/20 mm., d_4 1·673, which is converted by phosphorus pentabromide into *iso*butyl bromide. H. BURTON.

Oxidation of cacodyl oxide. A. VALEUR and P. GAILLIOT (Compt. rend., 1927, **185**, 70—71).—Cacodyl oxide is converted by a slow stream of oxygen under water at the ordinary temperature into cacodylic acid, trimethylarsine, monomethylarsine oxide, and arsenious acid with small amounts of trimethylarsine oxide and methylarsinic acid. The cacodylic acid is formed by direct oxidation, the trimethylarsine, monomethylarsine oxide, and arsenious acid are formed by simultaneous self-oxidation and reduction. E. A. LUNT.

A Grignard starter. R. W. HUFFERD (J. Amer. Chem. Soc., 1927, **49**, 1845—1846).—The preparation of Grignard reagents is often facilitated by the addition of a small quantity of anhydrous aluminium bromide, freshly prepared by heating aluminium with bromine. F. G. WILLSON.

Effect of some solvents on the yields of Grignar reagents. H. GILMAN and R. MCCRACKEN (Rec. trav. chim., 1927, **46**, 463—472).—A study of the yields of some Grignard reagents in ether–hydrocarbon mixtures and in varying concentrations of ether. Hydrocarbons have in general a retarding or an inhibiting effect, and although a higher yield is obtained by adding the alkyl halide dissolved in a hydrocarbon to a given amount of ether and magnesium than by adding the halide in a mixture of ether and hydrocarbon, neither procedure is as satisfactory as the use of ether alone. Thus, using 0·2 g.-mol. of ether to 1 g.-mol. of halide and 100 c.c. of benzene, the yields of magnesium *n*-butyl bromide and of magnesium phenyl bromide, after refluxing for 4 hrs., are reduced by 10% and that of magnesium benzyl bromide by 30% (cf. Gilman and McCracken, A., 1924, i, 23), but even these yields can be obtained only by adding a portion of the alkyl halide in ether alone in order to start the reaction. Toluene, xylene, and light petroleum have a similar retarding effect. Experiments carried out with ether alone at 20° show that the minimum amounts of ether (in g.-mol. per g.-mol. of halide) required for maximum yields are, with magnesium *n*-butyl bromide, 1·3—1·5 (yield 94%); with magnesium phenyl bromide, 4—5 (93%); with magnesium benzyl bromide, 6—7 (93%). Grignard reagents were prepared from the following halides, the figures quoted being the proportion of solvent (ether unless otherwise stated) and the yield: *n*-propyl bromide 7, 89·9; *n*-butyl bromide in di-*n*-butyl ether 5, 88·4; cetyl bromide 16, 81·1; cetyl iodide 50, 42·1; bromo*cyclo*hexane 3, 67·4; β-phenylethyl chloride 10, 73·7; γ-phenyl-*n*-propyl chloride 10, 88·3; δ-phenyl-*n*-butyl chloride 20, 83; phenyl β-chloroethyl ether 16, 35·5; phenyl γ-chloropropyl ether 16, 64·3; benzhydryl bromide 25, 13·0; bromobenzene, in di-*n*-butyl ether, 5, 55·9; in phenetole, 5, 41·7; α-bromonaphthalene 2, 72·5; β-bromonaphthalene 10, 64·6. W. J. POWELL.

Reaction of carbon monoxide with magnesium phenyl bromide in presence of chromium chloride. A. JOB and A. CASSAL (Bull. Soc. chim., 1927, [iv], **41**, 814—824).—Although neither magnesium ethyl bromide nor magnesium phenyl bromide reacts with carbon monoxide when pure, chromic chloride induces reaction. Thus in presence of about *M*/30 chromic chloride, magnesium phenyl bromide rapidly absorbs 1 mol. of carbon monoxide, the reaction product affording on fractional distillation traces of *chromium carbonyl*, phenol, and benzaldehyde and in addition about 10% of diphenyl, 15% of benzophenone, 15% of benzhydrol, 10% of triphenylvinylcarbinol, and 2% of triphenylcarbinol. The benzhydrol and benzophenone arise from decomposition of benzpinacone, fractional crystallisation of the reaction mixture affording about 33% of this product. Benzil is probably the primary product, the benzpinacone arising by the action of 2 mols. of magnesium phenyl bromide, $2PhMgBr + COPh{\cdot}COPh \longrightarrow CPh_2(OMgBr){\cdot}CPh_2{\cdot}OMgBr \longrightarrow CPh_2(OH){\cdot}CPh_2{\cdot}OH$. Traces of benzil were detected from the reaction product below 0°, and a little triphenylmethane was isolated. Triphenylvinyl alcohol is probably formed by dehydration of triphenylethylene glycol (from phenylbenzoin) and the triphenylmethane from β-benzpinacolin, from benzpinacone. It is suggested that a complex is primarily formed in which the chromium has the co-ordination number 6. The reducing action observed on decom-

position with water may be attributed to either reduced chromium or reduced magnesium.

R. BRIGHTMAN.

Action of magnesium organo-derivatives on *N*-diethylformamide. N. MAXIM (Bull. Soc. chim., 1927, [iv], **41**, 809—813).—Magnesium ethyl bromide or iodide and *N*-diethylformamide in ethereal solution afford exclusively *γ-diethylaminopentane*, b. p. 143°/760 mm. (*picrate*, m. p. 84°) (cf. Viguier, A., 1912, i, 7). With magnesium *iso*butyl bromide, however, the reaction affords in addition to about 22% of *δ-diethylamino-βη-dimethylheptane*, b. p. 95°/19 mm., 206°/760 mm. (*picrate*, m. p. 89—90°), about 29% of *iso*valeraldehyde, the reaction thus partly pursuing the course, $H{\cdot}CO{\cdot}NEt_2+RMgX \longrightarrow R{\cdot}CHO+NHEt_2$, observed by Bouveault (A., 1905, i, 116) and by Houben and Doescher (A., 1908, i, 27).

R. BRIGHTMAN.

Course of the Leuckart xanthate reaction [ethyl- and methyl-sulphonylbenzene-2 : 4-disulphonyl chlorides]. J. POLLAK, K. DEUTSCHER, and (FRL.) M. KRAUSS (Monatsh., 1927, **48**, 103—111; cf. Hurtley and Smiles, A., 1926, 948).—In attempting the preparation of benzene *as*-trisulphonic acid by treating diazotised anilinedisulphonic acid with potassium xanthate, it was found that whilst oxidation of the product by nitric acid gives apparently the desired acid, oxidation by potassium permanganate gives rise to a sulphone, owing to decomposition of the xanthate derivative to give an alkylthiol derivative. When nitric acid is used and the product is treated with phosphorus pentachloride, there is obtained, not benzenetrisulphonyl chloride, but 1-chlorobenzene-2 : 4-disulphonyl chloride, sulphur dioxide being lost.

When potassium permanganate is used, the product of chlorination is *ethylsulphonylbenzene-2 : 4-disulphonyl chloride*, m. p. 162·5—163°. This is identical with a specimen prepared by sulphonating thiophenetole to a mixture of *thiophenetole mono-* and *disulphonic acids* (*thiophenetole-2 : 4-disulphonyl chloride*, m. p. 72—73·5°, prepared), and treating the mixed potassium salts with potassium permanganate, whereby *ethylsulphonylbenzene-mono-* and *-di-sulphonic acids* (*potassium* salts) are obtained, and finally chlorinating the latter.

By similarly treating thioanisole, *methylsulphonylbenzene-2 : 4-disulphonyl chloride*, m. p. 154—156°, is obtained. The hydrolysis of these two acid chlorides requires 5 mols. of potassium hydroxide : the sulphone group is thus apparently hydrolysed.

E. W. WIGNALL.

Action of aqua regia on fluorene. E. BLUMENSTOCK-HALWARD (Monatsh., 1927, **48**, 99—101).—From the product of the prolonged action of aqua regia on fluorene (cf. Datta, A., 1916, i, 715) some β-dichlorofluorenone (Goldschmiedt, A., 1896, i, 174) is isolated.

E. W. WIGNALL.

Effect of mercury salts in the nitration of aromatic systems. P. V. MCKIE (J.S.C.I., 1927, **46**, 261—262T).—In the nitration of aromatic compounds by various methods the effect of small quantities of mercuric nitrate may be considerable, either the nitrating or the oxidising function of the acid being positively catalysed according to the conditions employed, although in a few instances, such as the nitration of salicylic acid, and the nitration of hydrocarbons in presence of small concentrations of mercury salts, the effect is a negative one. Increase of oxidation does not take place at the expense of nitration, since a larger proportion of the organic compound undergoes reaction, but if the temperature be carefully controlled direct oxidation is in every case little more than occurs in absence of mercury. As with ethylene and acetylene, there is a tendency, particularly with hydrocarbons, to form nitrohydroxy-compounds (cf. this vol., 643) and the evidence supports the view that nitration proceeds by preliminary addition of nitric acid to the aromatic nucleus (cf. Meisenheimer, A., 1901, i, 135; Straus and Ekhard, A., 1925, i, 1138). The increase (per cent.) of total nitration obtained by the addition of 0·1—0·5% of mercuric nitrate is, with xylene 0·8, naphthalene —2·7 to —6·8, phenanthrene 13·1, bromobenzene 2·56—3·99, phenol 21·7—25·0, chlorophenol 3·1—6·25, *o*-cresol 18·6—19·1, naphthol 10·7—11·4, benzaldehyde 8·3—9·6, *p*-hydroxybenzaldehyde 18·1—22·2. With anthracene, oxidation and mononitration are decreased, dinitration being increased.

W. J. POWELL.

Optical identification of the naphthalenesulphonic acids by means of their benzyl-ψ-thiocarbamide salts. R. M. HANN and G. L. KEENAN (J. Physical Chem., 1927, **31**, 1082—1090).—Optical data on the benzyl-ψ-thiocarbamide salts of α-, β-, 1 : 5-, 2 : 6-, 2 : 7-, and 1 : 6-naphthalene-mono- and -di-sulphonic acids are given in a form suitable for rapid identification by microscopical observation.

L. S. THEOBALD.

[Mechanism of the formation of diphenyl from benzene.] O. FUCHS (Ber., 1927, **60**, [*B*], 1663).—The arrangement of Pyl's main and control experiments are not sufficiently similar to justify the conclusion which he has reached (cf. this vol., 654).

H. WREN.

Hydrogenation under pressure of tetraphenylmethane and *p*-hydroxytetraphenylmethane. V. N. IPATIEV and B. N. DOLGOV (Compt. rend., 1927, **185**, 210—212).—Tetraphenylmethane, when hydrogenated at 275—285°/80—100 atm. using a nickel oxide catalyst, yields tri*cyclo*hexylmethane and di*cyclo*hexylmethane. *p*-Hydroxytetraphenylmethane, similarly treated, yields *cyclo*hexanol, di*cyclo*hexylmethane, and phenyldi*cyclo*hexylmethane.

B. W. ANDERSON.

Dehydrogenations and hydrogenations catalysed by metallic oxides. P. SABATIER and [illegible] FERNANDEZ (Compt. rend., 1927, **185**, 241—[illegible]). It has been found (cf. Sabatier, this vol., 737) metallic oxides dehydrogenate primary alcohols aldehydes, as well as dehydrating them to unsaturated hydrocarbons. Manganous oxide has no dehydrating, but a slight dehydrogenating action, which is greater with zinc oxide; alumina has scarcely dehydrogenating action. Piperidine, stable in a tube at 600°, is converted by manganous oxide this temperature into pyridine and dipyridyl, hydrogen being evolved.

Nitrobenzene vapour passed with hydrogen

heated manganous oxide is reduced slowly at 300°, rapidly at 600°, to aniline, with diphenylamine, triphenylamine, water, ammonia, and some benzene and carbon dioxide Zinc oxide gives similar results (cf. its catalysis of the reduction of carbon dioxide at high pressures to methyl alcohol); without a catalyst the reaction is slight.

Zinc oxide is more active than manganous oxide in catalysing the reduction of *iso*valeronitrile to di- and tri-*iso*amylamines, and that of *iso*butyronitrile to the corresponding primary and secondary amines. Hexonitrile is reduced by either oxide at 500° to dihexylamine, with mono- and tri-hexylamines.

Manganous oxide does not reduce satisfactorily ethylene or acetone derivatives. E. W. WIGNALL.

Diacylamides. III. Formation of amidines. K. BRUNNER, (FRL.) M. MATZLER, and V. MOSSMER (Monatsh., 1927, 48, 125—131; cf. A., 1924, i, 1310).—Diacetamide, when heated at 150—160° with aniline hydrochloride, gives mainly acetanilide, but also some NN'-*diphenylacetamidine*, NPh:CMe·NHPh, m. p. 130° (*oxalate*, m. p. 159°; *chloroplatinate*), with traces of N-*phenylacetamidine* (*oxalate*, m. p. 179°, *picrate*, m. p. 188·5°); the latter is obtained in larger quantity when aniline hydrobromide is used. *Triphenylacetamidine*, prepared from acetanilide and diphenylamine, has m. p. 93° (*picrate*, m. p. 164°).

The action of diacetamide on *p*-toluidine yields *di*-p-*tolylacetamidine*, m. p. 120·5° (*chloroplatinate*; *oxalate*; *picrate*, m. p. 156°; *benzoyl* derivative, m. p. 137°), with N-p-*tolylacetamidine* (picrate, m. p. 184°).

Since Wallach found (A., 1882, 958) that acetanilide reacts with aniline hydrochloride to form the amidine, it might be thought that acetanilide and acet-*p*-toluidide are intermediate products in the above reactions; at moderate temperatures, however, these are found not to react with the hydrochlorides of the respective amines. E. W. WIGNALL.

Diacylamides. IV. Formation of nitrophenylacetamidines. K. BRUNNER and F. HASLWANTER (Monatsh., 1927, 48, 133—137).—In the hope that more feebly basic aromatic amines would give better yields of the amidine and less of the amide, *o*- and *p*-nitroaniline hydrochlorides were heated with diacetamide; the yields were, however, not improved.

-*Di*-o-*nitrophenylacetamidine* has m. p. 62° (*picrate*, m. p. 198°; *hydrochloride*, m. p. 180—190°, omp.). *p*-Nitroaniline hydrochloride gave no amidine until heated with the diacetamide at 170°, when N-p-*nitrophenylacetamidine* (*picrate*, m. p. 170°) was obtained in small yield; heating for 6 hrs. at 200° necessary to obtain, in slightly better yield, -*ai*-p-*nitrophenylacetamidine*, m. p. 131°, which en evaporated with hydrochloric acid decomposed to give *p*-nitroaniline. E. W. WIGNALL.

Action of chlorosulphonic acid on aromatic amines. O. LUSTIG and E. KATSCHER (Monatsh., 1927, 48, 87—97).—Aniline dissolved in excess of chlorosulphonic acid and heated at 150—160° for 2 hrs. with sodium chloride slowly reacts to give, on adding water, *aniline*-2 : 4 : 6-*trisulphonyl chloride*, m. p. 175°. The constitution is established by hydrolysis, diazotisation, and rechlorination to 1-chlorobenzene-2 : 4 : 6-trisulphonyl chloride (Olivier, A., 1920, i, 303). *Aniline*-2 : 4 : 6-*trisulphonamide*, m. p. 291°, and -*trisulphonanilide*, m. p. 240—241°, were prepared. The acid chloride is obtained in only small yield if sodium chloride is absent (the free acid then being formed). It is also obtained when acetanilide, or aniline-mono- or -di-sulphonic acid is employed: these substances do not give the blue impurity obtained when aniline is used.

p-Toluidine gives similarly its 3 : 5-*disulphonyl chloride*, yellow, m. p. 156°, *disulphonamide*, m. p. 257°, *disulphonanilide*, m. p. 192°; *m*-phenylenediamine gives its 4 : 6-*disulphonyl chloride*, m. p. 274—275° (after sintering), which turns reddish-violet in sunlight, *disulphonamide*, m. p. 187°, *disulphonanilide*, m. p. 236°; *p*-phenylenediamine, however, gives its tetrachloro-derivative.

Sodium acetylanthranilate heated with sodium chlorosulphonate for 3 hrs. at 200° gives 4-keto-3-*o*-carboxyphenyl-2-methyldihydroquinazoline, $C_6H_4<\begin{matrix}N=CMe\\ |\\ CO\cdot N\cdot C_6H_4\cdot CO_2H\end{matrix}$, m. p. 246° (cf. Anschütz and Schmidt, A., 1903, i, 57). E. W. WIGNALL.

Simultaneous diazotisation and nitration of aromatic amino-compounds. I. J. RINKES (Rec. trav. Chim., 1927, 46, 506—508).—Repetition of the work of Varma and Krishnamurthy (this vol., 552) has in some cases led to different results. Aniline hydrochloride, on treatment with nitrous gases under the conditions given by Varma and Krishnamurthy, furnishes 2 : 4-dinitrophenol, not 2 : 5-dinitrophenol. *p*-Chloroaniline yields 4-chloro-2 : 6-dinitrophenol, not 4-chloro-2 : 3-dinitrophenol, whilst *m*-aminobenzoic acid affords 2 : 4 : 6-trinitro-3-hydroxybenzoic acid, m. p. 180° (uncorr.), (cf. Wolffenstein and Paar, A., 1913, i, 363), which when heated in a vacuum loses carbon dioxide and is converted into picric acid. The production of 5-nitro-3-hydroxybenzoic acid as reported by Varma and Krishnamurthy is unlikely in view of this result and the fact that the m. p. 166° given by these authors is 28° below that previously recorded (cf. Beyer, A., 1922, i, 37).

W. J. POWELL.

Migration of the triphenylmethyl group in aniline, and *o*- and *p*-toluidines. J. VAN ALPHEN (Rec. trav. chim., 1927, 46, 501—505).—When heated with zinc chloride at 160°, *N*-triphenylmethylaniline affords *p*-aminotetraphenylmethane by migration of the triphenylmethyl group. With similar treatment *N*-triphenylmethyl-*o*-toluidine yields α-o-*aminophenyl*-βββ-*triphenylethane*, m. p. 216°, which is converted into α-*o*-hydroxyphenyl-βββ-triphenylethane by diazotisation and subsequent hydrolysis (cf. this vol., 660). On boiling with alcohol the diazonium salt yields a *substance*, m. p. 143°, which is not the expected *as*-tetraphenylethane (mixed m. p. 110°) but probably α-o-*ethoxyphenyl*-βββ-*triphenylethane*. α-*o*-Aminophenyl-βββ-triphenylethane may also be prepared by heating triphenylcarbinol with *o*-toluidine hydrochloride and glacial acetic acid. When *N*-tripnenylmethyl-*p*-toluidine is heated with zinc chloride at 190°, the reaction takes a different course, triphenylmethane and a dye being produced, recalling the reaction of *p*-cresol with triphenylmethyl chloride (*loc. cit.*). W. J. POWELL.

Carbylamines. XVI. Reactions with hydroxylamine hydrochloride. M. PASSERINI (Gazzetta, 1927, 57, 452—456).—The reaction of carbylamines with hydroxylamine hydrochloride varies with the solvent. In alcohol, phenylcarbylamine gives anilinoformaldoxime (Nef, A., 1895, i, 11); it is suggested that diphenylformamidine is first produced, since this substance is the product in acetone solution, which removes excess of hydroxylamine. Alcoholic potassium hydroxide converts anilinoformaldoxime into phenylcyanamide. *p*-Carbylaminoazobenzene in acetone solution yields largely *di-p-benzeneazodiphenylformamidine*, $NPh:N\cdot C_6H_4\cdot N:CH\cdot NH\cdot C_6H_4\cdot N:NPh$, m. p. 196—197°; if the crude product is hydrolysed by alcoholic potassium hydroxide, *p*-aminoazobenzene is obtained, with a substance probably *p*-cyanamidoazobenzene, m. p. 163° (cf. Pierron, A., 1906, i, 772), since when boiled with hydrochloric acid it is converted into *p*-carbamidoazobenzene; *p*-formamidoazobenzene is also produced. E. W. WIGNALL.

Positive halogens attached to carbon in the aromatic series. IV. Selectivity of halogen removal. B. H. NICOLET and R. B. SANDIN (J. Amer. Chem. Soc., 1927, 49, 1806—1810; cf. this vol., 869).—In support of the theory which predicts that halogen atoms *ortho* or *para* to an amino-group should exhibit " positive " properties, it has been found that *o*-iodo-*p*-toluidine remains unaffected under conditions which result in the ready replacement of iodine by hydrogen in the hydrolysis of *m*-iodo-*p*-toluidine. Treatment of *o*-iodo-*p*-toluidine in ether with iodine, calcium carbonate, and water affords 2 : 5-*di-iodo*-p-*toluidine*, m. p. 110° (*acetyl* derivative, m. p. 193°), which is reconverted into *o*-iodo-*p*-toluidine by aqueous 10% hydrochloric acid. Bromination of *o*-iodo-*p*-acetotoluidide with bromine in glacial acetic acid yields 5-*bromo*-2-*iodoacet*-p-*toluidide*, m. p. 165—166°, from which 5-*bromo*-2-*iodo*-p-*toluidine*, m. p. 86—87°, is obtained on hydrolysis with aqueous 20% hydrochloric acid. Bromination of *o*-iodo-*p*-toluidine in glacial acetic acid affords 3 : 5-*dibromo*-2-*iodo*-p-*toluidine*, m. p. 109° (*acetyl* derivative, m. p. 228—229°). Treatment of *o*-iodo-*p*-toluidine with iodine monochloride in glacial acetic acid yields 2 : 3 : 5-*tri-iodo*-p-*toluidine*, m. p. 120—121°. Bromination of 2 : 5-di-iodo-*p*-toluidine in glacial acetic acid yields 3 : 5-dibromo-2-iodo-*p*-toluidine. When the above halogenated derivatives of *o*-iodo-*p*-toluidine are boiled with concentrated hydrochloric acid and glacial acetic acid in presence of stannous chloride, the halogen atoms *ortho* to the amino-group are in all cases replaced by hydrogen, with production of *o*-iodo-*p*-toluidine. This indicates the " positive " nature of these halogen atoms, whilst the non-production of *p*-toluidine shows that the presence of stannous chloride does not influence the course of the hydrolytic reaction. The rate of removal of iodine from *o*-iodoaniline under the above conditions is about 33% more rapid than that from 2 : 5-di-iodo-*p*-toluidine. F. G. WILLSON.

Oxidation of compounds containing the primary amino-group. I. Diphenylmethylamine. L. HELLERMAN and A. G. SANDERS (J. Amer. Chem. Soc., 1927, 49, 1742—1747).—Treatment of diphenylmethylamine hydrochloride in absolute alcohol with sodium ethoxide (3 mols.) and bromine (1 mol.), with subsequent acidification, affords benzophenone in 66% yield, presumably through the corresponding imine, formed by elimination of hydrogen bromide from the *N*-bromoamine. Treatment of diphenylmethylamine hydrochloride with aqueous sodium hypochlorite yields *N-chlorodiphenylmethylamine*, which is converted by absolute-alcoholic sodium ethoxide into benzophenoneimine. F. G. WILLSON.

Arylamine salts of naphthalenesulphonic acids. IV. Arylamine salts of α-naphthol-4-sulphonic acid, acetylation of naphthionic acid, and arylamine salts of acetylnaphthionic acid. R. B. FORSTER and R. WATSON (J.S.C.I., 1927, 46, 224—226T).—The following salts of α-naphthol-4-sulphonic acid have been prepared, and their solubilities in 100 parts of 1% acetic acid (*S*) determined: (*a*) from 1 mol. each of acid and base, *aniline*, m. p. 186—187°, *S* at 15° 5·38; o-*toluidine*, m. p. 203—204°, *S* at 20° 1·66; p-*toluidine*, m. p. 196°, *S* at 15° 0·68; m-*xylidine*, m. p. 228—229°, *S* at 12° 0·23; *ψ-cumidine*, m. p. 227—228°, *S* at 17° 0·216; α-*naphthylamine*, m. p. 216—217°, *S* at 19° 0·18; β-*naphthylamine*, begins to decompose at 270°, *S* at 18° 0·053; p-*chloroaniline*, m. p. 184—185°, *S* at 15° 0·53; p-*nitro*-o-*toluidine*, m. p. 249° (decomp.), *S* at 18° 0·28; o-*anisidine*, m. p. 202—203°, *S* at 17° 1·37; p-*anisidine*, m. p. 224°, *S* at 16° 0·45; (*b*) from 2 mols. of acid and 1 mol. of diamine, *benzidine*, begins to decompose at 310°, *S* at 14° 0·17; *tolidine*, m. p. 214—215°, *S* at 16° 0·12; *dianisidine*, m. p. 207—209°, *S* at 18° 0·25. Naphthionic acid does not yield arylamine salts, owing possibly to inner salt formation between the amino- and sulphonic groups of the acid. On acetylation, however, this inhibiting influence is removed and acetylnaphthionic acid (cf. Schroeter, A., 1906, i, 415), which is prepared in 95% yield by boiling the acid with acetic anhydride in presence of pyridine, yields the following salts: *aniline*, m. p. 231—232°, *S* at 14° 3·0; o-*toluidine*, m. p. 260—261°, *S* at 16° 0·28; p-*toluidine*, m. p. 232—233°, *S* at 16° 0·66; m-*xylidine*, m. p. 239—240°, *S* at 16° 0·46, *ψ-cumidine*, m. p. 266—267°, *S* at 17° 0·105; α-*naphthylamine*, m. p. 261—262°, *S* at 16° 0·183; β-*naphthylamine*, m. p. 255—256°, *S* at 16° 0·17; p-*chloroaniline*, m. p. 224°, *S* at 12° 0·28; p-*nitro*-o-*toluidine*, m. p. 264—265°, *S* at 16° 1·55; p-*anisidine*, m. p. 232—233°, *S* at 13·5° 3·85; o-*anisidine*, m. p. 254—255°, *S* at 12·5° 0·65; *benzidine*, m. p. 265—266°, *S* at 17·5° 0·22; *tolidine*, m. p. 279—280°, *S* at 13° 0·10, *dianisidine*, m. p. 278—279°, *S* at 16° 0·15. The re acid and its salts regenerate naphthionic acid on boi ing with dilute hydrochloric acid. W. J. POWELL.

Manufacture of aralkylamines and derivatives and intermediate products. FARBENIND. A.-G.—See B., 1927, 572.

Manufacture of amines of the *cyclo*hexane series. I. G. FARBENIND. A.-G.—See B., 1927, 5

Positive halogens attached to carbon in the aromatic series. II. Iodine derivatives *m*-phenylenediamine and of resorcinol. NICOLET and J. R. SAMPEY (J. Amer. Chem.

1927, **49**, 1796—1801; cf. A., 1922, i, 121).—Treatment of resorcinol in aqueous 20% hydrochloric acid with iodine monochloride (2 mols.) affords 4 : 6-*di-iodoresorcinol*, m. p. 145° (*dibenzoyl* derivative, m. p. 195—200°). 4-*Iodo*-3-*hydroxyphenyl benzoate*, decomp. 153—155°, is obtained from monobenzoylresorcinol and iodine chloride in glacial acetic acid, whilst 5-*iodo*-2 : 4-*dihydroxybenzoic acid*, m. p. 172°, is obtained similarly from resorcylic acid in ether. 3 : 5-*Di-iodo*-2 : 4-*dihydroxybenzoic acid*, decomp. 193—196°, is obtained by treatment of resorcylic acid in ether with iodine and litharge, whilst 4-*chloro*-6-*iodo*-m-*phenylenediamine* is obtained similarly from 4-chloro-*m*-phenylenediamine in methyl alcohol. 4-*Iododiacetyl*-m-*phenylenediamine*, decomp. 175—180°, is obtained by treating *m*-aminoacetanilide in aqueous 20% hydrochloric acid with iodine, with subsequent acetylation. 4 : 6-*Di-iodo*-m-*aminoacetanilide*, m. p. 172—174°, is obtained by treating *m*-aminoacetanilide with iodine chloride in warm aqueous 10% hydrochloric acid. All the above derivatives, as well as 4-iodoresorcinol, 4-iodo-*m*-phenylenediamine, 4 : 6-di-iodo-*m*-phenylenediamine, 2-iodo-*p*-phenylenediamine, and 3-iodo-*p*-toluidine, are hydrolysed with replacement of iodine by hydrogen when treated with aqueous 10% hydrochloric acid and stannous chloride in glacial acetic acid at 100°. The results obtained are in accordance with predictions based on the theory of induced alternate polarities (cf. Lapworth and Shoesmith, J.C.S., 1922, **121**, 1391). F. G. WILLSON.

Positive halogens attached to carbon in the aromatic series. III. Derivatives of *p*-phenylenediamine, *p*-nitroaniline, and mesitylene. B. H. NICOLET and W. L. RAY (J. Amer. Chem. Soc., 1927, **49**, 1801—1806; cf. this vol., 868).—Iodomesitylene is converted into mesitylene, indicating the positive nature of the halogen atom, when heated with hydrogen chloride in glacial acetic acid at 135—150°, or with acetic acid, hydrochloric acid, and stannous chloride at the same temperature. Iodobenzene is unaffected by hydrogen chloride in glacial acetic acid at 150°. 2-*Iodo*-p-*phenylenediamine*, m. p. 110·5° (*diacetyl* derivative, m. p. 211·5°; *dibenzoyl* derivative, m. p. 254°), obtained by reduction of 2-iodo-4-nitroaniline with stannous chloride, is converted into *p*-phenylenediamine when boiled with aqueous 10% hydrochloric acid, or with glacial acetic acid and hydrochloric acid, or when heated with concentrated hydrochloric acid at 105°. In the last two cases, 2 : 6-di-iodo-4-nitroaniline is formed. 2-Iodo-*p*-phenylenediamine is deiodinated similarly by hydrochloric acid in presence of stannous chloride, but much less rapidly than *o*-iodoaniline. 2-*Bromo*-p-*phenylenediamine*, m. p. 76° (*diacetyl* derivative, p. 200°), obtained by reduction of 2-bromo-4-nitroaniline, is debrominated more slowly than the corresponding iodo-derivative. Reduction of 2-bromo-4-nitroacetanilide affords 2-*bromo*-4-*aminoacetanilide*, m. p. 123°. Bromination of 3-bromo-4-aminoacetanilide in glacial acetic acid yields 2 : 3 : 5-*tribromo*-4-*aminoacetanilide*, m. p. 207°. F. G. WILLSON.

Positive halogens attached to carbon in the aromatic series. V. Analogy between positive and negative halogens. B. H. NICOLET (J. Amer. Chem. Soc., 1927, **49**, 1810—1814; cf. this vol., 868, and preceding abstract).—The theory of alternating polarities predicts correctly the respective negative and positive natures of the halogen atoms in 1-chloro-2 : 4-dinitrobenzene and 1-iodo-3 : 5-diaminobenzene. Accordingly, the halogen atom of 1-chloro-3 : 5-diaminobenzene and 1-iodo-3 : 5-dinitrobenzene should also exhibit negative and positive characteristics, respectively. It has now been found, however, that neither of these compounds can be dehalogenated, *i.e.*, that their halogen atoms show no indications of polar characteristics. It is therefore concluded that the possibility of reaction is conditioned by factors other than polar structure, and it is suggested that the removal of halogen from the *o*- or *p*-derivatives takes place through the intermediate formation of a quinonoid derivative, *e.g.*, according to the scheme $:C(NH_2)\cdot Cl: \longrightarrow :C(NH_3Cl)\cdot Cl: \longrightarrow \cdot C(:NH_2Cl)\cdot CH\cdot \longrightarrow \cdot C(NH_2):CH\cdot + ClI$. 1-*Iodo*-3 : 5-*dinitrobenzene*, yellow, m. p. 99°, was prepared from 3 : 5-dinitroaniline. On reduction and subsequent acetylation it yields 1-*iodo*-3 : 5-*diacetamidobenzene*, m. p. 291°. F. G. WILLSON.

Benzidine monohydrate. M. p. of benzidine. R. J. W. LE FEVRE and E. E. TURNER (J.S.C.I., 1927, **46**, 209—210T).—Benzidine forms a *monohydrate*, m. p. 104—105° (with effervescence) when taken very rapidly. The transition temperature benzidine hydrate $\rightleftharpoons$ water + benzidine is at about 71°. Benzidine separates anhydrous from aqueous solutions at temperatures above 80° and hydrated at temperatures below 60°. The commonly accepted m. p. of 122° for benzidine is shown to be traceable to the use, in error, of partly hydrated specimens.

Stereochemistry of aromatic compounds. III. Condensation of aromatic diamines with dicarboxylic anhydrides. R. KUHN, P. JACOB, and M. FURTER (Annalen, 1927, **455**, 254—271).—In agreement with the results of Le Fevre and Turner (A., 1926, 1131), monophthalylbenzidine [*hydrochloride*, decomp. 310°; *acetyl* derivative, m. p. 332° (all m. p. corr.); benzylidene derivative, m. p. 339°], monophthalyldi-*o*-anisidine, m. p. 221° (Kaufler and Borel, A., 1907, i, 794, 795) [*hydrochloride*, m. p. 278° (decomp.); *benzylidene* derivative, m. p. 200°; *acetyl* derivative, m. p. 298°], and monophthalyl-2 : 7-naphthylenediamine, m. p. 249° (*acetyl* derivative, m. p. 306°; *benzylidene* derivative, m. p. 150°), are shown to possess free amino-groups. They cannot, therefore, have a cyclic structure. 2 : 7-Diphthalimidonaphthalene, m. p. 314°, exists in yellow and colourless forms. Attempts to prepare a cyclic compound from *NN'*-dimethylbenzidine (Willstatter and Kalb, A., 1904, i, 1050) (dihydrochloride, m. p. 249°; *diacetyl* derivative, m. p. 242°) and phthalic anhydride at 160° gave a *monophthalyl* derivative, m. p. 276°. Since, however, this contains a free imino-group and gives an *acetyl* derivative, m. p. 216°, which is hydrolysed by alcoholic potassium hydroxide to a *phthalamic acid*, $C_{24}H_{22}N_2O_4$, m. p. 253°, it has probably the structure, $NHMe\cdot C_6H_4\cdot C_6H_4\cdot N<_{CO-C}$. Its ready hydrolysis by acids to dimethylbenzidine is

surprising. The above phthalyl derivatives give characteristic colour reactions with sulphuric and chromic acids. *Monosuccinyl*-NN'-*dimethylbenzidine*, m. p. 269°, gives an *acetyl* derivative, m. p. 292°. NN'-*Dimethylphthaldianilide* has m. p. 186·5°. *NN'*-Dimethylbenzidine and carbonyl chloride in toluene give an amorphous *product*, $(?)(C_{15}H_{14}ON_2)_4$. A monophthalyl derivative of *pp'*-diaminodiphenylmethane could not be prepared. The latter gives with *p*-toluenesulphonyl chloride in hot aqueous suspension, pp'-*di*-p-*toluenesulphonamidodiphenylmethane*, m. p. 164°, which is converted by methyl sulphate and alkali followed by hydrolysis into oily pp'-*dimethyldiaminodiphenylmethane* (*dinitroso*-derivative, m. p. 99°). This condenses with phthalic anhydride at 190° to a *diphthalyl* derivative, m. p. 221° (indef.). Thus, even under favourable conditions formation of cyclic derivatives of the Kaufler type does not take place; this is, however, not regarded as evidence against a similar formula for benzidine derivatives since *o*-phenylenediamine also fails to give a cyclic phthalyl derivative.

H. E. F. Notton.

Caoutchouc and guttapercha. II. Disazo-compounds from dihydroxy- and tetrahydroxy-diphenyldihydrocaoutchouc. E. Geiger (Helv. Chim. Acta, 1927, **10**, 539—543; see below).—4 : 4'-Dihydroxydiphenyldihydrocaoutchouc is coupled with diazobenzene to give a *dye*, m. p. 205—210° (decomp.); with *p*-nitrodiazobenzene giving a *dye*, m. p. 260—270°; with diazotised naphthionic acid and sulphanilic acid, and with tetrazotised benzidine. The analogue of diamine-green-B, *p*-nitroaniline ⟶ H-acid ⟵ benzidine ⟶ dihydroxydiphenyldihydrocaoutchouc, is bluer than the phenol (*para*) coupling. *p*-Nitrodiazobenzene (2 mols.) couples with 2 : 2' : 4 : 4'-tetrahydroxydiphenyldihydrocaoutchouc to give a *dye*, m. p. 210—215° (decomp.). The products are truly colloidal dyes, and coupling is about as rapid as with *p*-cresol.

C. Hollins.

Phenol tests. Velocity of indophenol formation. H. D. Gibbs (J. Physical Chem., 1927, **31**, 1053—1081).—The reaction between 2 : 6-dibromobenzoquinone-4-chloroimide and phenol, producing 2 : 6-dibromobenzenoneindophenol, has been studied quantitatively at various p_H values in the alkaline region, the velocity of reaction being measured by a spectrophotometric method. In buffered solutions containing an excess of phenol, the reaction is pseudo-unimolecular and can be expressed by an equation of the type $k = 2{\cdot}3026 \log [a/(a-x)]/tb\alpha$, where a, b, and α are the molar concentrations of 2 : 6-dibromobenzoquinonechloroimide, phenol, and phenoxide, respectively. When the concentrations of phenol and imide are nearly equal, the same value of k is obtained from an equation for a reaction of the second order. At 20°, k is $1{\cdot}63 \times 10^4$. The production of the blue colour given by the indophenol in alkaline solution is a very delicate test for phenol, and the velocity of reaction has been measured at concentrations below the limits of many usual tests, fair results being obtained at a dilution of 1 part in two million. The temperature coefficient of the reaction is considerable. The chloroimide decomposes in alkaline solutions, the reaction being pseudo-unimolecular and very sensitive to the hydroxyl-ion concentration. The value of k in this case is $6{\cdot}13 \times 10^3$. 2 : 6-Dibromobenzoquinoneoxime is probably the primary product of the reaction. This substance has a solubility in water $8{\cdot}5 \times 10^{-4}M$ at 20°, and its absorption spectrum, together with that of the chloroimide, is given.

L. S. Theobald.

[Nuclear condensation of phenols with nitriles.] J. Houben (Ber., 1927, **60**, [*B*], 1554).—A reply to Hoesch (this vol., 353). H. Wren.

Nature of the alternating effect in carbon chains. XX. Conditions underlying vicinal substitution in *o*-substituted benzenes containing *op*-orienting groups. C. K. Ingold and E. W. Smith (J.C.S., 1927, 1690—1695; cf A., 1926, 831, 833, 947).—Nitration of *o*-chloro-, *o*-bromo-, and *o*-iodo-anisole shows that the proportion of vicinal substitution of an *o*-disubstituted benzene containing *op*-orienting substituents increases with increasing disparity between the directive powers of the groups. The proportion of 6-isomeride formed in the nitration of different *o*-derivatives of anisole is: *o*-fluoro-, 66%; *o*-chloro-, 56%; *o*-bromo-, 52%; *o*-iodo-, <38%; *o*-methoxy-, 0%. M. Clark.

Caoutchouc and guttapercha. I. Condensation of caoutchouc and guttapercha dibromides with phenols and phenol ethers. *E.* Geiger (Helv. Chim. Acta, 1927, **10**, 530—538; *cf.* Weber, A., 1900, i, 353; Fisher, Gray, and McColm, A., 1926, 730).—Caoutchouc dibromide when heated at 90—120° with ferric chloride and excess of phenol gives 4 : 4'-dihydroxydiphenyldihydrocaoutchouc (*dibenzoate*, m. p. 195—200°). Similar *compounds* are obtained from *o*-cresol (m. p. 165—178°; *dibenzoate*, m. p. 190—195°), *m*- and *p*-cresols, resorcinol (not melted at 300°; *tetrabenzoate*, m. p. 240—245°), pyrogallol (*hexabenzoate* prepared), anisole (m. p. 150—160°, cf. Fisher, Gray, and McColm, *loc. cit.*), and phenetole (m. p. 210—215°). Guttapercha dibromide also condenses with phenol, *m*-cresol, and resorcinol, giving hydroxylated *diaryldihydroguttaperchas*, melting, respectively, at 170—175° (*dibenzoate*, m. p. 190—195°), 150—160° (*dibenzoate*, m. p. 175—180°), and above 300° [*tetrabenzoate*, m. p. 195—200° (decomp.)]. C. Hollins.

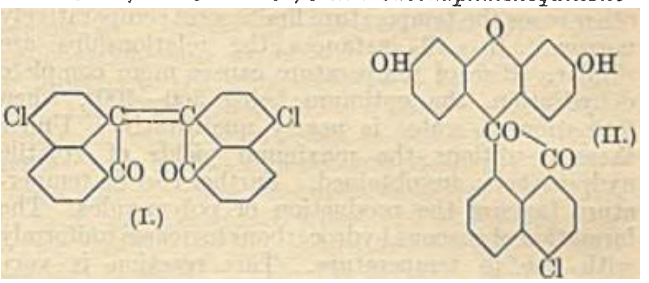
Monothioethylene glycol. III. Nitrophenyl thioethers. G. M. Bennett and W. A. Berry (J.C.S., 1927, 1666—1676).—The following were prepared by reaction of ethylenechlorohydrin with the potassium salts of *o*-, *m*-, and *p*-nitrothiophenol, respectively: *o-nitrophenyl* β-*hydroxyethyl sulphide*, m. p. 100°; m-*nitrophenyl* β-*hydroxyethyl sulphide*, m. p. 42·5° (p-*nitrobenzoyl* derivative, m. p. and *p*-nitrophenyl β-hydroxyethyl sulphide, m. p. (lit. 59°). p-*Nitrobenzyl* β-*hydroxyethyl sulphide*, m. p. 37·5°, and p-*nitrophenyl* γ-*hydroxypropyl sulphide*, m. p. 41·5°, were prepared by analogous methods. The following are also described: *o-nitrophenyl* β-*chloroethyl sulphoxide*, m. p. 84°; *o-nitrophenyl* β-*chloroethyl sulphide*, m. p. 62° (*sulphoxide*, m. p. 80°); m-*nitrophenyl* β-*chloroethyl sulphide*, m. p. 31°; p-*nitrobenzyl* β-*chloroethyl sulphide*, m. p. 47°; p-*nitrophenyl* γ-*chloropropyl sulphide*, m. p.

50°; o-*nitrophenyl* β-*bromoethyl sulphide*, m. p. 63° (*sulphoxide*, m. p. 112°); p-*nitrophenyl* β-*bromoethyl sulphoxide*, m. p. 100°; m-*nitrophenyl* β-*bromoethyl sulphide*, m. p. 32°; o-*nitrophenyl* β-*iodoethyl sulphide*, m. p. 64°; p-*nitrophenyl* β-*iodoethyl sulphide*, m. p. 67°; *di*-m-*nitrodiphenylthiol*cyclo*butane* (?), m. p. 136°. Crystallographic data are given for the o-nitro-hydroxy-, -chloro-, -bromo-, and -iodo-sulphides and the *p*-nitrochloro-, *p*-nitrobromo-, and *p*-nitro-iodo-sulphides. M. CLARK.

Influence of the sulphur atom on the reactivity of adjacent atoms or groups. II. Comparative reactivities of chlorine in some β- and γ-chloro-sulphides. G. M. BENNETT and W. A. BERRY (J.C.S., 1927, 1676—1684).—Certain chlorosulphides, including *o*-, *m*-, and *p*-nitrophenyl β-chloroethyl sulphides, *p*-nitrobenzyl β-chloroethyl sulphide, *p*-nitrophenyl γ-chloropropyl sulphide and the unsubstituted phenyl β-chloroethyl and phenyl γ-chloropropyl sulphides, have been compared as to their velocities of reaction with water in alcoholic solution at 75° and with potassium iodide in acetone solution at 55°. The order in which the substances are arranged with respect to the hydrolysis is the opposite of that indicated by the reaction with potassium iodide. This contrast, and the results of Conant, Kirner, and Hussey (A., 1925, i, 494) and of Olivier (A., 1923, i, 197), are all accounted for in accordance with the electronic theory of valency on the assumption that a positive charge on the chlorine atom facilitates the reaction with potassium iodide, the first and characteristic stage of the reaction being the formation of a complex between the chloro-compound and the iodide ion. The hydrolytic reaction, on the other hand, is accelerated by a negative charge on the chlorine atom (Oxford and Robinson, A., 1926, 397). Moreover, on this assumption, the results of this comparison are in agreement with one of the authors' previous conclusions (this vol., 355). The following are described: *phenyl γ-chloropropyl sulphide*, b. p. 137°/13 mm.; o-*nitrophenyl* β-*piperidinoethyl sulphide*, m. p. 45°; p-*nitrophenyl* β-*piperidinoethyl sulphide*, m. p. 52°. M. CLARK.

Synthesis of safrole and o-safrole. W. H. PERKIN, jun., and V. M. TRIKOJUS (J.C.S., 1927, 1663—1666).—When the monoallyl ether of pyrocatechol is heated at 170—180°, it undergoes the Claisen rearrangement, yielding a mixture of 1 : 2-*dihydroxy*-3-*allylbenzene*, m. p. 28°, b. p. 143·5—145°/15 mm. (*dibenzoyl* derivative, m. p. 60—61°), 1 . 2-dihydroxy-4-allylbenzene (cf. Kawai, A., 1926, 609). These substances are converted respectively by treatment with methylene iodide and anhydrous potassium carbonate in dry acetone solution into o-*safrole*, b. p. 102·5—103°/13 mm. and 226—227°/762 mm., n_D^{20} 1·5359 (*pentabromo*-derivative, m. p. 154°), and safrole, n_D^{20} 1·5381 (*pentabromo*-derivative, m. p. 169°). M. CLARK.

Acenaphthene. IV. 3-Chloroacenaphthene and its reactions. K. DZIEWONSKI and (MME.) M. ZIENSKA-BARANOWSKA (Bull. Acad. Polonaise, 1927, [A], A, 65—79).—3-Chloroacenaphthene, m. p. 69—70° (cf. Crompton and Walker, J.C.S., 1912, **101**, 958; Sachs and Mosebach, A., 1910, i, 726), with sulphuric acid (*d* 1·84) at 70° affords a *sulphonic acid* (*chloride*, m. p. 140—141°; *amide*, m. p. 235—236°). Nitration with nitric acid (*d* 1·47—1·48) at 15—20° affords 3-chloro-4-nitroacenaphthene, m. p. 136—138° (Farnell, J.C.S., 1923, **123**, 60), from which 3-*chloro*-4-*hydroxyacenaphthene*, m. p. 123°, is obtained through the amino-compound. 3-*Chloro*-4-*hydroxy*-5-*benzeneazoacenaphthene*, red, has m. p. 175—176°. Oxidation of 3-chloroacenaphthene with sodium dichromate in acetic acid at 40—50° affords 3 : 3′-*dichlorobisacenaphthenedione* (I), m. p. 324—325°; at 105—120°, 3-*chloroacenaphthenequinone*



m. p. 212—213°, is obtained, whilst excess of sodium dichromate affords 4-chloronaphthalic anhydride, m. p. 216—217°. With nitric acid (*d* 1·52) in sulphuric acid this affords a *dinitro*-derivative, m. p. 192—193°; and with resorcinol 5-*chloronaphthalfluorescein* (II), orange-red, giving a strong green fluorescence in alkaline solution.

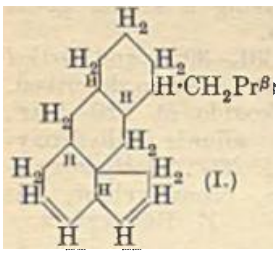
4-*Chloronaphthimide*, m. p. 301—302°, and *methyl* 4-*chloronaphthalate*, m. p. 91—93°, are also described. On fusion with sodium hydroxide at 220—230°, 4-chloronaphthalic anhydride affords 3-hydroxynaphthalic anhydride, m. p. 280°. 4-*Hydroxy*-4-*benzeneazonaphthalic anhydride*, bronze-yellow, has m. p. 261°. R. BRIGHTMAN.

Isomeric transformations of cyclic compounds under the influence of catalysts. II. Dehydration of the alcohols $C_5H_{10}O$; decomposition of the alcohols C_4H_8O with aluminium oxide as catalyst. M. DOJARENKO (Ber., 1927, **60**, [*B*], 1536—1553).—Methyl*cyclo*butanol is converted by passage over heated aluminium oxide mainly into isoprene accompanied by small amounts of β-methyl-Δ^{β}-butene, cymene, and caoutchouc-like polymerides; gaseous hydrocarbons are also evolved. At 370—375° the amount of volatile hydrocarbons is considerable, but diminishes at 400° owing to production of larger quantities of polymerides. *cyclo*Butylcarbinol is similarly isomerised, *cyclo*pentene being formed in more than 75% yield. Methyl*cyclo*propylcarbinol yields mainly piperylene accompanied by small amounts of divinylmethane. Enlargement of the ring with production of methyl*cyclo*butene is a very subsidiary process. Propylene is formed in about 2·5% yield at 350—360°. The alcohols C_4H_8O (*cyclo*propylcarbinol, *cyclo*butanol, and allylcarbinol) behave very similarly towards aluminium oxide, the reaction being complex. The initial stage consists in decomposition according to the scheme, $C_4H_8O = CH_3{\cdot}CH{:}CH_2 + H_2O + C$, in which formaldehyde is not a primary product. Isomerisation, $C_4H_8O = H_2O + CH_2{:}CH{\cdot}CH{:}CH_2$, takes place to a very limited

extent (3% in the case of allylcarbinol and not more than 7·5% with *cyclo*butanol and *cyclo*propylcarbinol). The change, $C_4H_8O=C_4H_6O+H_2$, leads to normal products with *cyclo*butanol and allylcarbinol, whereas *cyclo*propylcarbinol becomes isomerised to *cyclo*butanone and Δ^{γ}-butenaldehyde. The reaction, $C_4H_8O=CH_3{\cdot}CH{:}CH_2+CO+H_2$, is of little importance and the induced hydrogenation (butylene formation) is a secondary process, as also is the polymerisation observed at higher temperatures.

The influence of temperature on the course of the reaction has been most fully investigated with *cyclo*propylcarbinol and methyl*cyclo*propylcarbinol; in other cases the temperature limits were comparatively narrow. In all instances the relationships are similar. Rise of temperature causes more complete dehydration, the optimum being 350—400°, when formation of water is nearly quantitative. Under these conditions the maximum yields of volatile hydrocarbons are obtained. Further rise of temperature favours the production of polymerides. The formation of gaseous hydrocarbons increases uniformly with rise in temperature. This reaction is very subsidiary with the alcohols $C_5H_{10}O$, but is more important with the compounds C_4H_8O, from which propylene is mainly produced. H. WREN.

Derivatives of cholesterol. S. FRANKEL and P. DOMBACHER (Ber., 1927, **60**, [*B*], 1484—1487).—During unsuccessful attempts to prepare cholesteryl phosphates by the action of cholesterol on phosphoryl chloride, phosphoric anhydride, or hydrogen phosphates, or by fermentation, *hypocholesterol*, $C_{22}H_{36}O$, m. p. 83°, *hypocholesteryl ether*, $C_{44}H_{70}O$, m. p. 178°, and *hypocholestene* (I), m. p. 330°, have been isolated. H. WREN.



(I.)

Rape oil phytosterol. L. SCHMID and A. WASCHKAU (Monatsh., 1927, **48**, 139—144).—Rape oil phytosterol is most probably identical with sitosterol. Isolated from rich fractions of rape oil (cf. Windaus, A., 1909, i, 228) by extraction with light petroleum, hydrolysis, and recrystallisation from acetone, petroleum, and alcohol, it was acetylated by acetic anhydride and then brominated. Tetrabromobrassicasteryl acetate first separated, and was found to have the same crystalline form and optical properties as tetrabromostigmasteryl acetate. The filtrate from bromination when reduced by sodium amalgam and by zinc dust gave a phytosteryl acetate, softening 126—127°, m. p. 132—133° (corr.), hydrolysed to phytosterol, softening at 136—137°, m. p. 139—140°. This was suspected to be impure, and therefore a *digitonide* was prepared, from which the liberated sterol had m. p. 136—137° after softening at 132—133°; this preparation gave no depression of m. p. on mixing with sitosterol from wheat-germ, with which it was crystallographically identical. The acetate thence obtained, m. p. 127—128° after softening at 124·5°, was identical with sitosteryl acetate from the phytosterol of the calabar bean; the benzoate had m. p. 143°, the same as that of sitosteryl benzoate; the *anisate*, m. p. 147—148°, giving an orange-coloured, cloudy liquid with a violet fluorescence, clearing at 210—215°, indicated a molecular formula $C_{27}H_{46}O$.

No explanation is suggested for the change in m. p. of phytosterol when purified through the digitonide. E. W. WIGNALL.

Action of organo-magnesium compounds on oximino-ketones. Synthesis of some oximino-alcohols. A. OREKHOV and M. TIFFENEAU (Bull. Soc. chim., 1927, [iv], **41**, 839—843).—The action of Grignard reagents on oximino-ketones of the types Ar·CO·CH:NOH, Ar·CO·CAr′(NOH), and Ar·C(NOH)·CO·R, affords the corresponding oximino-alcohols, from which the amino-alcohols are obtained on reduction. Magnesium phenyl bromide and oximinoacetophenone afford, in 75% yield, *β-oximino-αα-diphenylethyl alcohol*, m. p. 121°. Similarly, magnesium phenyl bromide and β-benzilmonoxime afford β-oximino-ααβ-triphenylethyl alcohol, m. p. 153—154°, identical with the oxime of phenylbenzoin prepared by Delacre (A., 1895, i, 485), a reaction which indicates that the latter oxime possesses the same spatial configuration as β-benzilmonoxime. Magnesium methyl iodide and β-benzilmonoxime afford *α-oximino-αβ-diphenylisopropyl alcohol*, m. p. 120—121°. Since this is identical with the reaction product from magnesium phenyl bromide and phenyl oximinobenzyl ketone, it is concluded that the latter has a spatial configuration corresponding with that of β-benzilmonoxime (Meisenheimer, A., 1922, i, 152). R. BRIGHTMAN.

Dehydration in the trisubstituted secondary-tertiary glycol series (migration of the benzyl radical). (MLLE.) J. LEVY and R. LAGRAVE (Bull. Soc. chim., 1927, [iv], **41**, 833—839).—By dehydration with 50% oxalic acid, ααγ-triphenyl-αβ-propylene glycol affords 30% of ααβ-triphenylpropaldehyde (*oxime*, m. p. 91°) and 70% of benzyl diphenylmethyl ketone (cf. A., 1924, i, 283). The formation of the former product by migration of the benzyl group is interpreted as indicating that the migratory tendency of the benzyl group is equal or superior to that of hydrogen. The ketone probably results from the semihydrobenzoin transformation and only to a slight extent from isomerisation of the triphenylpropaldehyde, the latter change being effected under the influence of concentrated sulphuric acid. Vinyl dehydration without transposition is improbable. The fact that triphenylpropaldehyde is not formed in the dehydration of benzylhydrobenzoin (which also yields ααγ-triphenylpropan-β-one) supports the view of Orékhov that in this dehydration the secondary hydroxyl and not the tertiary is eliminated, $CH_2Ph{\cdot}CPh(OH){\cdot}CHPh{\cdot}OH \longrightarrow CH_2Ph{\cdot}CO{\cdot}CHPh_2$ (cf. A., 1919, i, 205). R. BRIGHTMAN.

Action of hydrobromic acid on diphenyldimethylbutinenediol. J. S. SALKIND and O. OUTKINA (J. Russ. Phys. Chem. Soc., 1927, **59**, 283—8[illegible]). This reaction was investigated to determine why tetramethylbutinenediol on treatment with hydrobromic or hydriodic acid gives chiefly $CMe_2X{\cdot}CX{\cdot}CMe_2$ (X=halogen), whilst diphenylbutinenediol with hydrobromic acid gives chiefly 3-bromo-2 : 5-diphenyl

hydrofuran, although the dibromide was also produced (A., 1926, 1121). Diphenyldimethylbutinenediol, CPhMe(OH)·C:C·CPhMe·OH, does not react with an aqueous solution of hydrobromic acid, but reacts readily on warming with a solution of hydrobromic acid in acetic acid. A small yield of a *dibromide*, m. p. 113°, was isolated, which did not decolorise a solution of bromine in chloroform. It is not hydrolysed at 70° by 25% aqueous potassium hydroxide, and therefore is probably CPhMe·CBr·CBr:CPhMe. The chief product was, however, 3-*bromo*-2 : 5-*diphenyl*-2 : 5-*dimethyldihydrofuran*, an oil, formed as in the case of the diphenylbutinenediol, not by decomposition of the dibromide, but by an independent parallel reaction. Diphenyldimethylbutinenediol resembles, therefore, the diaryl-substituted rather than the tetra-alkyl-substituted acetylene glycol.

J. KAYE.

Preparation of triarylmethane dyes. BRITISH DYESTUFFS CORPN., LTD., E. H. RODD, and F. W. LINCH.—See B., 1927, 598.

Three-carbon system. XII. Effect of positive substituents in the α-position on the tautomerism. G. A. R. KON and B. T. NARAYANAN (J.C.S., 1927, 1536—1546).—Acids, ketones, and nitriles of the general formulæ R·CEtX, where R is CMeEt· or the *cyclo*pentane or *cyclo*hexane radical and X is ·CO_2H, ·COMe, or ·CN, have been examined. It is shown that for acids and ketones, introduction of the α-ethyl group favours the βγ-position for the double linking and slightly retards the mobility of the system. The nitriles, however, are obtained in the αβ-form since they are produced by elimination of ethyl carbonate from cyano-esters of the type  This process is now shown to yield αβ-unsaturated compounds, not the βγ-isomerides as previously supposed (Birch and Kon, J.C.S., 1923, **123**, 2440). The presence of the α-ethyl group causes greater retardation of mobility in the nitriles than in the acids and ketones. When α-ethyl-Δ¹-*cyclo*hexenylacetic acid (*amide*, m. p. 115—116°; p-*toluidide*, m. p. 115°; *silver* salt) is boiled with potassium hydroxide, it is recovered largely unchanged together with a trace of the αβ-acid and a *lactone*, from which the *silver* salt of a hydroxy-acid is obtained. α-*Ethyl*cyclo*hexylideneacetic acid*, b. p. 164—166°/20 mm., $d_4^{19°}$ 1·01831, n_D 1·47977 (*silver* salt; *chloride*, p. 110—112°/20 mm.; *amide*, m. p. 104—105°; p-*toluidide*, m. p. 104°), from 1-*hydroxy*-α-*ethyl*cyclo*hexylacetic acid*, b. p. 167—170°/16 mm., $d_4^{18·8}$ 1·0010, $n_D^{18·8}$ ·46798 (*silver* salt), and acetic anhydride on equilibration with boiling potassium hydroxide is largely converted into the βγ-acid and the above-mentioned lactone. α-Ethyl-Δ¹-*cyclo*hexenylacetone, [illegible]er admixture with sodium ethoxide in alcohol, gives a mixture of *semicarbazones* of m. p. 185° and [illegible]5— and on oxidation with potassium hypobromite is converted into α-ethyl-Δ¹-*cyclo*hexenyl[illegible]e . When treated with ethyl sodiomalonate, [illegible]e ne forms a condensation *product*, m. p. 76—77° w[illegible] on hydrolysis, yields cyclo*hexane*spiro-2-[illegible]cy[illegible]*exane*-3 : 5-*dione*, m. p. 159—160°. Dehydration of 1-hydroxy-α-ethyl*cyclo*pentylacetic acid with sulphuric acid gives a mixture of α-*ethyl*-Δ¹-cyclo*pentenylacetic acid*, b. p. 138—142°/15 mm., $d_4^{17·4}$ 1·01909, $n_D^{17·4}$ 1·47525 (*silver* salt; *chloride*, b. p. 96—98°/20 mm.; *amide*, m. p. 102—103°; *dibromide*; *hydrobromide*), with less α-*ethyl*cyclo*pentylideneacetic acid*, m. p. 80—81° (*chloride*, 102—106°/16—18 mm.; *amide*, m. p. 97°; *dibromide*; *hydrobromide*). The α^{α}-acid is better obtained by dehydration of the hydroxy-acid with acetic anhydride. α-*Ethyl*cyclo*pentylideneacetonitrile*, b. p. 116—118°/20 mm., $d_4^{21°}$ 0·923586, 1·47555, gives on hydrolysis the corresponding *ethyl* ester, b. p. 116—118°/25 mm., $d_4^{19·5}$ 0·936298, $n_D^{19·5}$ 1·47417. Hydrolysis of this ester yields a mixture of acids in which the βγ-acid predominates. α-Ethyl-Δ¹-*cyclo*pentenylacetone after equilibration with alcoholic sodium ethoxide gives, in addition to the semicarbazone of m. p. 166—167° (Kon and Linstead, A., 1925, i, 633), a second *semicarbazone*, m. p. 143—145°. Condensation of the ketone with ethyl sodiomalonate yields after hydrolysis a liquid *diketone*, which, on oxidation with hypobromite, gives α-*ethyl*cyclo*pentane*-1 : 1-*diacetic acid* (*silver* salt). Ethyl β-hydroxy-β-methyl-α-ethylvalerate [*acid*, b. p. 132—136°/20 mm. (*silver* salt)], yields with phosphorus oxychloride ethyl β-methyl-α-ethyl-Δ$^{\beta}$-pentenoate [*acid*, b. p. 122—126°/20 mm., $d_4^{20·4}$ 0·95884, $n_D^{20·4}$ 1·45113 (*silver* salt; *chloride*, b. p. 76—78°/18—20 mm.; p-*toluidide*, m. p. 102—104°)]. β-*Methyl*-α-*ethyl*-Δ$^{\alpha}$-*pentenoic acid*, b. p. 126—130°/15—18 mm., $d_4^{20·4}$ 0·95930, $n_D^{20·4}$ 1·45193 (*silver* salt; *chloride*, b. p. 86—90°/20 mm.; p-*toluidide*, m. p. 112—113°; *hydrobromide*), is obtained from β-hydroxy-β-methyl-α-ethylpentanoic acid and acetic anhydride. δ-*Methyl*-γ-*ethyl*-Δ$^{\delta}$-*hexen*-β-*one*, b. p. 72—74°/16 mm., d_4 0·85068, $n_D^{19·7}$ 1·43908 (*semicarbazone*, m. p. 163—164°), after equilibration with alcoholic sodium ethoxide, yields a mixture of αβ- and βγ-unsaturated ketones, which forms a second *semicarbazone*, m. p. 151—152°, in addition to that of m. p. 163—164°.

M. CLARK.

Quantitative comparison of electron displacement and alternate polarity effects in aromatic compounds. G. BERGER (Rec. trav. chim., 1927, **46**, 541—548).—The general or electron displacement effect, like the alternate polarity effect, is considered to be transmitted by the carbon chain. The contention that the former decreases more slowly with increasing distance from the affected group than the latter may be answered by assuming that there is a difference in the mechanism of transmission in the two cases (cf. van Duin, this vol., 662). The theory of Højendahl (A., 1924, ii, 722) used by van Duin in the calculation of the hydrolysis constant of the substituted benzyl chlorides has not been experimentally verified, and in some cases is not in agreement with the facts. Thus, according to the theory, the effect of chlorine substitution in the β-position on the dissociation constant of crotonic acid should be three times the effect of the same substitution on the dissociation constant of butyric acid, assuming, with van Duin, that the general effect, which also causes an increase in the constant, decreases at the same rate as the alternating effect with increasing distance. Actually, the influence of the entry of the chlorine atom is only 10% higher for the

unsaturated acid. Again, the entry of a *m*-methyl group into the benzoic acid molecule causes a reduction in the dissociation constant, both general and alternating effects acting in the same sense. The effect of the entry of this group on the benzoic acid constant should be 3·3 times as large as its effect on the constant of hexahydrobenzoic acid; actually the methyl group is only 11% more effective in the first case.

Olivier has shown that the effect of the substituents in the isomeric dibromobenzyl chlorides on the hydrolysis constant varies as the product of the effects of the two substituents taken separately (A., 1926, 511). Assuming therefore that the total effect of a substituent varies as the product (or the quotient if the effects are in opposition) of the alternating effect, the general effect, and the special ortho-effect in the case of *o*-substituents, and, further, that the general effect decreases at the same rate as the alternating effect with the distance of the substituent from the affected atom, the relative influence of the three effects in the case of the substituted benzyl chloride has been calculated for the substituents Cl, Br, I, CO_2H, NO_2, and Me. Similar calculations have been carried out for two other reactions, viz., that between substituted phenols and ethylene oxide (Boyd and Marle, J.C.S., 1914, **105**, 2117) and the hydrolysis of substituted ethyl benzoates (cf. McCombie and Scarborough, J.C.S., 1915, **107**, 155). In all three reactions and for all substituents the general effect is greater than the alternating effect, the difference being smallest in the case of the methyl group (about 30%), and greatest for the nitro-group (6—18 times). The general effect varies most for the various substituents but the ratio of the general effects of two given substituents is approximately constant in the three reactions. The temperature coefficients of the three effects in the case of the substituted benzyl chlorides is small and, with the exception of the methyl group, negative.

W. J. Powell.

Imino-aryl ethers. V. Effect of substitution on the velocity of molecular rearrangement. A. W. Chapman (J.C.S., 1927, 1743—1751; cf. A., 1925, i, 1400).—The velocity of the imino-ether ⟶ amide change when the substituted *N*-phenylbenzimino phenyl ethers are heated is investigated for the three types of imino-ether (I) NPh:CPh·OR, (II) NR:CPh·OPh, (III) NPh:CR·OPh. The following substituent groups in type I are arranged in descending order of ease of migration: *o*-nitrophenyl > 2 : 4 : 6-trichlorophenyl > *p*-acetylphenyl > 2 : 4-dichlorophenyl > *o*-chlorophenyl > *m*-chlorophenyl > *p*-chlorophenyl and α- and β-naphthyl > phenyl and *o*-anisyl > *m*-anisyl > anisyl > methyl. The velocities of migration of a phenyl group for different substituents attached to the nitrogen atom (type II) are in the order: *p*-anisyl > phenyl > *p*-chlorophenyl and α-naphthyl > *m*- and *o*-chlorophenyl and 2 : 4-dichlorophenyl > 2 : 4 : 6-trichlorophenyl. For different substituents attached to the carbon atom (type III) the velocities of migration are in the order: *p*-anisyl > phenyl > *p*- and *o*-chlorophenyl > *p*-nitrophenyl and 2 : 4 : 6-trichlorophenyl. An electronic hypothesis is advanced to account for the migration.

The following are described: type I, N-*phenylbenzimino* m-*chlorophenyl ether*, m. p. 71°, 2 : 4-*dichlorophenyl ether*, m. p. 73—74°, 2 : 4 : 6-*trichlorophenyl ether*, m. p. 80—81°, o-*anisyl ether*, m. p. 113°, m-*anisyl ether*, a viscid oil, p-*anisyl ether*, m. p. 79—80°, p-*nitrophenyl ether*, m. p. 76—77°, α-*naphthyl ether*, m. p. 89°, β-*naphthyl ether*, m. p. 127—128°, p-*acetylphenyl ether*, m. p. 94—95°; type II, N-o-*chlorophenyl*-, m. p. 65—66° (prepared from *benz*-o-*chloroanilideiminochloride*, b. p. 204°/10 mm., and phenol), N-m-*chlorophenyl*-, m. p. 66° (from *benz*-m-*chloroanilideiminochloride*, b. p. 211—213°/14 mm.), N-p-*chlorophenyl*-, m. p. 110° (from benz-*p*-chloroanilideiminochloride, b. p. 220—224°/20 mm.), N-2 : 4-*dichlorophenyl*-, m. p. 57—58°, and N-2 : 4 : 6-*trichlorophenyl-benziminophenyl ether*, m. p. 88·5°; N-2 : 4 : 6-*trichlorophenylbenzimino* 2 : 4 : 6-*trichlorophenyl ether*, m. p. 141° (gives on heating *benzoyl*-2 : 4 : 6 : 2′ : 4′ : 6′-*hexachlorodiphenylamine*, m. p. 194—195°); N-p-*anisyl*-, m. p. 100° (from *benz*-p-*anisidideiminochloride*, m. p. 55°, b. p. 269—273°/162—180 mm. decomp.), N-o-*nitrophenyl*-, m. p. 67—68°, N-α-*naphthyl*- a viscid oil, and N-*methyl-benzimino phenyl ether*, m. p. 30—31°; type III, N-*phenyl*-o-*chloro*-, m. p. 100° (from o-*chlorobenzanilideiminochloride*, m. p. 59°, b. p. 235°/60 mm.), N-*phenyl*-p-*chloro*-, m. p. 64—65° (from p-*chlorobenzanilideiminochloride*, b. p. 219°/17 mm.), -*phenyl*-2 : 4 : 6-*trichloro*-, m. p. 94—95°, N-*phenyl*-p-*methoxy*-, m. p. 86—87° (dimorphous), N-*phenyl*-o-*nitro*-, m. p. 141—142°, and N-*phenyl*-p-*nitro-benzimino phenyl ether*, m. p. 102—102·5°; and the following diphenylamine derivatives: *benzoyl*-2 : 4-*dichloro*- m. p. 109°, *benzoyl*-2 : 4 : 6-*trichloro*-, m. p. 149°, *benzoyl*-o-*methoxy*-, m. p. 117°, *benzoyl*-p-*methoxy*-, m. p. 121°, *benzoyl*-o-*nitro*-, m. p. 134°, *benzoyl*-p-*acetyl*-, m. p. 136—137·5°, o-*chlorobenzoyl*-, m. p. 142—143°, p-*chlorobenzoyl*-, m. p. 138—138·5°, 2 : 4 : 6-*trichlorobenzoyl*-, m. p. 118—119°, p-*methoxybenzoyl*-, m. p. 139—140°, and p-*nitrobenzoyl-diphenylamine*, m. p. 156—157°; 2 : 4 : 6-*trichlorobenzanilide*, m. p. 197°. N-*Phenylbenzimino*-o-*acetylphenyl ether*, m. p. 92—93°, on heating yields 1 : 2-*diphenyl*-4-*quinolone*, m. p. 268°, by intramolecular transformation and elimination of water.

M. Clark.

Variations in the sweetening power of saccharin and of some of its derivatives. B. Oddo and Q. Mingoia (Gazzetta, 1927, **57**, 465 474). By the action of magnesium methyl iodide on saccharin, "C-*hydroxymethylsaccharin*," $C_6H_4\begin{cases}CO\\SO\end{cases}NH$, m. p. 110—111° (*dibenzoyl* derivative, m. p. 183—184°; *hydrochloride*, soluble in water), is prepared. The 3-*ethyl*-, m. p. 119—120° (*diacetyl* derivative, obtained by the action of acetyl chloride on reaction product of saccharin and magnesium e bromide, m. p. 138°), 3-*propyl*-, m. p. 1[illegible]4 (r *dibenzoyl* derivative), 3-*phenyl*-, m. p. [illegible], 3-*benzyl*-, m. p. 134°, analogues are similarly prepared. These substances are all tasteless after being ree from saccharin by washing with sodium hydrox solution, in which they are insoluble.

E. W. Wignall.

Reaction between cinnamyl chloride, magnesium, and carbon dioxide. H. Gilman

S. A. HARRIS (J. Amer. Chem. Soc., 1927, **49**, 1825—1828).—Addition of cinnamyl chloride to an ethereal suspension of magnesium through which carbon dioxide is bubbled affords methylatropic acid (cf. Oglialoro, A., 1886, 468), the formation of which probably indicates the rearrangement of magnesium cinnamyl chloride to the isomeride CPh(MgCl):CHMe, and throws doubt on Rupe and Bürgin's interpretation of their results (A., 1910, i, 161). F. G. WILLSON.

Action of organo-magnesium derivatives on α-trisubstituted primary amides. (MME.) RAMART, (MLLE.) LACLÔTRE, and ANAGNOSTOPOULOS (Compt. rend., 1927, **185**, 282—284).—Whereas mono- and di-substituted acid amides are converted by organo-magnesium derivatives into ketones, trisubstituted amides yield mainly the corresponding nitriles. It is suggested that the amide reacts in the hydroxyimide form; *N*-substituted amides do not react. Dimethylcampholamide, fencholamide, diphenylbenzylacetamide, phenylmethylethylacetamide, and phenyldiethylacetamide yield exclusively nitriles, the last-named amide losing 2 mols. of ethane from each mol. Benzyldimethylacetamide with magnesium phenyl bromide gives benzyldimethylacetophenone and benzyldimethylacetonitrile, but with magnesium ethyl bromide the nitrile only. Dimethylethylacetamide and trimethylacetamide give mainly the ketones, with some nitrile. E. W. WIGNALL.

Preparation of βββ-triphenylethylamine. Rearrangement of βββ-triphenylpropionhydroxamic acid. L. HELLERMAN (J. Amer. Chem. Soc., 1927, **49**, 1735—1742).—βββ-Triphenylpropionic acid (cf. Fosse, A., 1907, i, 764) was converted successively into the chloride, m. p. 132°, and the *amide*, m. p. 192°. The latter affords, when treated in alcoholic solution with aqueous sodium hypochlorite, the NN'-*dichloro*-derivative, m. p. 116°, which could not be fully purified. An impure N-*bromoamide*, obtained analogously, yielded βββ-*triphenylethylamine*, m. p. 132° [*hydrochloride*, m. p. 239—240°; *nitrate*, decomp. 237°; *chloroplatinate*, m. p. 183° (decomp.); *benzoyl* derivative, m. p. 157°; *urethane*, m. p. 94°], when subjected to rearrangement by the Lengfeld–Stieglitz method (A., 1894, i, 415). Treatment of the above acid chloride with hydroxylamine hydrochloride and sodium carbonate affords βββ-*triphenylpropionhydroxamic acid*, m. p. 182·5° (decomp.), the *benzoyl* derivative of which, m. p. 171·5°, yields, when boiled with aqueous potassium hydroxide, s-*di*-βββ-*triphenylethylcarbamide*, m. p. 218·5—219·5°. The latter yields the above triphenylethylamine on hydrolysis with aqueous-alcoholic hydrogen chloride at 150°. The non-production of βββ-triphenylethylamine by reduction of triphenylacetonitrile (Biltz, A., 1897, i, 533) is confirmed. F. G. WILLSON.

Introduction of the carbethionyl group by means of aluminium chloride. I. *p*-Hydroxydithiobenzoic esters. H. JÖRG (Ber., 1927, **60**, [B], 1466—1470).—When the Friedel–Crafts reaction is effected in the presence of carbon disulphide, aromatic acidic compounds containing sulphur are produced in amounts which attain their maximum when phenolic ethers are employed. Thus phenetole, carbon disulphide, and aluminium chloride give *ethyl* p-*hydroxydithiobenzoate*, $OH\cdot C_6H_4\cdot CS_2Et$, m. p. 57° (or $+\frac{1}{2}H_2O$, m. p. 42°), which yields a *benzoyl* derivative, m. p. 80°, and p-*nitrobenzoyl* compound, m. p. 119°, but cannot readily be benzylated. It is hydrolysed by alkali hydroxide to p-*hydroxythiobenzoic acid*, m. p. 208°, hydrogen sulphide, and ethyl sulphide and by hydrochloric acid to *p*-hydroxybenzoic acid, hydrogen sulphide, and ethyl mercaptan. It is oxidised by hydrogen peroxide to *p*-hydroxybenzoic acid. Phenetole in this reaction may be replaced by a mixture of phenol and ethyl bromide. Phenyl *iso*amyl ether, *p*- and ω-bromophenetole do not yield crystalline products; anisole gives *methyl* p-*hydroxydithiobenzoate*, m. p. 61°, in very small yield. Benzene, ethyl bromide, aluminium chloride, and carbon disulphide give ethyl dithiobenzoate. H. WREN.

Ring–chain tautomerism in γ-aldehydo-acids and δ-ketoaldehydes. H. MEERWEIN [with H. BRAKE, W. KOMANT, and H. MORSCHEL] (J. pr. Chem., 1927, [ii], **116**, 229—275).—Introduction of an α-alkyl group into γ-aldehydo-acids greatly favours lactone formation; both tautomerides of any one acid have not yet been isolated. Methyl γ-aldehydo-β-phenyl-γ-methylbutane-αα-dicarboxylate (I) (A., 1920, i, 844) is hydrolysed by potassium hydroxide, giving first γ-*aldehydo*-α-*carbomethoxy*-β-*phenyl*-γ-*methylvaleric acid* (II), m. p. 114—119° (decomp.), and then the corresponding *dicarboxylic acid* ($+H_2O$), m. p. 98—99° (decomp.), which does not form a lactone but is converted by boiling dilute sulphuric acid into γ-*aldehydo*-β-*phenyl*-γ-*methylvaleric acid* (III), m. p. 108—109° (also $+H_2O$). This behaves as a true aldehydo-acid, giving an *oxime*, m. p. 141·5°, and a *phenylhydrazone*, m. p. 151·5—152·5°, but with methyl alcohol and hydrogen chloride δ-*methoxy*-β-*phenyl*-γγ-*dimethylvalerolactone*, b. p. 169·5—170·5°/10 mm., d_4^{20} 1·071, n_D^{20} 1·4999, is formed. The normal *methyl* ester, b. p. 160°/10 mm., d_4^{20} 1·0838, n^{20} 1·5119, is obtained by heating the ester-acid, (II), at 130—140°. With cold acetic anhydride the aldehydo-acid gives a reactive mixed anhydride, converted by ammonia into γ-*aldehydo*-β-*phenyl*-γ-*methylvaleramide* ($+H_2O$), m. p. 162°, resolidifying, decomp. 192°, and by alcohols into esters. The anhydride is stable, even at 220°, but in presence of acetic anhydride it is rapidly transformed through the triacetate into δ-*acetoxy*-β-*phenyl*-γγ-*dimethylvalerolactone*, m. p. 146·5—147·5°, which regenerates the aldehydo-acid on hydrolysis. The lactone is converted by hydroxylamine into a mixture of the oxime (above) and the *hydroxamic acid*, $CHO\cdot CMe_2\cdot CHPh\cdot CH_2\cdot C(OH).NOH$ ($+H_2O$), m. p. 145·5—148°; and by phenylhydrazine into γ-*aldehydo*-β-*phenyl*-γ-*methylvalerphenylhydrazide*-*phenylhydrazone*, m. p. 186—187°. When the sodio-derivative of (I) is heated at 100° with methyl iodide *methyl* γ-*aldehydo*-β-*phenyl*-αγγ-*dimethylbutane*-αα-*dicarboxylate*, m. p. 94°, is produced. Hydrolysis gives (*a*) with potassium hydroxide, instead of the expected dicarboxylic acid, the corresponding *dilactone*, m. p. 134°, which is oxidised by alkaline permanganate to β-phenyl-ααγ-trimethylglutaric acid, m. p. 169° (Killing, Diss., Bonn, 1920); (*b*) with sodium methoxide, the monocarboxylic ester, hydrolysed by addition of water to a *product*, m. p. 123—124°.

Comparison of the last with the aldehydo-acid (III) shows that the former is much the weaker acid and that its physical properties are not those of a homologue of the latter. Its chemical behaviour is similar to that of the cyclic derivatives of (III), and it is therefore regarded as *δ-hydroxy-β-phenyl-αγγ-trimethylvalerolactone*. The corresponding free acid cannot be isolated. The hydroxylactone is converted by boiling acetic anhydride into its *acetate*, m. p. 123·5°; by hydroxylamine (*a*) in alkaline solution into the *oxime*, m. p. 168°, of γ-aldehydo-β-phenyl-αγ-dimethylvaleric acid; (*b*) in acetic acid into the *oxime-hydroxamic acid*, $NOH{:}CH{\cdot}CMe_2{\cdot}CHPh{\cdot}CHMe{\cdot}C(OH){:}NOH$ ($+0{\cdot}5CHCl_3$), m. p. 172°; and by phenylhydrazine into a mixture of the *phenylhydrazide* (66%), m. p. 166·5—168°, and *phenylhydrazone* ($+H_2O$) (33%), m. p. 176·5—177·5°, of γ-aldehydo-β-phenyl-αγ-dimethylvaleric acid. *Methyl γ-aldehydo-β-phenyl-γ-methyl-α-ethylbutane-αα-dicarboxylate*, m. p. 114—115°, prepared similarly to the α-methyl derivative, is hydrolysed by alcoholic potassium hydroxide to *δ-hydroxy-β-phenyl-γγ-dimethyl-α-ethylvalerolactone*, m. p. 97°, which is oxidised by alkaline permanganate to β-phenyl-αα-dimethyl-γ-ethylglutaric acid. The hydroxylactone is converted by hydroxylamine (*a*) in alkaline solution into the *oxime*, m. p. 179—180°, of γ-aldehydo-β-phenyl-γ-methyl-α-ethylvaleric acid, (*b*) in acetic acid into the *hydroxamic anhydride*, $\begin{matrix}CHEt{-}CO{-}N{\cdot}OH\\ |\qquad\quad |\\ CHPh{\cdot}CMe_2{\cdot}CH{\cdot}OH'\end{matrix}$, m. p. 174—175°.

Whilst δ-benzoyl-γδ-diphenylbutaldehyde behaves chemically in accordance with an open-chain structure (cf. A., 1919, i, 21), δ-benzoyl-γ-phenyl-β-propylbutaldehyde and δ-benzoyl-γ-phenyl-ββ-dimethylbutaldehyde (IV) (A., 1920, i, 844) frequently appear to react in the tautomeric dihydropyranol form. Thus, the ketoaldehyde (IV) reacts instantaneously with bromine, giving the *δ-bromo*-derivative, m. p. 106—107° (decomp.), and with iodine monochloride, and is hydrogenated in presence of platinum-black in the same way as the cyclic ether (V) to *ε-hydroxy-γε-diphenyl-ββ-dimethylvaleraldehyde*, m. p. 106—107·5°. With methyl-alcoholic hydrogen chloride the ketoaldehyde gives *2-methoxy-4 : 6-diphenyl-3 : 3-dimethyl-3 : 4-dihydro-1 : 2-pyran* (V), m. p. 121·5—122·5°. Bromination of (V) in carbon tetrachloride is accompanied by hydrolysis to the δ-bromoketoaldehyde (above). Catalytic hydrogenation gives *2-methoxy-4 : 6-diphenyl-3 : 3-dimethyltetrahydropyran*, m. p. 100—101° or 97—101° (stereoisomerism ?), which is hydrolysed to the ε-hydroxyaldehyde. When (V) is heated at 90—145° it decomposes into α-methoxy-β-methyl-Δ^{α}-propylene and phenyl styryl ketone. This supports the theory that the reversible addition of substances capable of enolisation to a double linking takes place through an intermediate cyclic compound, *e.g.*, $CHPh{:}CH{\cdot}COPh + CMe_2{:}CH{\cdot}OH \longrightarrow \begin{matrix}CH{:}CPh{-}\!-\!O\\ |\qquad\quad |\\ CHPh{\cdot}CMe_2{\cdot}CH{\cdot}OH\end{matrix} \longrightarrow CH_2Bz{\cdot}CHPh{\cdot}CMe_2{\cdot}CHO$.

H. E. F. Notton.

Action of hydrazine on meconine and 3-nitromeconine. A. Tasman (Rec. trav. chim., 1927, 46, 534—540).—Meconine, when warmed with an alcoholic solution of hydrazine hydrate, yields *2-hydroxymethyl-5 : 6-dimethoxybenzhydrazide*, m. p. 165°, which gives on boiling with acetone and benzaldehyde *acetone-2-hydroxymethyl-5 : 6-dimethoxybenzhydrazone*, m. p. 174°, and *benzylidene-2-hydroxymethyl-5 : 6-dimethoxybenzhydrazide*, m. p. 155°. When meconinehydrazide is boiled with acetic anhydride, meconine is regenerated, but at 0° *N-acetyl-2-hydroxymethyl-5 : 6-dimethoxybenzhydrazide*, m. p. 177°, is obtained. In 3-nitromeconine, m. p. 160° (cf. Anderson, Annalen, 1856, 98, 47), the mobility of the 6-methoxy-group is considerably increased since it is eliminated by alcoholic hydrazine hydrate solution, the chief product being *3-nitro-5-methoxy-6-hydrazinophthalide*, m. p. 220° (decomp.), and a small quantity of a *dihydrazide*, m. p. 248° (decomp.), which does not react with benzaldehyde. 3-Nitro-5-methoxy-6-hydrazinophthalide yields an *acetone* derivative, orange, m. p. 208°, a *benzylidene* derivative, red, m. p. 246°, and an *acetyl* derivative, yellow, m. p. 227°. W. J. Powell.

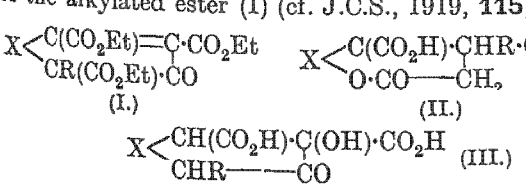
Diphenyl series. VI. Configuration of diphenyl derivatives. F. Bell and P. H. Robinson (J.C.S., 1927, 1695—1699).—Partial resolution of 6-nitrodiphenic acid is effected by fractionation of the *morphine* salt, m. p. 224°, $[\alpha]_{5461}$ −87·5° in pyridine, or of quinine hydrogen 6-nitrodiphenate. The impure d- and l-*acids* thus obtained have respectively m. p. 240—245°, $[\alpha]_{5461}$ +62°, and m. p. 239—245°, $[\alpha]_{5461}$ −66·7°. No resolution of 4-nitrodiphenic acid can be brought about. It is suggested that diphenyl derivatives should be resolvable when they have substituents in the 2- and 2′-positions which, owing to size or electrical character, are unable to pass the 6′- and 6-positions respectively. *Dimenthyl diphenate*, m. p. 126°, $[\alpha]_{5461}$ −120·4°, and d-β-*octyl hydrogen diphenate*, m. p. 70—73°, $[\alpha]_D$ +51°, show no change in rotation on fractionation. *4-Nitrodiphenic dichloride*, m. p. 90—92°, *6-nitrodiphenic dichloride*, m. p. 87°, *diphenic dichloride*, m. p. 97°, are obtained from the acids and thionyl chloride. 4 : 4′-Dinitrodiphenic acid and the corresponding acid chloride on boiling in acetic acid solution yield a double *compound* of 4 : 4′-dinitrodiphenic anhydride and acetic anhydride in equimolecular proportions from which *4 : 4-dinitrodiphenic anhydride*, m. p. 233—235°, is obtained by heating. *4-Nitrodiphenic anhydride*, m. p. 205—207°, is obtained by evaporating a solution of 4-nitrodiphenic acid in thionyl chloride in a vacuum. The following are described : *2 : 2′-dibenzamidotetramethylbenzidine*, m. p. 201°, *2 : 2′-di-p-toluenesulphonamidotetramethylbenzidine*, m. p. 203°, and *2 : 2′-diaminotetramethylbenzidine*, m. p. 138°. M. Clark.

Stereochemistry of aromatic compounds. Racemisation of optically active diphenic acids, and rotation of the benzene nucleus in diphenyl system. R. Kuhn and O. Albrecht (Annalen, 1927, 455, 272—299).—The stereochemistry of diphenyl compounds is reviewed and it is deduced from the theories of Weissenberg and of Reis (A., 1924, i, 934) that different derivatives must have different spatial formulæ. Contrary to the statement of Christie and Kenner (J.C.S., 1922, **121**, 614), solutions of *d*-6 : 6′-dinitrodiphenate does not racemise when kept or heated at 140—160° in aqueous solution. The optical activity of the acid is not changed by heating with sulphuric acid at 98°, or with alumi-

chloride at 140—150°. *l*-4 : 6′-Dinitrodiphenic acid, $[\alpha]^{17.3}$ +176°, $[\alpha]^{12.5}$ +142° in 2*N*-sodium hydroxide (*d*-acid, m. p. 303—304°, $[\alpha]_D^{21}$ −212·6° in 2*N*-sodium hydroxide; cf. Christie, Holderness, and Kenner, A., 1926, 518), shows a normal rotation dispersion. The velocity of racemisation of the *l*-acid at 73·5° and 98·2° in 2*N*-sodium hydroxide has been measured. In sulphuric acid at the same temperature the velocity is much smaller. Racemisation is not preceded in this case by enolisation (cf. Hückel, A., 1926, 1024). The reaction is unimolecular and the heat of activation of the free anion calculated from the temperature coefficient $(k_t+10)/k_t=5{\cdot}2$ is 26,000 g.-cal./mol. This is regarded as a measure of the energy required to rotate the benzene nuclei into a coplanar position. The constitution of 4 : 4′-dinitrodiphenic acid is proved by its decomposition in presence of copper bronze to 4 : 4′-dinitrodiphenyl (Willstatter and Kalb, A., 1906, i, 996). When the acid is converted into its *quinine* salt, it appears to undergo an asymmetric transformation (cf. Leuchs, A., 1921, i, 442), the homogeneous product (80% of theoretical) having m. p. 207—208°, $[\alpha]_D^{22}$ +110° in chloroform, from which the value $[\alpha]_D^{22}$ +700° is calculated for the free acid. In alcohol the activity varies greatly with the concentration and the ratio acid/base. Cinchonidine also gives a strongly dextrorotatory salt. Only inactive acid is regenerated from these salts. The series 4 : 4′-, 4 : 6′-, and 6 : 6′-dinitrodiphenic acids thus clearly illustrates the powerful effect of 6-nitro-groups in hindering the racemisation of active diphenic acids. H. E. F. Notton.

Alkaline oxidation of α-nitronaphthalene. J. H. Gardner (J. Amer. Chem. Soc., 1927, **49**, 1831—1833).—Oxidation of α-nitronaphthalene with alkaline permanganate, with subsequent treatment with aniline, affords the aniline derivative of phthalonic acid, as previously reported for the similar oxidation of naphthalene (cf. Fuson, A., 1926, 612). F. G. Willson.

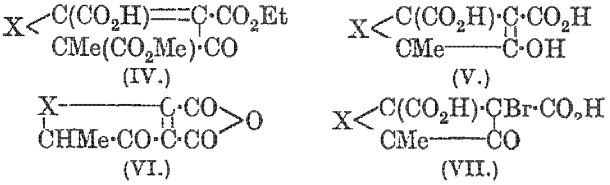
Chemistry of polycyclic structures in relation to their homocyclic unsaturated isomerides. VIII. Differing effects of the *gem*-dimethyl and *spirocyclo*hexane groupings on the direction of blocking of an intra-annular tautomeric system by substitution. C. K. Ingold and E. A. Seeley (J.C.S., 1927, 1684—1689).—Ethyl 5-*cyclo*hexane-*spirodicyclo*penten-3-ol-1 : 2 : 4-tricarboxylate is methylated exclusively in the unbridged form. automerism of the *spirocyclo*hexane five-carbon nucleus is, therefore, affected by methylation in a irection conforming to the general chemical differences etween this series and the corresponding *gem*-methyl series of intra-annular tautomeric compounds (cf. J.C.S., 1923, **123**, 853, 3303). The revised ormulæ (II) and (III) are accordingly advanced as e most probable structures for the fission products of the alkylated ester (I) (cf. J.C.S., 1919, **115**, 320).



(I.) (II.)

(III.)

where X=C_5H_{10}>C. When the methylation product obtained from the sodio-derivative of ethyl 5-*cyclo*hexane*spirodicyclo*penten-3-ol-1 : 2 : 4-tricarboxylate is boiled with hydrochloric acid, it yields an acid ester (IV), *methyl ethyl hydrogen* 4-*methyl*-5-cyclo*hexane*spiro-Δ¹-*cyclopenten*-3-*one*-1 : 2 : 4-*tricarboxylate*, m. p. 92—93°, which on hydrolysis with alcoholic potassium hydroxide, gives 4-*methyl*-5-cyclo*hexane*spiro-(0 : 1 : 2)-dicyclo*penten*-3-*ol*-1 : 2-*dicarboxylic acid* (V), m. p. 214—216°. This compound gives a deep violet colour with ferric chloride and yields a stable cyclic *anhydride*, m. p. 95°, reverting to the original acid on hydrolysis. Bromination of the dibasic acid yields 2-*bromo*-4-*methyl*-5-cyclo*hexane*spiro-(0 : 1 : 2)-dicyclo*pentan*-3-*one*-1 : 2-*dicarboxylic acid*, m. p. 197—198°; (VI) and (VII) are regarded as the most probable constitutions of the last two compounds.



(IV.) (V.)

(VI.) (VII.)

Treatment of (I) with hydriodic acid gives 4-*methyl*-5-cyclo*hexane*spirocyclo*pentan*-3-*one*-1-*carboxylic acid*, m. p. 114—116° (*semicarbazone*, m. p. 223°). M. Clark.

The Reimer–Tiemann reaction with *m*-chlorophenol. H. H. Hodgson and T. A. Jenkinson (J.C.S., 1927, 1740—1742).—A mixture of 4-*chloro*-2-*hydroxybenzaldehyde*, m. p. 52·5° (*copper* and *chromium* salts; *oxime*, m. p. 155°; p-*nitrophenylhydrazone*, m. p. 257°; *semicarbazone*, m. p. 212°; *benzoate*, m. p. 98·5°), and 2-chloro-4-hydroxybenzaldehyde [*copper* and *chromium* salts; p-*nitrophenylhydrazone*, m. p. 288° (decomp.); *semicarbazone*, m. p. 214°; *acetate*, m. p. 51·5°; *benzoate*, m. p. 96·5°] in almost equal proportions is obtained from *m*-chlorophenol by the Reimer–Tiemann reaction. The constitutions of the aldehydes are established by conversion of the methyl ethers into the corresponding methoxy- and hydroxy-benzoic acids and confirmed by preparation of 4-chloro-2-methoxybenzaldehyde from 4-nitro-2-methoxytoluene and of 2-chloro-4-hydroxybenzaldehyde from 2-chloro-4-nitrotoluene. The following are described: 4-*chloro*-2-*methoxybenzaldehyde*, m. p. 74° (*oxime*, m. p. 132°; p-*nitrophenylhydrazone*, m. p. 238°; *semicarbazone*, m. p. 228°); 4-*chloro*-2-*methoxybenzoic acid*, m. p. 148°; 4-chloro-2-hydroxybenzoic acid, m. p. 211 (lit. 207°); 2-chloro-4-methoxybenzaldehyde (p-*nitrophenylhydrazone*, m. p. 249°; *semicarbazone*, m. p. 240°); 2-*chloro*-4-*hydroxybenzoic acid*, m. p. 159°. M. Clark.

Aromatic aldehydes. I. G. Farbenind. A.-G. —See B., 1927, 572.

***cyclo*Propane derivatives.** P. Bruylants (Ann. Soc. scient. Bruxelles, 1927, **47**, B, [ii], 27—38). *cyclo*Propyl alkyl ketones (cf. A., 1909, i, 226) have been prepared in fair yield from magnesium alkyl halides and cyano*cyclo*propane. Using magnesium *iso*propyl bromide a *polymeride*, $(C_4H_5N)_3$, m. p.

199—200°, of the nitrile was isolated from the non-volatile by-products. It contains one secondary amino-group and gives a *hydrochloride*, m. p. 237°, *chloroplatinate*, decomp. 190—250°, and *nitroso*-derivative, m. p. 169—170°. It is not attacked by alkali, but is converted by hydrochloric acid into the *hydrochloride* of an isomeric monoacid *base*, m. p. 123—125° (*chloroplatinate*, decomp. 180°). The density of the *cyclo*propyl alkyl ketones decreases on ascending the homologous series, the differences being alternately larger and smaller as in the case of the *cyclo*propyldialkylcarbinols (this vol., 653). The mol. refraction $[R_L]_{Na}$ and mol. dispersion of the series show mean exaltations of 0·71 and approx. 10%, respectively. In the phenyl and benzyl *cyclo*propyl ketones the effect is still more marked. The exaltation is ascribed to the conjugation of the *cyclo*propyl and carbonyl groups which is favoured by the introduction of aryl radicals. New or revised values are quoted for the b. p., d_4^{20}, and n^{20}, respectively, of the following *cyclo*propyl ketones: methyl, 111·6—111·8°/751·7 mm., 0·8983, 1·4251; ethyl, 131·8°/769 mm., 0·8927, 1·4299; *propyl*, 151—151·4°/754 mm., 0·8808, 1·4325; *iso*propyl, 141·0—141·4°/761 mm., 0·8753, 1·4299; *butyl*, 173·8—174·0°/757 mm., 0·8788, 1·4371; iso*butyl*, 163·8—164·2/761 mm., 0·8667, 1·4330; n-*amyl*, 194—195°/760 mm., 0·8721, 1·4397; phenyl (m. p. 3—3·5°), 116—117°/10·5 mm., 1·0545, 1·5567; *benzyl*, 124—125°/10 mm., 1·0261, 1·5374; and of cyclo*propylethyl*iso*butylcarbinol*, 191—192°/762 mm., 0·8725, 1·4474, and cyclo*propyl*-n-*propyl*iso*butylcarbinol*, 89—90°/12 mm., 0·8674, 1·4478. H. E. F. NOTTON.

Preparation of unsaturated ketones from the chlorides of hydroxy-acids. G. A. R. KON and B. T. NARAYANAN (J.C.S., 1927, 1546—1549).—Certain unsaturated ketones can be obtained by the action of zinc methyl iodide on the chlorides prepared from cyclic β-hydroxy-acids without previous dehydration of the last-named compounds. *cyclo*Pentenylacetone is obtained in this way from 1-hydroxy*cyclo*pentane-1-acetic acid. The action of thionyl chloride on cyclic β-hydroxy-acids leads to formation of the corresponding chloride in addition to the chlorides of the two possible unsaturated acids and thence, by treatment with zinc methyl iodide, to the same unsaturated ketones. Substitution of zinc ethyl iodide gives the corresponding ethyl ketones in very poor yield, owing to simultaneous formation of the ethyl ester of the βγ-unsaturated acid. Investigation of certain cyclic α-hydroxy-acids showed that these had no practical value for the synthesis of ketones, owing to the extreme instability of the chlorides. The following are described: Δ^1-cyclo*pentenylacetanilide*, m. p. 98°; cyclo*pentylidene*-*acetanilide*, m. p. 152—153°; a constant-melting mixture, m. p. 121—122°, of the two semicarbazones (m. p. 138° and 189°) of *cyclo*pentenylacetone; Δ^1-cyclo*hexenylacetanilide*, m. p. 117°; cyclo*hexylidene*-*acetanilide*, m. p. 138—139°; *semicarbazone* of cyclo*hexylidenemethyl ethyl ketone* (?), m. p. 184—185°.

1-Hydroxy-α-ethyl*cyclo*pentane-1-acetic acid yields with thionyl chloride a chloride mixture which, on treatment with ammonia, gives a mixture of the αβ- and βγ-unsaturated amides, together with a third *amide*, m. p. indef. 70°. A third *amide*, similarly obtained from 1-hydroxy-α-ethyl*cyclo*hexane-1-acetic acid, has m. p. 108—109°. M. CLARK.

α-Trimethyl- and tetramethyl-*cyclo*hexanones. Separation of ketones by fractional oximation. R. CORNUBERT (Bull. Soc. chim., 1927, [iv], **41**, 894—901).—By successive treatment with about half the theoretical amount of hydroxylamine hydrochloride in presence of sodium acetate in boiling alcohol (fractional oximation), crude α-tetramethyl-*cyclo*hexanone, b. p. 185—186°/770 mm. (Cornubert, Ann. Chim., 1921, **16**, 141), is shown to contain a tetramethyl*cyclo*hexanone, b. p. 184°/735 mm., 86°/30 mm., $d_4^{15·5}$ 0·892, $n^{15·5}$ 1·4484 (oxime, m. p. 151·5°). Similarly crude α-trimethyl*cyclo*hexanone, b. p. 174—176°, consists mainly of 2 : 2 : 6-trimethyl- and 2 : 2-dimethyl-*cyclo*hexanone, together with a little 2 : 6-dimethyl and 2 : 2 : 6 : 6-tetramethyl-*cyclo*hexanone. The α-trimethyl*cyclo*hexanone, b. p. 176—178°, consists of 2 : 2 : 6-trimethyl*cyclo*hexanone, b. p. 180°/750 mm., $d_4^{17·5}$ 0·9008, $n^{17·5}$ 1·4488 (oxime, m. p. 104·5—105°), together with traces of dimethyl*cyclo*hexanone. It is concluded that there is no great tendency for the introduction of a second *gem*-dimethyl group. The tetramethyl*cyclo*hexanone may be produced direct from either of the two dimethyl-*cyclo*hexanones or from the trimethyl derivative. The following constants are recorded for the dimethyl-*cyclo*hexanones obtained by hydrolysis of the oximes prepared in the above way: 2 : 2-dimethyl-, b. p. 171·5°, d_4^{20} 0·9143, n_D^{20} 1·4480; 2 : 6-dimethyl-, b. p. 174°, d_4^{20} 0·9140, n_D^{20} 1·4479. R. BRIGHTMAN.

Chloromethylacetophenones. C. F. H. ALLEN and M. P. BRIDGESS (J. Amer. Chem. Soc., 1927, **49**, 1846).—2-Chloro-5-methylacetophenone, b. p. 245·8—246°/760·1 mm., n_D^{25} 1·5419, and 4-chloro-3-methylacetophenone, b. p. 254·2—254·4°/753·4 mm., 1·5521, are obtained, in 70% and 34% yields, respectively, by the condensation of acetic anhydride with the appropriate chlorotoluene in presence of aluminium chloride (cf. Claus, A., 1892, 1200). F. G. WILLSON.

Ethylideneacetophenone (phenyl propenyl ketone) and β-methoxybutyrophenone. DUFRAISSE and M. DEMONTVIGNIER (Bull. Soc. chim., 1927, [iv], **41**, 843—850).—Condensation of acetophenone with acetaldehyde in methyl alcohol at —10° to 10° in presence of sodium methoxide affords a 56% yield of β-*methoxybutyrophenone*, b. p. 121°/8 mm., d_4^{20} 1·0349, n_D^{20} 1·5168, which on distillation in presence of zinc chloride at 150—160°/150 mm. gives 86% of the theoretical yield of phenyl propenyl ketone, m. p. 20—21°, b. p. 111—112°/9 mm., d^{15} 1·0250, n_D^{18} 1·5626. With bromine in carbon disulphide β-methoxybutyrophenone rapidly affords (yield 70%) αβ-dibromobutyrophenone, m. p. [illegible] which on reduction in alcoholic solution at [illegible] iron (reduced by hydrogen) in presence of acetic acid affords phenyl propenyl ketone. It is suggested that the higher fractions obtained in the distillation of the condensation product contain a product of the structure $COPh\cdot CH_2\cdot CHMe\cdot O\cdot CHMe\cdot OMe$, the decomposition of which would explain the pr[illegible]

of acetaldehyde as well as the formation of the β-methoxybutyrophenone. R. BRIGHTMAN.

Reduction of oximes of unsymmetrical ketones and of β-ketonic esters. P. BILLON (Ann. Chim., 1927, [x], **17**, 314—384).—Oximes of unsymmetrical ketones, when reduced in absolute alcoholic solution with three times the theoretical amount of sodium, afford the corresponding amine in yields of 85% and upwards of the theoretical, as compared with 55% by electrolytic reduction in sulphuric acid and 60% by reduction with sodium amalgam. Oximes of β-ketonic esters similarly afford the corresponding amino-alcohols, but owing to difficulties in alkylating ethyl acetoacetate, the oximes were not obtained in sufficient quantity for a complete study of the reduction products. Unsymmetrical diaryl ketones always afford a mixture of stereoisomeric oximes melting at a higher temperature than the more stable form, and these oximes readily decompose, affording the ketone. Oximes derived from aryl alkyl ketones are much more stable and no cases of stereoisomerism of these oximes were observed. Ketones of the type, $Ar{\cdot}CO{\cdot}CR_3$, however, afford oximes which slowly turn yellow and appear to decompose by oxidation of the nitrogen. Attempts to resolve the amines obtained were unsuccessful except in the case of α-phenyl-*n*-propylamine, which was resolved with *d*-tartaric acid. Indications of partial resolution were obtained with α-phenyl-ββ-dimethyl-*n*-propylamine and α-phenyl-ββ-dimethyl-*n*-butylamine.

The stereoisomeric oximes of phenyl *p*-tolyl ketone afford a quantitative yield of phenyl-*p*-tolylmethylamine, b. p. 296°/760 mm., 172°/14 mm., m. p. 40° (*hydrochloride*, m. p. 250° [decomp.]). Phenyl-*p*-anisylmethylamine (85%), b. p. 205°/30 mm. (hydrochloride, m. p. 190°), *phenyl-o-anisylmethylamine* (72%), b. p. 185°/14 mm. (*hydrochloride*, m. p. 250°; *chloroplatinate*, yellow), *o*-hydroxydiphenylmethylamine (70% as hydrochloride, m. p. 190°; *chloroplatinate*, orange), α-phenylethylamine (85%), b. p. 183°/760 mm., 84°/22 mm. (hydrochloride, m. p. 158°), α-phenyl-*n*-propylamine, (100%) b. p. 204°/760 mm., 88°/16 mm., $[\alpha]_D$ −10·5° (hydrochloride, m. p. 194°; d-*hydrogen tartrate*, m. p. 180°; l-*hydrogen tartrate*, m. p. 195°; *dl*-mixture, m. p. 166°), α-phenyl-*n*-butylamine (90%), b. p. 220°/760 mm., 102°/14 mm. (hydrochloride, m. p. 265°), α-phenyl*iso*butylamine (95%), b. p. 213—215°/760 mm., 95°/14 mm. (hydrochloride, m. p. 275°), *α-phenyl-ββ-dimethyl-n-propylamine* (95%), b. p. 115°/22 mm. [*hydrochloride*, m. p. (decomp.); *hydrogen tartrate*, m. p. 152°] and *α-phenyl-ββ-dimethyl-n-butylamine*, b. p. 130°/22 mm. (*hydrochloride*; *hydrogen tartrate*, m. p. 158°), are analogously obtained in the yield indicated.

The action of thionyl chloride on *o*-methoxybenzoic acid affords in addition to *o*-methoxybenzoyl chloride, b. p. 126—138°/17 mm., a little *o-methoxybenzoic hydride*, m. p. 62°, b. p. 215°/4 mm. Condensation of *o*-methoxybenzoyl chloride with benzene in presence of aluminium chloride affords one part of *o*-methoxybenzophenone and 3 parts of the hydroxy-ketone. *o*-Methoxybenzophenoneoxime (quantitative yield) has m. p. 145° 148°, falling to 130° on recrystallisation; prepared in the cold the oxime has m. p. 159°, falling to 130° on fusion and recrystallisation. Both isomerides give benz-*o*-anisylamide, m. p. 62—63°. *o-Methoxybenzanilide* has m. p. 62°.

Methyl αα-dimethylacetoacetate, b. p. 171°/760 mm., affords an *oxime*, m. p. 62°, which on distillation yields 3 : 4 : 4-trimethyl*iso*oxazolone, b. p. 102—103°, which, unlike the oxime, on treatment with ammonia, affords βγ-oximino-ββ-dimethyl-*n*-butyramide. Reduction of the oxime with sodium and alcohol affords a basic *product*, b. p. 95°/25 mm. (*hydrochloride*, m. p. 117—118°; *chloroplatinate*, orange), which is probably a mixture of *γ-amino-ββ-dimethylbutyl alcohol* and its ethyl ether (*phenylcarbamide-phenylurethane*, m. p. 104°). Similarly ethyl αα-diethylacetoacetate, b. p. 210°/760 mm., 102°/18 mm., affords an oxime, m. p. 54°, b. p. 148°/15 mm., yielding on reduction *ethyl β-amino-αα-diethylbutyrate*, b. p. 110°/22 mm. (*hydrochloride*; *chloroplatinate*), and *γ-amino-ββ-diethyl-n-butyl alcohol*, m. p. 42°, b. p. 132°/22 mm. (*hydrochloride*, m. p. 115°; *chloroplatinate*; *benzoate hydrochloride*, m. p. 168°, possesses anæsthetic powers; *phenylcarbamide-phenylurethane*, m. p. 74°). Ethyl αα-dipropylacetoacetate, b. p. 235°/760 mm., 130°/18 mm., gives an *oxime*, m. p. 80°, affording on reduction α-propylvaleric acid, b. p. 220°/760 mm., a neutral substance, b. p. 110°/40 mm., methyl α-propylbutyl ketoxime, b. p. 140°/40 mm., δ-(*α-aminoethyl*)-n-*heptane*, b. p. 92—94°/30 mm., (*chloroplatinate*) and δ-(*α-aminoethyl*)-δ-*hydroxymethyl*-n-*heptane*, b. p. 140°/18 mm. (*hydrochloride*, m. p. 175°; *chloroplatinate*, m. p. about 120°; *phenylcarbamide-phenylurethane*, m. p. 163°; d-*tartrate*, m. p. 133°; the *benzoate hydrochloride*, m. p. 176°, possesses anæsthetic powers). *Ethyl αα-dibutylacetoacetate*, b. p. 146°/18 mm., yields an *oxime*, m. p. 72°, affording on reduction a neutral product, b. p. 130°/18 mm., either the ester $CH_2Me{\cdot}CBu_2{\cdot}CO_2Et$ or the alcohol, $CH_2Me{\cdot}CBu_2{\cdot}CH_2{\cdot}OH$; *methyl α-butyl-n-amyl ketoxime*, b. p. 165°/18 mm.; *β-amino-γ-butylheptane*, b. p. 105°/18 mm. (*chloroplatinate*), and ε-(*α-aminoethyl*)-ε-*hydroxymethyl*-n-*nonane*, b. p. 160°/18 mm. (*hydrochloride*, m. p. 146°; *chloroplatinate*, m. p. 178°; *phenylcarbamide-phenylurethane*, m. p. 152°; the *benzoate hydrochloride*, m. p. 148°, has anæsthetic powers).

Ethyl α-butylacetoacetate, b. p. 126°/22 mm., obtained from ethyl acetoacetate and butyl iodide in 70% yield, gives only a small yield of the dibutyl derivative on alkylation; further treatment of the unchanged monobutyl ester affords ethyl αα-dibutylacetate, b. p. 110°/6 mm. Ethyl αα-diethylbenzoylacetate, b. p. 152°/6 mm., was obtained in only 10% yield from ethyl α-ethylbenzoylacetate, b. p. 146°/6 mm., ethyl iodide, and sodium in alcohol. Ethyl benzoylacetate and sodium in benzene with allyl bromide afford ethyl α-allylbenzoylacetate, b. p. 151—154°/6 mm. (yield 68%), and *ethyl αα-diallylbenzoylacetate*, b. p. 168°/6 mm. (yield 54% in small-scale experiments only). A similar observation was made on alkylation with sodamide in xylene, benzyl chloride affording ethyl α-benzylbenzoylacetate, b. p. 187°/1 mm., and *ethyl αα-dibenzylbenzoylacetate*, b. p. 220—230°/1 mm., in yields of 70% and 50%, respectively, in small-scale experiments.

The action of Crismer's salt on the following

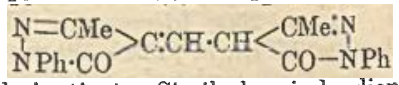
ketones affords a double *compound* of zinc chloride with 2 mols. of the oxime, having the m. p. indicated: acetone, m. p. 104°; methyl ethyl ketone, m. p. 71°; methyl *iso*propyl ketone, m. p. 94°; diethyl ketone, 51°; dipropyl ketone, 52°. The same compounds are obtained by the action of zinc chloride on the oxime in absolute alcohol. With aldehydes, Crismer's salt affords limpid liquids containing zinc and chlorine, but no definite compounds could be isolated. Analogous compounds with cadmium chloride or magnesium chloride could not be isolated. With acetylacetone, Crismer's salt gives no oxime but a *compound*, $C_{10}H_{14}O_2N_2,ZnCl_2$, m. p. 92—93°, decomposed by water to give dimethyl*iso*oxazole. Ethyl benzoylacetate and Crismer's salt afford only phenyl*iso*oxazolone (cf. Haller and Bauer, A., 1911, i, 568). Reduction of the phenyl*iso*oxazolone with sodium and alcohol affords β-phenylalanine. R. BRIGHTMAN.

Hydrogenation of distyryl ketone and of di-β-phenylethyl ketone. V. IPATIEV and ORLOV (Bull. Soc. chim., 1927, [iv], **41**, 862—864).—Hydrogenation of distyryl ketone in benzene solution at 170—180°/70—100 atm. in presence of 15% of nickel oxide affords di-β-phenylethyl ketone, b. p. 335—340°/760 mm., 209°/10 mm., m. p. 13—14° (oxime, m. p. 91°), the yield being 60% in 15% solution, 25% in 35% solution, and 10% in 50% solution. In 20% alcoholic solution the yield is 20%. In *cyclo*hexane the reduction does not take place. In presence of copper oxide as catalyst a tarry mass results. Hydrogenation of di-β-phenylethyl ketone in *cyclo*hexane at 240° affords αε-di*cyclo*hexylpentane, b. p. 315°, d^0 0·8836, n^0 1·478. R. BRIGHTMAN.

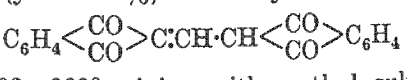
Reality of the semipinacolinic transposition. Study of anisyl methyl ethyl glycol. (MLLE.) J. LEVY and P. WEILL (Compt. rend., 1927, **185**, 135—137).—The results of Danilov (A., 1923, i, 680, 787) and of Orekhov and Tiffeneau (A., 1926, 171) have thrown doubt on the actuality of the semipinacolinic transformation observed in the dehydration of aryl dialkyl glycols by concentrated sulphuric acid and consisting in the elimination of a secondary hydroxyl group and the formation, by migration of an alkyl radical, of a ketonic product (cf. Tiffeneau and Levy, A., 1926, 818). It is now found that, by semipinacolinic transposition and migration of the ethyl group, anisyl methyl ethyl glycol is converted into α-anisyl-*n*-propyl methyl ketone, $OMe\cdot C_6H_4\cdot CH(OH)\cdot CMeEt\cdot OH \longrightarrow OMe\cdot C_6H_4\cdot CHEt\cdot CO\cdot Me$, whereas the action of concentrated sulphuric acid on α-anisyl-α-methylbutaldehyde gives α-anisyldiethyl ketone, $OMe\cdot C_6H_4\cdot CMeEt\cdot CHO \longrightarrow OMe\cdot C_6H_4\cdot CHMe\cdot CO\cdot Et$. Further, when distilled at about 250°, α-anisyl-β-methyl-α-butylene oxide yields α-anisyl-*n*-propyl methyl ketone, $OMe\cdot C_6H_4\cdot CH\cdot CMeEt \longrightarrow OMe\cdot C_6H_4\cdot CHEt\cdot CO\cdot Me$, this change being a semipinacolinic transposition analogous to that of the corresponding glycol. These results demonstrate the reality of the semipinacolinic transposition and show that, in this reaction, the ethyl radical migrates more readily than methyl. T. H. POPE.

Substituted phenyl styryl ketones. Condensation of cinnamic acid with resorcinol and pyrogallol. T. E. ELLISON (J.C.S., 1927, 1720—1724).—The statements of Bargellini and Marantoni (A., 1908, i, 801) and of Dutta and Watson (J.C.S., 1912, **101**, 1238) that 2 : 4-dihydroxyphenyl styryl ketone and 2 : 3 : 4-trihydroxyphenyl styryl ketone may be prepared respectively by condensation of cinnamic acid with resorcinol and with pyrogallol in presence of zinc chloride are shown to be incorrect. More complex colouring matters only are obtained in these cases. Condensation of resacetophenone and benzaldehyde in alcoholic potassium hydroxide solution yields a mixture of 2 : 4-*dihydroxyphenyl styryl ketone*, m. p. 133—134°, and the isomeric 7-*hydroxyflavanone*, m. p. 189° (*acetyl* derivative, m. p. 98°). Similar condensations of gallacetophenone with benzaldehyde, *m*-hydroxybenzaldehyde, and salicylaldehyde yield respectively 2 : 3 : 4-*trihydroxyphenyl styryl ketone*, m. p. 165—166°, 2 : 3 : 4-*trihydroxyphenyl* 3-*hydroxystyryl ketone*, m. p. 219—220°, and 2 : 3 : 4-*trihydroxyphenyl* 2-*hydroxystyryl ketone*, m. p. 224—225° (decomp.). The action of anhydrous hydrogen chloride on an ethereal suspension of the last-named compound causes slow conversion into 2′ : 3′ : 4′-*trihydroxy-2-phenylbenzopyrylium chloride*. M. CLARK.

Action of substances containing an active methylene group on urotropine (hexamethylenetetramine). II. M. V. IONESCU and V. N. GEORGESCU (Bull. Soc. chim., 1927, [iv], **41**, 881—894; cf. this vol., 651).—Deoxybenzoin, indene, and fluorene do not decompose hexamethylenetetramine in alcoholic solution. 1-Phenyl-3-methyl-5-pyrazolone affords in about 70% yield methenylbis-1-phenyl-3-methyl-5-pyrazolone (I), m. p. 180° (yellow *monosodium* derivative). Similarly, indandione rapidly affords (yield 25%) methenylbisindandione (II),

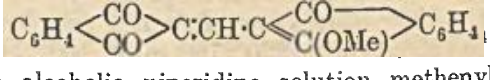


(I.)



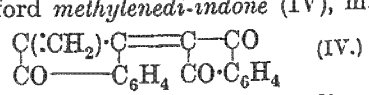
(II.)

m. p. 302—303°, giving with methyl sulphate the *methyl ether* (III), m. p. 274°, together with an *anhydro*-derivative, m. p. 232—234°.



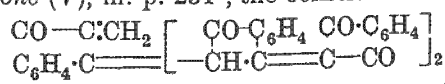
(III.)

In alcoholic piperidine solution methenylbisindandione is accompanied by a substance, m. p. ..., probably a mixture of mono-substituted di-indones. In xylene solution hexamethylenetetramine an di-indone afford *methylenedi-indone* (IV), m. p. ,



(IV.)

together with a little *methyleneindandionylidenebis di-indone* (V), m. p. 234°, the constitution of which is



(V.)

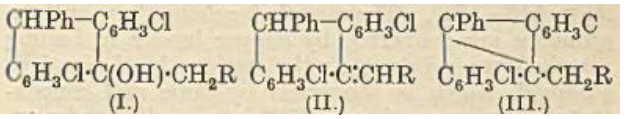
supported by its genetic relation to methylenedi indone and by the fact that methylenedi-in one presence of "nascent" di-indone (indandione piperidine solution) affords *methyleneindandionylideneindandionedi-indone* (VI), m. p. ..., from

which the formation of (V) is intelligible. The formation of (VI) indicates that the more active ethylene linking in methylenedi-indone is that connecting the two rings. Attempts to obtain similar additive products from methylenedi-indone and acetylacetone, dimethyldihydroresorcinol, and 1-phenyl-3-methyl-5-pyrazolone in xylene solution were unsuccessful; in the last case a *substance*, $C_{30}H_{20}O_2N_6$,AcOH, m. p. above 290° (decomp.), probably from auto-condensation of the pyrazolone, was obtained. In view of the fact that these substances containing a reactive methylene group will not condense with methylenedi-indone, it is concluded that the additive properties of a conjugated system are modified, not only by the different substituents within the system, but also by the nature and structure of the added substance. Di-indone thus appears to contain the most reactive methylene group.

R. BRIGHTMAN.

Synthesis of *meso*alkyl- and *meso*aryl-anthracene derivatives. II. E. DE B. BARNETT, J. W. COOK, and J. L. WILTSHIRE (J.C.S., 1927, 1724—1732). —The low and variable yield of 9 : 10-diphenyl-9 : 10-dihydroanthraquinol, m. p. 260—263°, obtained by the action of magnesium phenyl bromide on anthraquinone, is ascribed to reduction of anthraquinone to anthraquinol by the Grignard reagent and to formation of 9 : 10-diphenylanthracene. That the reducing action of the Grignard reagent on anthraquinones is general, is shown by the formation of 1-chloro-9 : 10-diphenylanthracene and 1-chloroanthraquinol and of 2-chloro-9 : 10-diphenylanthracene from 1-chloro- and 2-chloro-anthraquinones, respectively. 1 : 5-*Dichloro*-9 : 10-*diphenyl*-9 : 10-*dihydroanthraquinol*, m. p. 320°, is obtained (with much dichloroanthraquinol) from 1 : 5-dichloroanthraquinone, and yields with dry hydrogen chloride 1 : 5 : 9 : 10-*tetrachloro*-9 : 10-*diphenyl*-9 : 10-*dihydroanthracene*, m. p. 250°. Anthrone is so rapidly enolised by Grignard solutions that good yields of alkyl- or aryl-anthracenes are rarely obtained. 9-*Benzyldihydroanthranol*, m. p. 50°, from anthrone and magnesium benzyl chloride, dehydrates on keeping to 9-benzylanthracene. The less ready enolisation of 9-phenylanthrone is evinced by the fact that good yields of the 9-phenyl-10-alkyl(or aryl)-anthracenes are produced by the action of Grignard reagents. The primarily formed dihydroanthranol may be isolated and is converted into the anthracene by treatment with acid. The following are prepared in this way: 9-*phenyl*-10-*ethylanthracene*, m. p. 110°; 9-*phenyl*-10-n-*propyldihydroanthranol*, m. p. 148—150°, 9-*phenyl*-10-n-*propylanthracene*, m. p. 115—116°, 9-*phenyl*-10-iso*propylanthracene*, m. p. 166—, 9-*phenyl*-10-n-*butylanthracene*, m. p. 156°; -*phenyl*-10-iso*amylanthracene*, m. p. 203—204°; -*phenyl*-10-*benzyldihydroanthranol*, m. p. 177°; *phenyl*-10-*benzylanthracene*, m. p. 155°; 9-*phenyl*--α-*naphthyldihydroanthranol*, m. p. 260—262°; -p enyl-10-α-naphthylanthracene, m. p. 244—245°. e dihydroanthranols (I) from 1 : 5-dichloro-9-p enylanthrone (m. p. 254°) and Grignard reagents, equen y pass into the alkylidene derivatives (II) by ss of water and may also dehydrate to the anthracene) since 1 : 5-*dichloro*-9-*phenyl*-10-n-*propyldihydro-*

anthranol yields 1 : 5-*dichloro*-9-*phenyl*-10-n-*propylanthracene*, m. p. 196°, as well as 1 : 5-*dichloro*-9-*phenyl*-10-*propylidene*-9 : 10-*dihydroanthracene*, m. p. 135°.



The following are described: 1 : 5-*dichloro*-9-*phenyl*-10-*methylene*-9 : 10-*dihydroanthracene*, m. p. 150°; 1 : 5-*dichloro*-9-*phenyl*-10-*ethylidene*-9 : 10-*dihydroanthracene*, m. p. 159°; corresponding 10-*propylidene* derivative, m. p. 135°; 1 : 5-*dichloro*-9-*phenyl*-10-iso*propylanthracene*, m. p. 195°; 1 : 5-*dichloro*-9-*phenyl*-10-*benzylanthracene*, m. p. 209°; 1 : 5-*dichloro*-9-*phenyl*-10-*benzyl*-9 : 10-*dihydroanthranol*, m. p. 173°, 1 : 5-*dichloro*-9 : 10-*diphenyl*-9 : 10-*dihydroanthranol*, m. p. 201°; 1 : 5-*dichloro*-9 : 10-*diphenylanthracene*, m. p. 236°. 9-Phenyl-10-alkylanthracenes show reversible deepening of colour in mesitylene solution on heating and cooling, but the hypothesis of Ingold and Marshall (this vol., 141) that this phenomenon indicates the existence of a dissociable "bridge" linking is not accepted. 9 : 10-Di-*p*-anisyl-9 : 10-dihydroanthraquinol on reduction with hydriodic acid and phosphorus gives 9 : 10-dihydroanthracene, not octahydrodiphenylanthracene (Ingold and Marshall, *loc. cit.*).

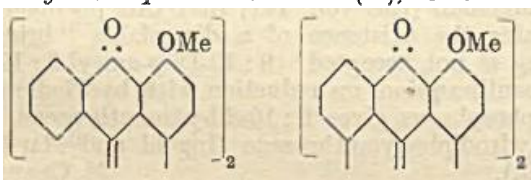
M. CLARK.

Oxidations in light. A. ECKERT (Ber., 1927, **60**, [*B*], 1691—1693; cf. A., 1925, i, 413).—A solution of potassium anthraquinone-1-sulphonate in hydrochloric acid (1 : 1) on exposure to light evolves chlorine and yields 1-chloroanthraquinone, m. p. 162°. Potassium anthraquinone-1 : 8-disulphonate similarly gives 1 : 8-dichloroanthraquinone, whereas potassium anthraquinone-1 : 5-disulphonate yields mainly potassium 1-chloroanthraquinone-5-sulphonate with very little 1 : 5-dichloroanthraquinone. Sodium anthraquinone-2 : 6-disulphonate affords little 2 : 6-dichloroanthraquinone and much sodium 2-chloroanthraquinone-6-sulphonate. Anthraquinone-2 : 7-disulphonic acid yields only products soluble in water; 2-chloroanthraquinone-7-sulphonic acid and an isomeric compound are isolated. The nitroanthraquinonesulphonic acids react with greater difficulty; 5-, 8-, and 6-chloro-1-nitroanthraquinones have been obtained from the corresponding sulphonic acid. The bromoanthraquinones could not be isolated by exposing solutions of anthraquinone-1- and -2-sulphonates in hydrobromic acid to light, although bromine is readily liberated.

H. WREN.

Preparation of 1 : 1′-dianthraquinonyl derivatives. A. ECKERT and J. HAMPEL (Ber., 1927. 60, [*B*], 1693—1703).—Addition of hydrochloric acid to a solution of 1-methoxyanthraquinone and potassium chlorate in aqueous acetic acid yields small quantities of a product of high m. p. and two monochloro-1-methoxyanthraquinones, m. p. 136—140° and 164—165°, respectively, the latter of which is identified as 4-*chloro*-1-*methoxyanthraquinone* by its hydrolysis to 4-chloro-1-hydroxyanthraquinone, m. p. 183—184°. Treatment of 1-methoxyanthraquinone dissolved in glacial acetic acid with an excess of

bromine in the presence of anhydrous sodium acetate and a little ferric chloride affords mainly 2 : 4-*dibromo*-1-*methoxyanthraquinone*, m. p. 235°, with smaller amounts of 4-*bromo*-1-*methoxyanthraquinone*, m. p. 148—151°. The monohalogenomethoxyanthraquinones are converted by copper bronze in boiling nitrobenzene into 4 : 4′-*dimethoxy*-1 : 1′-*dianthraquinonyl*, which is converted by boric and concentrated sulphuric acids at 150° into 4 : 4′-dihydroxy-1 : 1′-dianthraquinonyl. The latter compound is brominated in nitrobenzene at 120—130° to 3 : 3′-*dibromo*-4 : -*dihydroxy*-1 : 1′-*dianthraquinonyl* (*potassium* salt), also obtained from 3 : 3′-*dibromo*-4 : 4′-*dimethoxy*-1 : 1′-*dianthraquinonyl*; replacement of the bromine atoms in this compound by the methoxy- or hydroxy-group could not be effected. The following compounds are incidentally described: 4 : 4′-*dimethoxy*mesobenzdianthrone (I), from 4 : 4′-dimethoxy-1 : 1′-dianthraquinonyl in concentrated sulphuric acid and copper bronze, converted by the action of sunlight in the presence of chlorobenzene into 4 : 4′-*dimethoxy*mesonaphthadianthrone (II), 3 : 3′-*dibromo*-

(I.)  (II.)

4 : 4′-*dimethoxy*mesobenzdianthrone, 3 : 3′-*dibromo*-4 : 4′-*dimethoxy*mesonaphthadianthrone. 4 : 4′-Dihydroxy-1 : 1′-dianthraquinonyl suspended in acetic acid is converted by nitric acid (*d* 1·48) into a *nitro*-4 : 4′-*dihydroxy*-1 : 1′-*dianthraquinonyl*; a dinitro-derivative could not be prepared.

1 : 2-Diketo-1 : 2-dihydroanthracene is converted by sulphuric acid into an amorphous quinhydrone, which is oxidised by chromic acid in glacial acetic acid to 3 : 4 : 3′ : 4′-*tetraketo*-3 : 4 : 3′ : 4′-*tetrahydro*-1 : 1′-*dianthracene*; the corresponding *azine* formed by the action of *o*-phenylenediamine is described. The ketone is transformed by reductive acetylation into 3 : 4 : 3′ : 4′-*tetra*-*acetoxy*-1 : 1′-*dianthracene*, which could not be caused to crystallise. The latter substance is oxidised by chromic acid to 3 : 4 : 3′ : 4′-*tetra*-*acetoxy*-1 : 1′-*dianthraquinonyl*, which is converted by acids or alkalis into 3 : 4 : 3′ : 4′-*tetrahydroxy*-1 : 1′-*dianthraquinonyl* [*dializarin*] (*potassium* salt). The action of copper bronze and concentrated sulphuric acid on 3 : 4 : 3′ : 4′-tetrahydroxy-1 : 1′-dianthraquinonyl leads to the production of 3 : 4 : 3′ : 4′-*tetrahydroxy*mesobenzdianthrone (3 : 4 : 3′ : 4′-*tetrahydroxy*helianthrone), which is converted with difficulty by exposure of its solution in concentrated sulphuric acid to light into 3 : 4 : 3′ : 4′-*tetrahydroxy*mesonaphthadianthrone. A strong positive colour change such as is usual with similar enlargements of the molecule does not occur with alizarin and 3 : 4 : 3′ : 4′-tetrahydroxy-1 : 1′- or -2 : 2′-dianthraquinonyl.

H. WREN.

Synthesis of morindone. R. BHATTACHARYA and J. L. SIMONSEN (J. Indian Inst. Sci., 1927, **10A**, 6—9).—Reduction of 2 : 4′-dimethoxy-3-methylbenzophenone-6-carboxylic acid by the method of Scholl and Neovius (A., 1911, i, 452) affords 2 : 4′-*dimethoxy*-3-*methyldiphenylmethane*-6-*carboxylic acid*, m. p. 103—104°, in good yield, together with 2 : 4′-*dimethoxy*-3-*methylphenylphthalide*, m. p. 78—79°. The former gives with sulphuric acid (*d* 1·84) 2 : 5-*dimethoxy*-6-*methyl*-9-*anthrone*, m. p. 111—112°, which is oxidised by chromic and acetic acids to 2 : 5-dimethoxy-6-methylanthraquinone, m. p. 192°, not 182° as previously stated (J.C.S., 1921, **119**, 1339). This is demethylated by aluminium chloride at 200° to 2 : 5-dihydroxy-6-methylanthraquinone, which is converted by potassium hydroxide at 220—230° in presence of sodium arsenate into 1 : 2 : 5-trihydroxy-6-methylanthraquinone, m. p. 275°, identified with morindone (cf. Jacobson and Adams, A., 1925, i, 273) by conversion into its triacetyl derivative.

H. E. F. NOTTON.

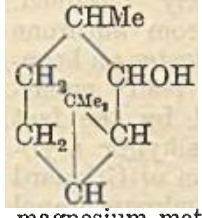
α-Aroyl-β-naphthols and condensation products of the benzanthrone series. I. G. FARBENIND. A.-G.—See B., 1927, 550.

Manufacture of [hydrogenated] anthraquinone derivatives. I. G. FARBENIND. A.-G.—See B., 1927, 597.

Betulin. II. R. VESTERBERG (Ber., 1927, 60, [*B*], 1535—1536; cf. A., 1923, i, 590).—The two acetyl groups of betulin diacetate are retained with such varying resistance to hydrolysis that the possibility of preparing betulin monoacetate is indicated. Boiling formic acid converts betulin monoacetate into *allo*-betulin monoacetate. Betulin diacetate is readily hydrogenated in glacial acetic acid solution in the presence of platinum to *dihydrobetulin diacetate*, m. p. 253°, $[\alpha]^{20}$ −6·50°, which is hydrolysed to *dihydrobetulin*, m. p. 277°, $[\alpha]_D^{20}$ −19·14°. The latter compound is transformed by formic acid into the corresponding *diformate*.

H. WREN.

Reactions of carone. K. N. MENON and J. L. SIMONSEN (J. Indian Inst. Sci., 1927, **10A**, 1—). *d*-Carylamine, b. p. 86—89°/15 mm., $[\alpha]_D^{21}$ +7·3 in alcohol, prepared by Baeyer's method (A., 1895, i, 15) is converted by nitrous acid into



l-carol (annexed formula), b. p. 141—142°/100 mm., d_{30}^{30} 0·9181, n_D^{30} 1·47, $[\alpha]^{26}$ −42·92, which has the abnormally high mol. refraction, $[R_L]_D$ is only slowly oxidised by alkaline permanganate; with chromic acid it gives carone. It is dehydrated by magnesium methyl iodide to a mixture containing principally doubly unsaturated monocyclic hydrocarbons. This gives with hydrogen chloride in acetic acid a little terpinene dihydrochloride and distils in two main fractions, (*a*) b. p. 172—174°, 0·839, n_D [illegible] $[\alpha]_D^{26}$ −46·52°, and (*b*) b. p. 180—190°/683 mm. d_{30}^{30} 0·8624, n_D^{30} 1·4745, $[\alpha]_D^{30}$ −58·48°. Sodium *l*-caryloxide is converted by carbon disulphide into oily *l*-[illegible] *carylxanthate*, which decomposes on distillation at atmospheric pressure into a hydrocarbon, b. p. 170°, d_{30}^{30} 0·8551, n_D^{30} 1·473, $[\alpha]_D$ −5·96° in acetic acid (hydrochloride, m. p. below −15°, appa[illegible] identical with Δ^4-carene. *d*-Carone behaves normally (cf. A., 1926, 1042) towards hydrogen cyanide, an oily *cyanohydrin* from which it is quantitatively regenerated by potassium hydroxide. It reacts with ethyl sodiocyanoacetate. H. [illegible]

Catalytic action of boroacetic anhydride in the combination of organic acids with pinene and nopinene. DUPONT and PASCAUD (Bull. Inst. Pin, 1926, 437).—Interaction of a mixture of *d*-pinene (68 g.), acetic acid (50 g.), boron trioxide (10 g.), and acetic anhydride (15 c.c.) is almost complete after 1 hr. at the b. p. The product contains 22·8 mols. of secondary alcohols (mainly borneol, with some fenchol), 12·2 mols. of tertiary alcohols, and 65·0 mols. of monocyclic hydrocarbons per 100 mols. of pinene. The interaction is appreciable at the ordinary temperature. In the presence of formaldehyde or oxalic acid polymerisation of the hydrocarbon takes place.

CHEMICAL ABSTRACTS.

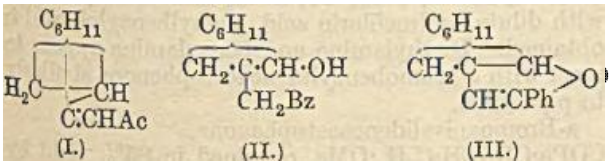
Production of terpineol from α-pinene in acid solution. F. G. GERMUTH (Amer. J. Pharm., 1927, 99, 402—405).—The conversion of α-pinene into terpineol in glacial acetic acid solution in presence of benzenesulphonic acid ($+1{\cdot}5H_2O$) is aided by heating and somewhat retarded by addition of water.

E. H. SHARPLES.

Camphor oils. VIII. Catalytic action of Japanese acid clay on cineole. K. ONO and S. MIYAZAKI (Bull. Chem. Soc. Japan, 1927, **2**, 207—209; cf. A., 1925, i, 941; this vol., 156, 464).—Japanese acid clay dehydrates cineole, yielding dipentene, *p*-cymene, and dipinene.

H. BURTON.

Camphene and the Friedel–Crafts synthesis of ketones. P. LIPP, P. KÜPPERS, and M. HOLL (Ber., 1927, **60**, [*B*], 1575—1581).—The action of aluminium chloride and acetyl chloride on camphene in the presence of anhydrous ether gives much resinous matter, *iso*bornyl chloride, and ω-*acetylcamphene* (I), b. p. 76°/3 mm. [*semicarbazone*, decomp. 199—200·5° (corr.)], which could not be obtained if carbon disulphide was used as solvent. Replacement of aluminium chloride by anhydrous magnesium bromide or of acetyl chloride by acetic anhydride does not give greatly improved results. The constitution of the ketone is established by its preparation from the magnesium compound of ω-bromocamphene and acetonitrile. Camphene and benzoyl chloride in the presence of aluminium chloride and carbon disulphide afford ω-*benzoylborneol* (II), m. p. 85—86° [*semi-*



carbazone, decomp. 212—214° (corr.); *oxime*, m. p. 159—160°; *acetate*, b. p. 179—184°/1·5 mm.], which is oxidised by chromium trioxide to ω-*benzoylcamphor*, m. p. 69—70° [*dioxime*, decomp. 225° (corr.); *monosemicarbazone*, m. p. 198° (corr. decomp.) when rapidly heated]. Dehydration of ω-benzoylborneol with potassium hydrogen sulphate at 180—185° gives ω-*phenyl*-2 : 3-*camphylidene*-2 : 3-*dihydrofuran* (III), b. p. 133—135°/0·3 mm., which gives the pine-shaving reaction and does not yield a semicarbazone. It is converted by hydrogen bromide in glacial acetic acid into the unstable ω-*benzoylbornyl bromide*, m. p. 71—, which is hydrolysed to ω-benzoylborneol.

H. WREN.

Azo-dyes from aminodiphenylene oxide. E. GLIETENBERG, and GRASSELLI DYESTUFF CORP.—See B., 1927, 627.

α-[3-]Phenylcoumarins. G. BARGELLINI (Gazzetta, 1927, **57**, 457—461).—The synthesis of 3-phenylcoumarin by the condensation of salicylaldehyde with sodium phenylacetate in the presence of acetic anhydride (Oglialoro, A., 1880, 164) is extended to hydroxycoumarins by the use of di- and tri-hydroxyaldehydes; the acetoxycoumarins are obtained, and are hydrolysed to the hydroxycoumarins; these have also been methylated. Of the substances described by Jacobson and Ghosh (A., 1915, i, 442, 831, 832) and by Ghosh (A., 1916, i, 281) as γ-pyrones, and regarded by Robinson and Baker (A., 1925, i, 1300) and by Baker (A., 1926, 74) as α-pyrones, "7 : 8-dihydroxy-3-phenyl-γ-benzopyrone," m. p. 215°, acetyl derivative, m. p. 184° (Ghosh, *loc. cit.*), is probably identical with 7 : 8-dihydroxy-3-phenylcoumarin, m. p. 213—215° (7 : 8-diacetoxy-, m. p. 180°, 7 : 8-*dimethoxy*-3-*phenylcoumarin*, m. p. 142—144°, prepared by use of diazomethane), now obtained from 2 : 3 : 4-trihydroxybenzaldehyde. The "7-hydroxy-3-phenylbenzo-γ-pyrone," m. p. 131° (Jacobson and Ghosh, *loc cit.*, 1057), is not, however, identical with 7-*hydroxy*-3-*phenylcoumarin*, m. p. 206—208° (7-*acetoxy*-, m. p. 182—184°, 7-*methoxy*-, m. p. 118—120°, derivatives), obtained from 2 : 4-dihydroxybenzaldehyde, and may be a true γ-pyrone. 5 : 7-*Dihydroxy*-, m. p. 258—260°, 5 : 7-*diacetoxy*-, m. p. 155—156°, and 5 : 7-*dimethoxy*-3-*phenylcoumarin*, m. p. 180°, are also described.

E. W. WIGNALL.

Preparation of 4 : 6-dihydroxy-α-(*p*-hydroxyphenyl)coumarin [5 : 7 : 4′-trihydroxy-3-phenylcoumarin]. G. BARGELLINI and (SIGNA.) L. MONTI (Gazzetta, 1927, **57**, 462—464).—The synthesis by Baker and Robinson (A., 1926, 1253) of 5 : 7 : 4′-trihydroxy-2-methyl*iso*flavone, identical with methylprunetol, proved that prunetol (genistein) is not, as Bargellini (A., 1926, 302) had suggested, a coumarin. This is now confirmed by the synthesis of the suggested 5 : 7 : 4′-*trihydroxy*-3-*phenylcoumarin*, decomp. from 280°, from sodium *p*-hydroxyphenylacetate and phloroglucinaldehyde, which when heated with acetic anhydride yield 5 : 7 : 4′-*triacetoxy*-3-*phenylcoumarin*, m. p. 206°, hydrolysed to the hydroxy-compound. This is methylated to the corresponding *trimethoxy* compound, $C_{18}H_{16}O_5,2H_2O$, m. p. 163—165°, which in acetic acid solution gives no colour on addition of nitric acid.

E. W. WIGNALL.

Synthesis of flavones and flavonols. S. HATTORI (Bull. Chem. Soc. Japan, 1927, **2**, 171—175).—3′ : 4′-*Methylenedioxyflavanone*, m. p. 127—128°, prepared from *o*-hydroxyphenyl 3 : 4-methylenedioxystyryl ketone (Feuerstein and Kostanecki, A., 1899, i, 369) and alcoholic sulphuric acid at 100°, is converted by phosphorus pentachloride in benzene (Lowenbein, A., 1924, i, 1221) into 3′ : 4′-*methylenedioxyflavone*, m. p. 206°, and by nitrous acid (Kostanecki, A., 1904, i. 764) directly into 3′ : 4′-*methylenedioxyflavonol*, m. p. 214—215° (*methyl ether*, m. p. 155°). Similarly *o*-*hydroxyphenyl* 3 : 4-*dimethoxystyryl ketone*, m. p. 117° (*acetate*, m. p. 90°), from veratraldehyde and *o*-hydroxyacetophenone, yields 3′ : 4-*dimethoxy*-

flavanone, m. p. 126°, and 3′ : 4′-*dimethoxyflavone*, m. p. 156°. With nitrous acid the flavanone gives a 3-iso*nitroso*-derivative, m. p. 125—127° (indef.), from which 3′ : 4′-*dimethoxyflavonol*, m. p. 202° (*methyl ether*, m. p. 168—169°), is obtained.

H. E. F. NOTTON.

Styrylpyrylium salts. IX. Colour phenomena associated with benzonaphtha- and dinaphtha-*spiro*pyrans. R. DICKINSON and I. M. HEILBRON (J.C.S., 1927, 1699—1705; cf. this vol., 251).—Condensation of 2-naphthol-1-aldehyde with 2-hydroxystyryl methyl ketone in presence of perchloric acid and dry hydrogen chloride, followed by decomposition of the crystalline pyrylium salt with concentrated ammonia, gives *benzo*-β-*naphtha*spiro*pyran*, m. p. 168—169°. Certain solutions of this substance, like those of 3-*methylbenzo*-β-*naphtha*spiro*pyran*, m. p. 149° (from 2 : 3-dimethylbenzopyrylium chloride and 2-naphthol-1-aldehyde), are colourless when cold and wine-red when warm. On the other hand, 3′-*methylbenzo* β-*naphtha*spiro*pyran*, m. p. 177—178°, prepared by condensation of 2-naphthol-1-aldehyde with 2-hydroxystyryl ethyl ketone, 3 : 3′-*dimethyldi*-β-*naphtha*spiro*pyran*, m. p. 238°, 3 : 3′-*trimethylenedi*-β-*naphtha*spiro*pyran*, m. p. 233—234°, and *ethyl di*-β-*naphtha*spiro*pyran*-3 : 3′-*dicarboxylate*, m. p. 205—207°, remain colourless in hot solution. It is concluded that for colour development at least one naphthalene nucleus must be present and that the 3′-carbon atom in the naphthapyran ring must be unsubstituted. In explanation of the colour changes, primary formation of a heteropolar ion is assumed (cf. Dilthey, A., 1926, 1254), followed by chelate formation through the agency of the free hydrogen atom attached to carbon atom 3′, equilibrium being established between the neutral *spiro*pyran and the ionised chelate compound. 4 : 2′-*Hydroxy*-1′-*naphthylidene*-1 : 2 : 3 : 4-*tetrahydro*-8 : 9-*benzoxanthylium chloride*, isolated as an intermediate product in the preparation of 3 : 3′-trimethylenedi-β-naphtha-*spiro*pyran from 2-naphthol-1-aldehyde and *cyclo*hexanone, is described.

M. CLARK.

Quinonedithiosalicylic acid and quinonedithioxanthen. V. V. SCHARVIN and A. M. LUKIN (J. Russ. Phys. Chem. Soc., 1927, **59**, 217—220).—*Quinonedithiosalicylic acid* is obtained when xylene solutions of thiosalicylic acid and *p*-benzoquinone (2 : 3) are mixed together, as red cubes, m. p. 213°. When this compound is warmed with 66% sulphuric acid at 80°, ring closure is effected, and *quinonedithioxanthen* is formed as a greyish-yellow powder, insoluble in the ordinary organic solvents. The compound is insoluble in alkali, but a red colour is formed, probably due to hydrolysis. Silk and wool are dyed yellow. The compound differs from the analogous quinonediacridone (A., 1915, i, 1004) by the fact that it yields no coloured hydrosulphide.

E. ROTHSTEIN.

Action of *p*-toluenesulphonamide on αδ-dibromobutane : new pyrrolidine synthesis. A. MÜLLER and A. SAUERWALD (Monatsh., 1927, **48**, 155—161).—αδ-Dibromobutane, obtained from *cyclo*hexanol by way of adipamide (prepared better from adipyl chloride than from adipic acid by the action of ammonia), condenses with *p*-toluenesulphonamide in the presence of potassium hydroxide solution to give a good yield of N-*p*-*toluenesulphonylpyrrolidine*, m. p. 123°. This is not hydrolysed by sulphuric acid, and hydrolysis by chlorosulphonic acid (cf. Marckwald and Droste-Huelshoff, A., 1899, i, 289) followed by treatment with excess of potassium hydroxide gives no pyrrolidine; the latter is, however, obtained in good yield by hydrolysis with hydrochloric acid at 160°.

E. W. WIGNALL.

Action of piperidine on some α-bromo-αβ-unsaturated ketones. C. DUFRAISSE and H. MOUREU (Bull. Soc. chim., 1927, [iv], **41**, 850—862).—The action of piperidine on other α-bromo-αβ-unsaturated ketones is analogous to the behaviour of α-bromobenzylideneacetophenone (this vol., 571), but the saturated compound $R{\cdot}CO{\cdot}CBr(NC_5H_{10}){\cdot}CH_2R'$ could not be isolated. According to the nature of the original ketone the reaction product is either an unsaturated monopipiperidide, $COR{\cdot}C(NC_5H_{10}){:}CHR'$, or a dipiperidino-compound of the type $COR{\cdot}C(NC_5H_{10})_2{\cdot}CH_2R'$ or $COR{\cdot}CH(NC_5H_{10}){\cdot}CHR'{\cdot}NC_5H_{10}$. The same compounds are obtained by the direct action of piperidine on the dibromides of αβ-unsaturated ketones, the first stage of this reaction being the formation of the α-bromo-αβ-unsaturated ketone by elimination of hydrogen bromide; this reaction affords a convenient means of preparing α-bromomesityl oxide, $CMe_2{:}CBr{\cdot}COMe$. The monopiperidino-derivatives behave on hydrolysis like α-piperidinobenzylideneacetophenone. The dipiperidino-derivatives present similar analogies and on hydrolysis afford the αβ-diketone and an amino-ketone in proportions depending on the nature of the original α-bromo-unsaturated ketone. As the dipiperidino-compounds are crystalline it is improbable that they are mixtures of isomerides and decision between the αα- and αβ-dipiperidino-structures is reserved. The action of ammonia on α-bromobenzylideneacetophenone affords a *substance*, m. p. 203°, containing nitrogen and 17·4% Br, and α-aminobenzylideneacetophenone, m. p. 95—97 (*hydrochloride*, m. p. 184°; *hydrobromide*, m. p. 189°), in 40% yield, and not the β-amino-compound (cf. Watson, J.C.S., 1904, **85**, 1323) since on hydrolysis with dilute hydrochloric acid phenylbenzylglyoxal is obtained. Diethylamine and benzylamine appear to react with α-bromobenzylideneacetophenone similarly to piperidine.

α-Bromoanisylideneacetophenone, $COPh{\cdot}CBr{:}CH{\cdot}C_6H_4{\cdot}OMe$, obtained in 95% yield by decomposition of α-bromo-β-ethoxyanisylideneacetophenone with potassium hydrogen sulphate at 170°, affords *α-pipiperidinoanisylideneacetophenone*, m. p. 79°, yielding on hydrolysis α-phenyl-β-anisylmethylglyoxal, $COPh{\cdot}CO{\cdot}CH_2{\cdot}C_6H_4{\cdot}OMe$. α- m mesityl oxide, n_D^{13} 1·4962, is obtained in 40% yield by the action of bromine on mesityl oxide in c o form at −5° and treatment with dilute alco o potassium hydroxide at −10°, or in 70% yie the action of 1 mol. of bromine in ether and t ment with 3 mols. of piperidine. It is conver (85% yield) by 3 mols. of piperidine into a *piperidino*-derivative, $C_6H_9O{\cdot}NC_5H_{10}$, b. p. 101°/10 0·9395, n_D^{22} 1·4710, giving a crystalline *sulphate*,

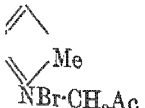
m. p. 82—84°. Only partial hydrolysis to acetyl*iso*butyryl (β-methylpentane-γδ-dione) occurs with acids, and it is possible that partial isomerisation occurs under the influence of the sulphuric acid. The dibromide of phenyl vinyl ketone affords 90% of *dipiperidinomethylacetophenone*, m. p. 73°, hydrolysis of which to acetylbenzoyl in high yield indicates an αα-structure. *Dipiperidinoethylacetophenone*, m. p. 113·5—114·5°, obtained from the dibromide of ethylideneacetophenone in 65%, on hydrolysis, however, affords about 80% of ω-piperidinoacetophenone together with acetaldehyde and only small amounts of propionylbenzoyl, thus indicating the αβ-structure for the dipiperidide. α-Bromoethylideneacetone, b. p. 62·5—63·5°/11 mm., obtained in 44% yield by the action of bromine in chloroform on ethylideneacetone at −10 to −5° and treatment with dilute alcoholic potassium hydroxide at −15°, affords a mixture of piperidides, yielding on hydrolysis acetylpropionyl and piperidinoacetone (1-acetonylpiperidine), indicating the formation of both a mono- and a di-piperidino-compound. R. BRIGHTMAN.

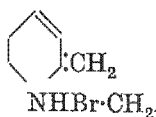
Transformations of ethyl isatin-*N*-carboxylate. N. PUTOCHIN (Ber., 1927, 60, [*B*], 1636—1639).—Contrary to the observations of Heller (A., 1918, i, 309), ethyl isatin-*N*-carboxylate, m. p. 115°, is converted by boiling water into *o-carbethoxyaminobenzoylformic acid*, $CO_2Et{\cdot}NH{\cdot}C_6H_4{\cdot}CO{\cdot}CO_2H$, m. p. 144° (Heller's dihydroxydihydroindolecarboxylic acid), which is oxidised by potassium dichromate and sulphuric acid to *o-carbethoxyaminobenzoic acid*, m. p. 126—127° (Heller's 2 : 4-dihydroxy-1 : 2 : 3 : 4-tetrahydroquinoline-2-carboxylic acid). Distillation of the latter acid with calcium oxide yields aniline. H. WREN.

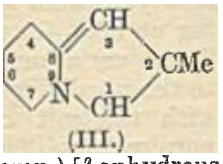
Manufacture of chloro-iodo-compounds of 2-aminopyridine and its derivatives. CHEM. FABR. AUF AKTIEN VORM. E. SCHERING.—See B., 1927, 572.

Production of 3-pyridylhydrazine and its derivatives. DEUTSCHE GOLD-U. SILBER-SCHEIDEANSTALT VORM. ROESSLER.—See B., 1927, 572.

Tautomerism in the pyridine series. A. E. TSCHITSCHIBABIN (Ber., 1927, 60, [*B*], 1607—1617).—The action of benzoic anhydride on 2-methylquinoline at 240—260° affords small quantities of *dibenzoyl-2-methylquinoline*, m. p. 189—190°, and benzoyl-2-methylquinoline, isolated as the *chloroplatinate*, $(C_{17}H_{13}ON,HCl)_2PtCl_4,2H_2O$. Similarly from 2-methylpyridine and benzoic anhydride the *chloroplatinates* of dibenzoyl-α-picoline and benzoyl-α-picoline ($+2H_2O$) are derived. 2-Methylpyridine and bromoacetone give an additive *compound*, (I) or (II), m. p. 196°, from which the *chloroplatinate*


(I.)

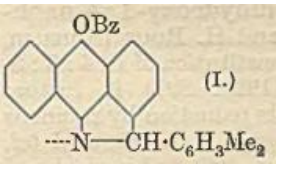

(II.)


(III.)

$(C_9H_{12}ONCl)_2PtCl_4$, m. p. 202° (decomp.) [? anhydrous and $+3H_2O$), is obtained. Treatment of the aqueous solution of the bromide with potassium hydroxide separation of the base (probably $CH_2{\cdot}C_4H_3N{\cdot}CH_2Ac$); if, however, the bromide is distilled with steam in the presence of sodium hydrogen carbonate, 2-*methylindolizine* (III), m. p. 68°, volatilises. The compound resembles indole in its behaviour towards light and air; it gives the pine-shaving reaction and the oxalic acid test. As vapour and in dilute solution it gives a strong violet fluorescence. Phenacyl bromide and 2-methylpyridine give the *compound*, $C_{14}H_{14}ONBr_4$, m. p. 215° (decomp.) after blackening at 210°, from which 2-*phenylindolizine*, m. p. 215°, is derived. Reaction proceeds less smoothly with halogenated aldehydes but from bromoacetaldehyde and 2-methylpyridine indolizine, m. p. 75° (the pyrrocoline of Scholtz, A., 1913, i, 514), is obtained in small amount. Bromoacetone and 2 : 6-dimethylpyridine afford 2 : 7-*dimethylindolizine*, b. p. 238—240°, whilst 3-*phenyl*-2-*methylindolizine* is derived from 2-benzylpyridine and bromoacetone. H. WREN.

Derivatives of acenaphthpyridine. I. S. U. NAIR and J. L. SIMONSEN (J. Indian Inst. Sci., 1927, **10A**, 10—13).—See this vol., 159.

Free organic radicals. VI. Azylium salts, metallic salts, and the benzoylation of *m*-xylyl-*peri*pyrrolinoanthranolazyl. R. SCHOLL, E. STIX, and H. SEMP (Ber., 1927, 60, [*B*], 1685—1691; cf. this vol., 675).—Aryl*peri*pyrrolinoanthranolazyls differ from most organic radicals since they can undergo chemical change without forfeiting their radical nature. Thus they are converted by strong acids into crystalline salts, by suitable metallic compounds into metallic salts, and by benzoylating agents, even when distillation with steam is employed, into crystalline benzoyl derivatives which are themselves radicals and are readily converted into the original azyls. In solution they resemble the free azyls


(I.)

since they are very sensitive to light and give a characteristic band spectrum. The benzoyl derivatives are easily converted by acids into relatively stable radical salts. The following compounds have been isolated: py-m-*xylyl*peri*pyrrolinoanthranol*-*azylium perchlorate*; the *potassium* salt of m-*xylyl*-peri*pyrrolinoanthranolazyl*; *benzoyl*-1-m-*xylyl*-1 : 9-peri-*pyrrolinoanthranolazyl* (I), m. p. 196°, and its *perchlorate*. H. WREN.

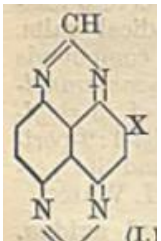
Curtius rearrangement of carbamyl azides. Formation of benzpyrazolones and bimolecular carbonylhydrazines. R. STOLLÉ [with N. NIELAND and M. MERKLE] (J. pr. Chem., 1927, [ii], **116**, 192—204; cf. A., 1924, i, 881).—Phenylmethylcarbamyl azide is converted in boiling xylene into 1-methylbenzpyrazolone, m. p. 154° [*hydrochloride*, m. p. 150° (decomp.)] (cf. Milrath, A., 1908, i, 1014), together with diphenyldimethylcarbohydrazide. *Phenylethylcarbamyl azide*, m. p. 43°, prepared from the chloride and sodium azide, yields similarly 1-*ethylbenzpyrazolone*, m. p. 134° [*hydrochloride*, m. p. 83° (decomp.)], together with diphenyldiethylcarbazide. Similarly *o-tolylmethylcarbamyl azide*, obtained from *o-tolylmethylcarbamyl chloride*, m. p. 62°, and sodium azide, gives 1 : 7-*dimethylbenzpyrazolone*, m. p. 240°, to-

gether with *bis*-as-*carbonyl*-o-*tolylmethylhydrazine*, $(C_6H_4Me{\cdot}NMe{\cdot}N{:}CO{\cdot})_2$, m. p. 160°. This last substance when heated with aniline in decahydronaphthalene solution yields the dimethylbenzpyrazolone together with a small quantity of what is probably 4-phenyl-1-*o*-tolyl-1-methylsemicarbazide. *o-Tolylethylcarbamyl chloride*, b. p. 145°/12 mm., m. p. 38°, is converted into the *azide*, which on decomposition yields 7-*methyl*-1-*ethylbenzpyrazolone*, m. p. 175°, *bis*-as-*carbonyl*-o-*tolylethylhydrazine*, m. p. 149°, and a *substance*, m. p. 39°. The carbonyl compound is converted by boiling aniline into the pyrazolone, diphenylcarbamide, and 4-*phenyl*-1-o-*tolyl*-1-*ethylsemicarbazide*, $C_6H_4Me{\cdot}NEt{\cdot}NH{\cdot}CO{\cdot}NHPh$, m. p. 129°, also obtained from *o*-tolylethylhydrazine and phenylcarbimide. H. BURTON.

1 : 8-Naphthyridine and its derivatives. G. KOLLER (Ber., 1927, 60, [*B*], 1572—1575; cf. this vol., 367).—The conversion of 2 : 4-dichloro-1 : 8-naphthyridine into 1 : 8-naphthyridine is accompanied by considerable difficulty and is most easily effected by hydrogen in the presence of palladised charcoal whereby a mixture of 1 : 8-naphthyridine (identified as the corresponding chloroaurate, decomp. 225°) and a dihydronaphthyridine (*picrate*, m. p. 173—175° after softening) is produced. Methyl 2 : 4-dihydroxy-1 : 8-naphthyridine-3-carboxylate is converted through the corresponding *amide*, m. p. 315° (decomp.), into 2 : 4-*dichloro*-3-*cyano*-1 : 8-*naphthyridine*, m. p. 212° after softening. 2 : 4-*Dimethoxy*-1 : 8-*naphthyridine* m. p. 145—146° after softening at 144°, is obtained from 2 : 4-dichloro-1 : 8-naphthyridine and methyl-alcoholic sodium methoxide. H. WREN.

Preparation of [naphthaphenazine] vat dyes. I. G. FARBENIND.—See B., 1927, 578.

Naphthazarin and 5 : 6-dihydroxy-1 : 4-naphthaquinone. O. DIMROTH and H. ROOS (Annalen, 1927, 456, 177—192).—The constitution of 1 : 4 : 5 : 8-tetranitronaphthalene (A., 1926, 297) is further established by its reduction by stannous chloride in presence of formic acid (cf. Sachs, A., 1909, i, 426) to brownish-red *diperimidine dihydrochloride*, which is oxidised by ferric chloride to *diperimidinequinone* (I, X=H). When the latter is boiled with 20% hydrochloric acid it yields *chlorodiperimidine hydrochloride* which is oxidised to yellow *chlorodiperimidinequinone* (I, X=Cl). Similarly a second chlorine atom may be introduced.



(I.)

Nitration of 6-hydroxy-1 : 4-naphthaquinone (Fischer and Bauer, A., 1916, i, 718) affords principally the 5-*nitro*-derivative. This is reduced by stannous chloride and hydrochloric acid to 5-*amino*-1 : 4 : 6-*trihydroxynaphthalene hydrochloride*, which is oxidised by ferric chloride in dilute aqueous solution to 5 : 6-*dihydroxy*-1 : 4-*naphthaquinone* (o-*naphthazarin*), m. p. 201—202° [*pyridine* salt; 5-*acetate*, m. p. 155—160° (decomp.); 6-*acetate*, m. p. 140—145°, sintering from 130°; 5 : 6-*diacetate*, m. p. 152° (decomp.); 5-*benzoate*, m. p. 160—170°; 6-*benzoate*]. This substance, which has the formula previously ascribed to naphthazarin, is unexpectedly inferior to the latter in dyeing properties and gives a less intensely coloured black chromium lake. The unusual ease with which it undergoes 5-acylation is explained by the observation that the 6-acyl derivatives, obtained in pyridine solution are transformed by acids into the corresponding 5-acyl derivatives. *o*-Naphthazarin and its 6-acyl derivatives give a positive reaction with boroacetic anhydride. It is reduced by stannous chloride and hydrochloric acid to 1 : 4 : 5 : 6-*tetrahydroxynaphthalene*, m. p. 180° (decomp.) (*tetra-acetate*, m. p. 202°), and oxidised by manganese dioxide and sulphuric acid to naphthapurpurin (*monopyridine* salt), identical with the products obtained by Jaubert (A., 1900, i, 42) from naphthazarin and by Thiele and Winter (A., 1900, i, 504) from naphthazarin diacetate. Hydroxynaphthaquinones in which the hydroxyl and carbonyl groups are adjacent are more volatile than those with hydroxyl groups in other positions. H. E. F NOTTON.

α-Hæmatin, Kuster's tetramethylhæmatoporphyrin, and Nencki's hæmatoporphyrin. O. SCHUMM (Z. physiol. Chem., 1927, 168, 1—10).—When α-hæmatin is heated with methyl alcohol containing 1—2% of hydrochloric acid, and iron removed from the product, a "porphyrin" is formed which is regarded as a derivative of Nencki's hæmatoporphyrin. Two different substances are obtained when this porphyrin is heated for 1 hr. with 25% hydrochloric acid, and, by spectroscopical investigation, these two products are identified as Nencki's hæmatoporphyrin and hæmateric acid. Kuster's tetramethylhæmatoporphyrin and Nencki's hæmatoporphyrin give the same products. A state of equilibrium is probably reached, and after removal of the hæmateric acid, a further yield of this acid is obtained by heating the remainder with hydrochloric acid. The iron-free hæmatin derivative is probably the methyl ester of a methylhæmatoporphyrin. When heated with glacial acetic acid for several hours, Nencki's hæmatoporphyrin is mainly transformed into a product which is identified spectroscopically as hæmateric acid, and this is regarded as a further distinction between this hæmatoporphyrin and coproporphyrin. A. WORMALL.

Simple method of preparation of the iron salt of tetramethylhæmatoporphyrin. H. FISCHER and F. LINDNER (Z. physiol. Chem., 1927, 168, 15–170).—This compound was prepared by heating hæmin with methyl alcohol and sulphuric acid, treating e reaction mixture with hydrochloric acid, cooling, an filtering. On keeping, the filtrate gave the iron sa , m. p. 185°, as tetragonal plates, or occasionally a pointed prisms. Crystallisation from chloroform methyl alcohol gave only tetragonal plates, not me ing at 300° (in one case m. p. 225° was observe). These variations in m. p. are discussed with rega to the possibility of isomeric forms, but a compari with the salt obtained from tetramethylhæma porphyrin and ferric chloride in acetic acid is impo ble, since this has no m. p. On oxidation with c o acid, the iron salt of tetramethylhæmatoporphyn behaves like tetramethylhæmatoporphyrin, an two compounds yield the same methoxylated u

(m. p. 64°). Iron can be removed from combination with tetramethylhæmatoporphyrin, with simultaneous hydrolysis, by hydrobromic acid in acetic acid, and crystalline hæmatoporphyrin is obtained. The iron salt can also be reduced readily to mesoporphyrin. Attempts to effect addition of methyl alcohol by heating with hæmin and acids other than sulphuric acid or hydrobromic acid, were unsuccessful. Protoporphyrin, heated with methyl alcohol and sulphuric acid, yielded protoporphyrin ester quantitatively and no tetramethylhæmatoporphyrin. Coprohæmin, esterified by hydrochloric acid and methyl alcohol, gave the ester of coprohæmatoporphyrin quantitatively. Protoporphyrin, prepared from hæmochromogen and free from mesoporphyrin, on oxidation gave traces of methylethylmaleinimide. Spectroscopic data for deuteroporphyrin and various derivatives (the iron salt, copper salt, ester, copper salt ester, and the dibromo-ester) are given.

A. WORMALL.

Thiolthiazoles. I. J. TEPPEMA and L. B. SEBRELL (J. Amer. Chem. Soc., 1927, **49**, 1748—1758).—Reduction of 2 : 2′-dinitrodiphenyl disulphide with aqueous ammonium or sodium hydrosulphide, or with sodium hyposulphite in aqueous or alcoholic solution, yields the corresponding 2 : 2′-diamino-derivative, which affords 1-thiolbenzthiazole in 32% yield when boiled with carbon disulphide. A 96% yield of 1-thiolbenzthiazole is obtained by treating the 2 : 2′-dinitrodiphenyl disulphide with aqueous sodium or ammonium hydrosulphide, but not with sodium hyposulphite, in presence of carbon disulphide. It is concluded that the formation of the thiazole derivative is due to the interaction of nascent *o*-aminothiophenol with nascent carbon disulphide (the former being derived from the reduction of the disulphide, the latter from dissociation of sodium trithiocarbonate formed from the carbon disulphide and the sodium sulphide or hydrosulphide), and this conclusion is supported by the production of 1-thiolbenzthiazole in 87·5% yield direct from *o*-chloronitrobenzene by treatment with sodium hydrosulphide in presence of carbon disulphide. 1 : 4-Dichloro-2-nitrobenzene affords similarly 4-*chloro*-1-*thiolbenzthiazole*, m. p. 192°, whilst 4-bromo-3-nitrobenzenesulphonic acid yields *sodium* 1-*thiolbenzthiazole*-4-*sulphonate*. 1-Chloro-2 : 4-dinitrobenzene yields, when treated similarly, *dithiolbenzdithiazole*, p. not below 270°, but 4-*amino*-1-*thiolbenzthiazole*, p. 216°, can be obtained by reduction of 2 : 4 : 2′ : 4′-tetranitrodiphenyl disulphide with tin and hydrochloric acid, followed by treatment with sodium hydrosulphide and carbon disulphide as above, probably through the intermediate formation of 2 : 4-minothiophenol. 2-Chloro-3-nitrotoluene affords analogously 1-*thiol*-6-*methylbenzthiazole*, m. p. 184°, whilst 4-chloro-3-nitrotoluene yields 1-*thiol*-4-*methylbenzthiazole*, m. p. 171—173°, from which it is concluded that Sebrell and Boord's product, obtained from *m*-toluidine (A., 1924, i, 89), is a mixture of the 4- and 6-methyl derivatives. 4-Chloro-3-nitrobenzoic acid affords analogously 1-thiolbenzthiazole-4-carboxylic acid, m. p. not below 270°, but 1-thiolbenzthiazoles could not be obtained in this way from 2 : 5 : 4 : 5-tetrachloro-2 : 2′-dinitrodiphenyl disulphide or 2 : 4 : 2′ : 4′-tetrachloro-6 : 6′-dinitrodiphenyl disulphide.

F. G. WILLSON.

Thiazoles. II. Nitration and reduction of 2-thiolbenzthiazole and its substituted derivatives. J. TEPPEMA and L. B. SEBRELL (J. Amer. Chem. Soc., 1927, **49**, 1779—1785; cf. preceding abstract).—Treatment of 1-thiolbenzthiazole with nitric and sulphuric acids affords 5-*nitro*-1-*thiolbenzthiazole*, m. p. 255—257°, which is reduced by sodium hydrosulphide to the 5-*amino*-derivative, m. p. 260°, the structure of the latter being established by its identity with the 5-amino-1-thiolbenzthiazole, m. p. 263°, obtained by treatment of the tin–hydrochloric acid reduction product of 5-nitro-2-aminothiophenol with sodium hydrosulphide in presence of carbon disulphide. 5-*Benzylideneamino*-1-*thiolbenzthiazole*, m. p. 226°, is described. Diazotisation and application of the Sandmeyer reaction to 5-amino-1-thiolbenzthiazole resulted in the formation of yellowish-brown 5-*chloro*-1-*thiolbenzthiazole disulphide*, which was reduced directly with aqueous sodium hydrosulphide to 5-*chloro*-1-*thiolbenzthiazole*, m. p. about 245°. The latter is also obtained in small yield by treating 1-thiolbenzthiazole disulphide with chlorine in chloroform solution in presence of iron, followed by reduction with sodium hydrosulphide. Nitration of 4-chloro-1-thiolbenzthiazole yields a *nitro*-derivative, m. p. 190—192°, from which the corresponding *amino*-compound, m. p. 240° (*benzylidene* derivative, m. p. 242°), is obtained by reduction with tin and hydrochloric acid. Treatment of *m*-tolylenediamine disulphide with sodium hydrosulphide in presence of carbon disulphide affords 4-*amino*-1-*thiol*-5-*methylbenzthiazole*, m. p. 220° (*benzylidene* derivative, m. p. 253°), from which the corresponding 4-*chloro*-derivative was prepared by the Sandmeyer reaction.

F. G. WILLSON.

Modified Kjeldahl method for the determination of nitrogen in alkaloids with the piperidine grouping. A. GUILLAUME (Bull. Sci. pharmacol., 1927, 4; Ann. Chim. anal., 1927, [ii], **9**, 202—203).—By using a mixture of 5 g. of sulphuric acid, 5 g. of potassium sulphate, and 15 c.c. of 50% phosphoric acid and heating for 3·5 hrs., 0·00651 g. of nitrogen was found in sparteine (theory 0·0066); with 1 c.c. of phosphoric acid and heating for 4·5 hrs., 0·00672 for creatine (theory 0·00673); for 3 hrs. with 1 c.c. of acid, 0·00742 for nicotine (theory 0·00746); under the same conditions 0·01148 for pilocarpine (theory 0·01145); for ψ-pelletierine with 3·5 hrs. 0·0062 (theory 0·00611); for pelletierine unsatisfactory results were obtained.

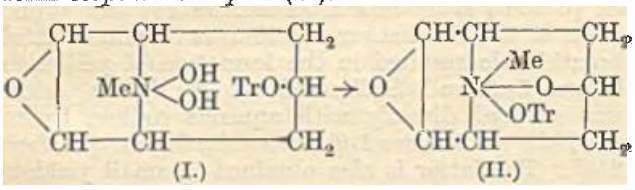
D. G. HEWER.

Sparteine. R. WOLFFENSTEIN and J. REITMANN (Biochem. Z., 1927, **186**, 269—277).—Sparteine is oxidised by sodium hypobromite to a very stable *dehydrosparteine*, $C_{15}H_{24}N_2$, m. p. 173°, $[\alpha]^{18}$ −255·0° in chloroform, which decolorises acid permanganate but cannot be reduced by zinc or tin and hydrochloric acid, and does not add hydrogen chloride or bromide when heated with the aqueous solutions of the latter in a sealed tube at 100°. It gives a *hydrochloride* and a *perbromide*, $C_{15}H_{24}N_2Br_6$ (cf. spartyrine, A., 1905, i, 544). It is catalytically reduced in presence of platinum-black to *sparteine*, b. p. 325°, $[\alpha]_D$

—49·8°, in chloroform (*picrate*, m. p. 201°, $[\alpha]_D^{18}$ —13·6° in chloroform). The bearing of this work on the structure of sparteine and dehydrosparteine is discussed. P. W. CLUTTERBUCK.

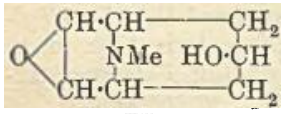
Preparation of derivatives of methylhydrastinine. E. MERCK CHEM. FABR.—See B., 1927, 572.

Scopinium derivative : reduction to ψ-scopine and degradation to *m*-hydroxybenzaldehyde. M. POLONOVSKI and M. POLONOVSKI (Compt. rend., 1927, **185**, 277—279; cf. Willstatter and Berner, A., 1923, i, 701).—By the action of hydrogen peroxide on scopolamine, the hydrate of the *N*-oxide (I) is presumably first formed, followed by migration of the tropyl group, OH·C_8H_8·CO· (for which Tr is written), from a *C*-oxygen to an *N*-oxygen atom, to form *scopinium tropate* (II).



(I.) (II.)

This is converted by hydrobromic acid into *scopinium bromide*, m. p. 209—210°, neutral to litmus; the quaternary base (*nitrate*, m. p. 203°) is unstable. The bromide is not reduced by sulphur dioxide, but is converted by zinc and hydrochloric acid into the hydrobromide of a strong tertiary base, which is a geometrical isomeride of scopine (Willstatter, *loc. cit.*), and is named *ψ-scopine* (III), m. p. 126° (*hydrochloride*, m. p. 257—258°; *picrate*, m. p. 229°; *chloroplatinate*, m. p. 223°; *chloroaurate*, m. p. 237—238°). ψ-Scopine gives an oily O-*acetyl* derivative (*picrate*, m. p. 187°; *chloroaurate*, m. p. 203°), and a *methiodide*, m. p. 249°, which is degraded to a mixture of ψ-scopine with other basic substances. *ψ-Scopine N-oxide*, $C_8H_{13}O_3N,3H_2O$, m. p. 177°, forms a *hydrobromide*, m. p. 188°, acid to litmus; it is reduced by sulphur dioxide to ψ-scopine. An attempt at resolution of *ψ-scopine* d-*tartrate*, m. p. 181°, gave negative results, in agreement with the formula (III).



(III)

On heating the reaction product of scopinium bromide and moist silver oxide, methylamine is evolved, and *m*-hydroxybenzaldehyde is obtained, with ψ-scopine. E. W. WIGNALL.

Quebracho alkaloids. I. G. HAHN (Ber., 1927, **60**, [*B*], 1681—1684).—Although quebrachine and yohimbine are very closely similar in themselves and their salts, their supposed identity (cf. Fourneau and Page, A., 1914, i, 862) cannot be maintained. Quebrachine hydrochloride, isolated from the total alkaloids of *Cortex Quebracho blanco*, has $[\alpha]_D^{16}$ +102·8° in water, whereas yohimbine and *iso*yohimbine hydrochlorides have $[\alpha]_D^{20}$ +103—104° and +103·8°, respectively. Quebrachine, m. p. 235°, has $[\alpha]_D^{17}$ +54·2° and +107·9° in alcohol and pyridine respectively, whereas the similar figures for yohimbine are $[\alpha]_D$ +53·6° and $[\alpha]_D^{20}$ +84·1°. Quebrachine hydrochloride is hydrolysed by alcoholic sodium hydroxide to *quebrachoic acid*, $C_{20}H_{24}O_3N_2,H_2O$, decomp. 269—270°, which has $[\alpha]_D^{17}$ +138·8° in pyridine, in which yohimboaic and *iso*yohimboaic acids have $[\alpha]_D^{20}$ +79·2° and +147·0°, respectively. *Quebrachoic anhydride* has m. p. 298°. *Ethyl quebrachoate hydrochloride* has m. p. 304—305° (decomp.); *ethyl quebrachoate*, m. p. 189°, is not affected in m. p. by ethyl yohimboate. H. WREN.

Strychnine and brucine. IV. G. R. CLEMO, W. H. PERKIN, jun., and R. ROBINSON (J.C.S., 1927, 1589—1627; cf. *ibid.*, 1910, **97**, 305; A., 1924, i, 1337; 1925, i, 831).—The chemistry of strychnidine (Tafel, A., 1892, 1012; 1898, i, 703) is investigated. Strychnine [*methosulphate*, decomp. 282°; *methobromide*, m. p. 320° (decomp.)] is reduced by an improved electrolytic method to a mixture of strychnidine, m. p. 246° (*methosulphate; methochloride*, decomp. 310°; *methobromide;* methiodide; *hydriodide*, decomp. 305°), and tetrahydrostrychnine, m. p. 202°, easily separated by crystallisation from benzene. Since strychnidine methosulphate is obtainable both from strychnidine and by electrolytic reduction of strychnine methosulphate, the nitrogen atom methylated is not the amide nitrogen atom. It is converted by methyl-alcoholic potassium hydroxide into *methoxymethyldihydrostrychnidine*, $C_{23}H_{30}O_2N_2$, m. p. 125—126°, b. p. 235—237°/1 mm. (crystallographic data by T. V. BARKER), a mono-acid base, giving a *hydriodide*, *methiodide*, m. p. 278° [(decomp.); $+H_2O$, m. p. 175° (decomp.)], and *methohydroxide*, m. p. 117°. The base is converted by methyl iodide in *methyl alcohol* into two *oxymethoxymethyldihydrostrychnidines*, $C_{23}H_{30}O_3N_2$, (*A*), m. p. 235°, and (*B*), m. p. 270° *B* is also obtained from the base by the action of dilute nitric acid or of acetic anhydride, and from *A* by boiling with xylene, alcohol, etc. Methoxymethyldihydrostrychnidine combines slowly in boiling benzene with 2 mols. of methyl sulphate, giving two *dimethosulphates*, from which two *dimethiodides*, one crystalline, m. p. 297° (decomp.), are obtained. The crystalline dimethiodide gives with silver chloride a *dimethochloride*, m. p. 255—257° (decomp.), which regenerates the original base when treated with alkali, and must be $C_{20}H_{22}O(OMe)(:NMe_2)\langle\begin{matrix}CH_2\\NMe\end{matrix}\rangle Cl_2$. Oxidation of methoxymethyldihydrostrychnidine with alkaline hydrogen peroxide gives the amino-acid, *methoxymethylstrychnidonic acid*, $C_{21}H_{28}O_5N_2$, which forms an *anhydro*-compound, $C_{21}H_{26}O_4N_2$, m. p. [illegible]. By the action of ethyl-alcoholic potassium hydroxide on strychnidine methosulphate the corresponding *ethoxymethyldihydrostrychnidine*, m. p. 98°, [illegible]me.

Methyl-ψ-strychnidine, $C_{20}H_{21}O(:NMe)\langle$[illegible], m. p. 203—204°, distillable in a vacuum [*hydriodide*, m. p. 265—270° (decomp.); *methiodide*, m. p. 312° (decomp.), *methochloride*, m. p. 202—203°], is obtained (i) by distilling the mother-liquors from the preparation of methoxymethyldihydrostrychnidine, (ii) by heating the dimethochloride (m. p. 255—257°) of this base, or (iii) by heating methyl*neo*strychnidinium chloride (see below). Methyl-ψ-strychnidine is not changed by electrolytic reduction, but is oxidised by permanganate in acetone at 15° to a diketone, $C_{21}H_{24}O_3N_2$, m. p. 152° [*monoxime*, decomp. 170—175°, *disemicarbazone*, m. p. 252° (decomp.)], which [illegible]

verted by methyl-alcoholic potassium hydroxide at 100° into the isomeric allo*strychnidone*, decomp. 260—265°, stable to permanganate and giving no oxime or semicarbazone.

When boiled with dilute sulphuric acid, methoxymethyldihydrostrychnidone loses methyl alcohol and gives a solution of two isomeric *methyl*neo*strychnidinium sulphates*, from which are obtained two *iodides*, $C_{22}H_{27}ON_2I$, *A*., m. p. 300° (decomp.), and *B*, m. p. 277° (decomp.); the corresponding *chlorides*, *A*, m. p. 270° (decomp.) (crystallographic data by T. V. Barker), and *B*, m. p. 255° (decomp.), are described.

Electrolytic reduction of methoxymethyldihydrostrychnidine gives *methoxymethyltetrahydrostrychnidine*, $C_{23}H_{32}O_2N_2$, m. p. 220—222°, b. p. 230—235°/1 mm. As a mono-acid base this compound forms a *hydriodide*, m. p. 235° (decomp.), and with difficulty a *methiodide* (*a*), m. p. 227° (decomp.), from which the *methochloride* (*a*) is obtained. The base yields two stereoisomeric series of dimetho-salts, (*A*) and (*B*), $C_{20}H_{24}O(OMe)(:NMe_2)\ll^{CH_2}_{Me}\rangle X_2$. The *dimethosulphate* (*A*), formed together with the more soluble (*B*) *isomeride* by long boiling with methyl sulphate in benzene, is converted into the *dimethiodide* (*A*), m. p. 315° (decomp.), and thence into the *dimethochloride* (*A*), which when heated gives methyl-ψ-dihydrostrychnidine (below). The soluble dimethosulphate is similarly converted into the *dimethiodide* (*B*), decomp. 165°, and the *dimethochloride* (*B*), which when heated gives methoxymethyltetrahydrostrychnidine. The dimethiodide (*B*), when boiled in dry mesitylene, loses methyl iodide and yields a *methiodide* (*b*), decomposing at 325° into methoxymethyltetrahydrostrychnidine. It is suggested, from their behaviour with diazo-salts, that the methiodide (*a*) is $C_{20}H_{24}O(OMe)(:NMe_2)\ll^{CH_2}\rangle I$, the *b* isomeride being $C_{20}H_{24}O(OMe)(:NMe)\ll^{CH_2}_{Me}\rangle I$.

Methyl-ψ-dihydrostrychnidine, $C_{20}H_{23}O(:NMe)\ll^{CH}_{N}$, m. p. 212° [*methiodide*, m. p. 330—335° (decomp.); *methochloride*, m. p. 315° (decomp.)], results when the dimethiodide (*B*) or methyl*neo*dihydrostrychnidine chloride (below) is heated.

By heating methoxymethyltetrahydrostrychnidine hydriodide cautiously at 230°, water and methyl alcohol are evolved and *methyl*neo*dihydrostrychnidinium iodide*, $C_{22}H_{29}ON_2I$, m. p. 350° (decomp.), is formed. The *chloride* has m. p. 345° (decomp.).

Methylstrychnine (Tafel, A., 1890, 1447), m. p. 318—320° (decomp.), readily obtained by adding potassium hydroxide to a solution of strychnine methosulphate, loses methyl alcohol when heated in a vacuum, giving *normethylstrychnine*, $C_{21}H_{22}O_2N_2$ [*methiodide*, m. p. 315° (decomp.); *methochloride*, m. p. [illegible] Decomposition of methylstrychnine by methyl-alcoholic potassium hydroxide at 250° yields [illegible], p. 52°, and a little carbazole, m. p. 236°; or by soda-lime carbazole and an oil, b. p. 93°/25 mm. [illegible] p. [illegible] which is probably an ethylindole.

Methylstrychnine, electrolytically reduced in dilute sulphuric acid, gives on treatment with barium carbonate *methylstrychnidinium hydrogen carbonate*, $C_{22}H_{27}ON_2,HCO_3,H_2O$, which with methyl-alcoholic potassium hydroxide yields methoxymethyldihydrostrychnidine, m. p. 126°. C. Hollins.

Strychnine and brucine. V. J. M. Gulland, W. H. Perkin, jun., and R. Robinson (J.C.S., 1927, 1627—1662; cf. preceding abstract).—Tafel's "tetrahydrobrucine," m. p. 200—201° (A., 1902, i, 53), is identical with the same author's "brucidine," m. p. 198° (impure), and the latter name is adopted. Brucine is reduced electrolytically at 17—18° to a mixture of brucidine, m. p. 203—203·5° [*dihydrochloride*, m. p. 310° (decomp.); *dihydriodide*, m. p. 255° (decomp.); *methosulphate*, m. p. 291° (decomp.); *methiodide*, m. p. 322° (decomp.)], and *tetrahydrobrucine*, m. p. 177° [*dihydrochloride*, m. p. 305° (decomp.); *dihydriodide*, m. p. 225° (decomp.); *methiodide*, m. p. 290° (decomp.); *nitrosoamine*, m. p. 213—214° (decomp.); *nitrosoamine hydrochloride*, m. p. 288° (decomp.)], separated by crystallisation from methyl alcohol and ethyl acetate. Tetrahydrobrucine is converted into brucidine by dehydration with phosphoryl chloride.

Brucine methosulphate, m. p. 278° (decomp.; Leuchs and Anderson, A., 1911, i, 1018, give 268°), gives the methiodide, m. p. 295° (decomp.; cf. Claus and Röhre, A., 1881, 749; Hanssen, A., 1885, 63), from which the *methohydrogencarbonate*, m. p. 202—203° (decomp.), is prepared. Methylbrucine, m. p. 300° (decomp.), obtained from brucine methosulphate and hot dilute sodium hydroxide, is electrolytically reduced in dilute sulphuric acid, giving on treatment with barium carbonate *brucidine methohydrogencarbonate*, $C_{25}H_{32}O_6N_2,2H_2O$, m. p. 265° (decomp.), convertible by 30% potassium hydroxide solution into *brucidine methohydroxide*, $(+2H_2O)$, m. p. 268° (decomp.).

Brucidine methosulphate when heated with methyl-alcoholic potassium hydroxide yields *methoxymethyldihydrobrucidine*, $C_{25}H_{34}O_4N_2$, m. p. 115°, b. p. 265—267°/1·5 mm. [*dihydriodide*, m. p. 217—218° (decomp.)]. It gives at 100° a *methiodide* (*A*), m. p. 190° (or, +0·5EtOH, 179°), together with a little *oxymethoxymethyldihydrobrucidine*, $C_{25}H_{34}O_5N_2$, m. p. 277° (decomp.), and an intermediate iodine-free *substance*, m. p. 210—218°; a *dioxymethoxymethyldihydrobrucidine* (*X*), $C_{25}H_{34}O_6N_2$, m. p. 270° (decomp.), may also be isolated. The methiodide (*A*) and *methochloride* (*A*) regenerate methoxymethyldihydrobrucidine by the action of methyl-alcoholic potassium hydroxide. A *dimethiodide* (*A*), m. p. 215°, is formed slowly at 140°; a *methosulphate* (*A*), m. p. 231—232° (decomp.), and, more slowly, a *dimethosulphate* (*B*) at 100°. The latter is converted into a *dimethiodide* (*B*), m. p. 290° $(+0·5H_2O$, decomp.), and a *dimethochloride* (*B*), which in boiling nitrobenzene loses methyl chloride and gives the *methochloride* (*B*), m. p. 164° (decomp.); the corresponding *methiodide* (*B*), m. p. 291° (decomp.), has only been obtained from the methochloride. By the successive action of silver sulphate and methyl-alcoholic potassium hydroxide on the dimethiodide (*B*) methoxymethyldihydrobrucidine is regenerated, but when

the dimethochloride (*B*) or methyl*neo*brucidinium chloride (below) is heated the product is *methyl-ψ-brucidine*, $C_{24}H_{30}O_3N_2$, m. p. 198—199° [*dihydriodide*, m. p. 259° (decomp.); *methiodide*, m. p. 297° (decomp.)]; from the dimethochloride (*B*) there is also formed, when inorganic salts are present, a *substance* which seems to be an important fission product of the brucine molecule. Methyl-ψ-brucidine is unchanged by electrolytic reduction and by hydrogen and palladium, but is oxidised by permanganate to an oily *brucidone*, $C_{23}H_{28}O_5N_2$ [*semicarbazone*, decomp. 226° (+1·5EtOH), separable into fractions of m. p. 220—257° (decomp.)]. The colour reactions of the reduced brucidine derivatives suggest the formulæ $(OMe)_2(C_{20}H_{20}O)(OMe)(:NMe)\left\langle \begin{matrix} CH_2 \\ NMe \end{matrix} \right\rangle I$ for the methiodide (*A*), and $(OMe)_2(C_{20}H_{20}O)(OMe)(:NMe_2)\left\langle \begin{matrix} CH_2 \\ N \end{matrix} \right\rangle I$ for (*B*), the more basic nitrogen atom of brucidine becoming the less basic one of methoxymethyldihydrobrucidine.

Methylneobrucidinium iodide, m. p. 298° (decomp.), is prepared by boiling methoxymethyldihydrobrucidine with 10% sulphuric acid, adding small excess of ammonia, acidifying with sulphur dioxide and adding sodium iodide. The *chloride* melts at 188°, or 163° (+H_2O). The *sulphate* (solution) is unchanged by electrolytic reduction.

By the action of dilute nitric acid at 100° methoxymethyldihydrobrucidine yields the *nitro*-derivative, m. p. 276—278° (+EtOH, decomp.). Oxidation of the base with permanganate in acetone at −10° gives two *dioxymethoxymethyldihydrobrucidines*, $C_{25}H_{31}O_6N_2$, *Y*, m. p. 185—186° [*methiodide*, plates, m. p. 225—226°, or needles, m. p. 223—224° (+ 2EtOH)], and *Z*, m. p. 110—111° (+0·5EtOH; no methiodide and no picrate), isomeric with the *X* compound, m. p. 270° (above).

Brucidine methosulphate reacts with sodium ethoxide to form *ethoxymethyldihydrobrucidine methiodide*, m. p. 176° (decomp.).

Methoxymethyltetrahydrobrucidine, $C_{25}H_{36}O_4N_2$, m. p. 133—135°, b. p. 253°/2 mm. [*dihydriodide*, m. p. 212° (decomp.); *dihydrochloride*, decomp. 150°; *methiodide* (*A*), m. p. 166—167° (regenerating the base); *methochloride* (*A*)], is obtained by electrolytic reduction of methoxymethyldihydrobrucidine. It reacts slowly with methyl sulphate to give a mixture of *dimethosulphates* (*A*) and (*B*), from which are prepared the easily separable *dimethiodide* (*A*), m. p. 230—232° [decomp.; *dimethochloride* (*A*), glassy], and *dimethiodide* (*B*), m. p. 287° [decomp.; *periodide* (*B*), m. p. 230° (decomp.); *dimethochloride* (*B*), m. p. 138° (decomp., +1EtOH) or 214° (decomp.)]. The dimethiodide (*A*) is also obtained directly from the base, and when heated yields the *methiodide* (*B*), m. p. 298° (decomp.), also obtained from the dimethiodide (*B*) or from the *methochloride* (*B*), decomp. 210°, produced by heating the dimethochloride (*B*). The structures of the *A* and *B* methiodides are analogous to those of the dihydro-compounds.

The tetrahydro-base is not changed by boiling with dilute sulphuric acid, but *methylneodihydrobrucidinium iodide*, $C_{24}H_{33}O_3N_2I$, m. p. 283° (decomp.), is prepared from the glassy *chloride* obtained when methoxymethyltetrahydrobrucidine dihydrochloride is heated in mesitylene at 180°.

Methoxymethyltetrahydrobrucidine dimethohydrogencarbonate (*A*), m. p. 92—94° (+5H_2O; 103—104° in sealed capillary), is prepared from the dimethiodide (*A*). The *isomeride* (*B*), m. p. 109° (+6H_2O), from the dimethiodide (*B*), yields when heated at 135° the *methohydrogencarbonate* (*B*), and at higher temperatures *methyl-ψ-dihydrobrucidine*, $C_{24}H_{32}O_3N_2$, m. p. 220—221° [*dihydriodide*, m. p. 215—217° (decomp.)], which cannot be obtained by heating the methochloride (*B*) or dimethochloride (*B*), more profound decomposition taking place.

C. HOLLINS.

Arsenic compounds of the pyridine series. II. A. BINZ and C. RATH (Annalen, 1927, 455, 127—139; cf. this vol., 580).—Some 3-aminopyridines have been converted through the diazonium salts into unexpectedly stable arsinic acids which show no basic properties. These are reducible in the normal way to arsines, arsinoxides, and yellow, amorphous arsenopyridines. The preparation of some of the intermediate aminopyridines will be described later. The following are obtained: (*a*) from 5-amino-2-hydroxypyridine: *2-hydroxypyridine-5-arsinic acid*, m. p. above 317° [*barium* (+H_2O), *mercury*, *copper*, and *silver* salts); *2-hydroxy-5-pyridylarsinoxide*; *2 : 2′-dihydroxy-5 : 5′-arsenopyridine*, and *2-hydroxy-5-pyridylarsine*; (*b*) from 2-chloro-5-aminopyridine: *2-chloropyridine-5-arsinic acid*, m. p. 178—179°; *2-chloro-5-pyridylarsinoxide*, decomp. 138°; *2 : 2′-dichloro-5 : 5′-arsenopyridine*, decomp. 140°; *2-chloro-5-pyridylarsine*, decomp. 135°; (*c*) from 2-bromo-5-aminopyridine: *2-bromopyridine-5-arsinic acid*, m. p. 175°; *2-bromo-5-pyridylarsinoxide*, decomp. 159°; *2 : 2′-dibromo-5 : 5′-arsenopyridine*; *2-bromo-5-pyridylarsine*; (*d*) from 2-iodo-5-aminopyridine: *2-iodopyridine-5-arsinic acid*, m. p. 173°; *2-iodo-5-pyridylarsinoxide*, decomp. 145°; *2-iodo-5-pyridylarsine*, decomp. 140°; *2 : 2′-di-iodo-5 : 5′-arsenopyridine*; (*e*) from 3-chloro-5-amino-2-hydroxypyridine: *3-chloro-2-hydroxypyridine-5-arsinic acid*, m. p. 237°; *3-chloro-2-hydroxy-5-pyridylarsinoxide*, decomp. 195°; *3 : 3-dichloro-2 : 2′-dihydroxy-5 : 5′-arsenopyridine*; (*f*) from 3-bromo-5-amino-2-hydroxypyridine: *3-bromo-2-hydroxypyridine-5-arsinic acid*, m. p. above 300°, *3-bromo-2-hydroxy-5-pyridylarsinoxide*, decomp. 3…, *3 : 3′-dibromo-2 : 2′-dihydroxy-5 : 5′-arsenopyridine*; (*g*) from 3-iodo-5-amino-2-hydroxypyridine: *3-iodo-2-hydroxypyridine-5-arsinic acid*, decomp. 289°, which loses iodine when boiled with water; *3-iodo-2-hydroxy-5-pyridylarsinoxide*, decomp. 200°; *3 : 3-di-iodo-2 : 2′-dihydroxy-5 : 5′-arsenopyridine*; and (*h*) from 2 : 5-diaminopyridine: *2-aminopyridine-5-arsinic acid*, which gives arsenic acid in boiling water, *2-amino-5-pyridylarsinoxide*, decomp. 90°, and *2 : 2′-diamino-5 : 5′-arsenopyridine tetrahydrochloride*, decomp. 120°.

H. E. F. NOTTON.

Dimagnesium derivative of *p*-dibromobenzene. R. QUELET (Bull. Soc. chim., 1927, [iv], 41, 936).—Magnesium reacts with an ethereal solution *p*-dibromobenzene, yielding, in addition to monomagnesium derivative, about 15% of the dimagnesium compound together with *pp*-dibromophenyl. The reaction must be carried out in

atmosphere of hydrogen. Some dimagnesium derivative is formed whether magnesium is present in excess or otherwise. H. BURTON.

Manufacture of mercurimononitro-o-cresol [3-nitro-4-acetoxymercuri-o-cresol etc.] and salts. G. W. RAIZISS, Assr. to ABBOTT LABORATORIES.—See B., 1927, 573.

Metallic derivatives of thiophen. I. Tin tetra-α-thienyl and lead tetra-α-thienyl. E. KRAUSE and G. RENWAUZ (Ber., 1927, **60**, [*B*], 1582—1583).—The magnesium compound from 2-iodothiophen is converted by tin tetrachloride in the presence of ether into *tin tetra-2-thienyl*, $C_{16}H_{12}S_4Sn$, m. p. 156° (corr.). *Lead tetra-2-thienyl*, m. p. 154·5° (corr.), is produced analogously from lead dichloride. The compounds resemble closely the corresponding tetraphenyl derivatives. H. WREN.

Transformations of lead diphenyl dihalides. L. ZECHMEISTER and J. CSABAY (Ber., 1927, **60**, [*B*], 1617—1621).—Lead diphenyl di-iodide is converted by silver cyanide in methyl-alcoholic suspension into *lead diphenyl dicyanide*, decomp. 245—255°, which is stable towards water at 160° but is converted by dilute nitric or hydrochloric acids into lead diphenyl dinitrate and lead diphenyl dichloride. Lead diphenyl di-iodide is rapidly and quantitatively converted by similar methods into the bromide or the chloride and the bromide into the chloride. Potassium hydroxide in ethyl-alcoholic solution converts the lead diphenyl dihalides into lead diphenyl oxide, whereas in methyl-alcoholic solution a basic iodo-derivative of somewhat varying composition is obtained from the di-iodide.

Lead tetraphenyl distils unchanged at about 240°, whereas at 270° it is partly decomposed into lead and diphenyl. Lead diphenyl oxide at 270° gives a similar sublimate and a residue of lead oxide. The basic iodo-compound (see above) yields lead tetraphenyl at 240° and diphenyl at 270°. Lead diphenyl dibromide remains almost unchanged at 240° or 270°. H. WREN.

Constitution of proteins. K. SHIBATA (Acta Phytochim., 1926, **2**, 193—198).—Glycine, alanine, leucine, tyrosine, and tryptophan, when heated with a mixture of asparagine and glycerol at 170° give dark, pasty masses, the methyl-alcoholic solutions of which are precipitated by the addition of barium or calcium chloride. The resulting hygroscopic powder, obtained by such a process and containing ash, has many protein characteristics since it is readily soluble in water, is not easily dialysable, and gives the protein colour reactions. It is precipitated from aqueous solution by silver nitrate and other heavy metal salts, and by acidified tannic acid solution, and is flocculated by saturation with ammonium sulphate. It contains no free amino-acid and gives a strong anhydride reaction with alkaline sodium picrate or dinitrobenzoate solutions. Less complex anhydride formation is brought about by heating asparagine alone with glycerol whence it is concluded that the resulting mixture contains diketopiperazine-2 : 5-diacetamide, diketopiperazine-2-acetic acid-5-acetamide, and diketopiperazine-2 : 5-diacetic acid. From alcoholic solutions of the mixture neutral salts or many metallic hydroxides precipitate a polymeride containing 2 mols. of these diketopiperazine derivatives with one atom of a bivalent metal. This polymeride after removal of the metal, is hydrolysed to aspartic acid by long boiling with hydrochloric acid or to aspartylaspartic acid by cold barium hydroxide solution. It serves as a nutrient for *Aspergillus* and *Penicillium*. It is concluded that these experiments support the anhydride constitution of proteins. L. M. CLARK.

Nucleotides of triticonucleic acid. H. O. CALVERY and D. B. REMSEN (J. Biol. Chem., 1927, **73**, 593—597).—Triticonucleic acid was hydrolysed with cold dilute sodium hydroxide and the nucleotides were prepared by the method of Jones and Perkins (A., 1925, i, 182) with the modification that the solution of lead salts was highly concentrated and treated with alcohol; this prevented the loss of uracil nucleotide owing to the solubility of its lead salt in presence of sodium acetate. There were isolated guanine, adenine, cytosine, and uracil nucleotides; the hypothesis of the identity of triticonucleic acid with yeast-nucleic acid is therefore supported. C. R. HARINGTON.

Determination of carbon in organic substances in the wet way. II. Determination of halogens and of nitrogen. B. LUSTIG (Biochem. Z., 1927, **185**, 349—354; cf. this vol., 687).—After destruction of organic matter by boiling with acid permanganate in presence of platinum, the nitrogen in the residual solution can be determined by the method of Devarda (A., 1893, ii, 343); this is applicable to all nitrogenous substances except azo- and diazo-compounds. For the determination of chlorine and bromine, the oxidation is conducted in presence of silver nitrate; the residual solution is treated with hydrogen peroxide and nitric acid, the silver halide filtered off, dissolved in ammonia, and titrated. Iodine, if present, is liberated from the residual solution by treatment with ferric ammonium alum (after removal of excess of permanganate with oxalic acid), steam-distilled into a solution of potassium iodide, and titrated. C. R. HARINGTON.

Direct iodometric determination of dextrose. A. VOORHIES and A. M. ALVARADO (Ind. Eng. Chem., 1927, **19**, 848—849).—Dextrose is readily oxidised by iodine to gluconic acid at ordinary temperatures in a strongly alkaline medium, and preliminary results indicate that the reaction may provide a new method for its determination. In presence of weak alkalis, *e.g.*, *N*-sodium hydrogen carbonate solution, dextrose is not completely oxidised to gluconic acid by iodine even at 70°. W. J. POWELL.

Determination of allantoic acid in the form of xanthylcarbamide. R. FOSSE and (MLLE.) V. BOSSUYT (Compt. rend., 1927, **185**, 308—310; cf. Fosse, A., 1926, 548).—Allantoic acid is determined by acid hydrolysis to carbamide, which is precipitated as xanthylcarbamide; dilute acids do not hydrolyse alloxan, although uroxanic acid gives carbamide. Allantoic acid is present in the juice expressed from *Acer pseudoplatanus*, which yields 0·68 g. from 1 kg. of fresh leaves, corresponding with 2·70 g. from 1 kg. of dried leaves. E. W. WIGNALL.

Spectrophotometric determination of pigments in the presence of coloured impurities. A. TREIBS (Z. physiol. Chem., 1927, **168**, 68—91).—Extinction coefficients have been determined for pyridine solutions of hæmin, hæmochromogen, coproporphyrin, and the copper salt of coproporphyrin in 0·1*N*-sodium hydroxide. Pyridine, specially purified by warming with chromium trioxide, treating with potassium hydroxide, and distilling in a vacuum over potassium hydroxide, must be used for the determinations, but the presence of 10% of water in the pyridine does not affect the extinction coefficients of hæmochromogen and coproporphyrin. Mixtures of hæmin and coproporphyrin give additive effects. Details are given of the determination of the concentration of hæmin and coproporphyrin in pyridine extracts of yeast, and of the procedure for the determination of hæmin in yeast. A. WORMALL.

Determination of tyrosine and tryptophan in proteins. O. FOLIN and V. CIOCALTEU (J. Biol. Chem., 1927, **73**, 627—650).—Addition of lithium sulphate to the original reagent of Folin and Looney (A., 1922, ii, 539) prevents the formation of turbidity during the colorimetric determination of tyrosine; a large excess of the modified reagent may therefore be used, and, in this way, true proportionality of colour development is obtained both with tyrosine and tryptophan. Moreover, the degree of colour given by these two substances is in inverse proportion to their mol. wt., so that standard solutions of tyrosine may be used for the determination of tryptophan. Tyrosine itself is, however, more conveniently determined by a modification of Millon's reaction (described).

Figures are given for the tyrosine and tryptophan content of a number of proteins determined in this way; in general, the figures are higher for tyrosine and lower for tryptophan than those obtained by the method of Folin and Looney (*loc. cit.*). A method for purifying mercuric sulphate is described.

C. R. HARINGTON.

Biochemistry.

Variations in the p_H and hydrogen carbonate of the plasma and of the alveolar carbon dioxide during forced breathing. E. H. LEPPER and M. MARTLAND (Biochem. J., 1927, **21**, 823—830).—During forced breathing the p_H of the blood rises rapidly, reaching a maximal increase of 0·20—0·24 in 10—15 min. When forced breathing is stopped the p_H falls rapidly, returning to normal within 5 min. The rise in the p_H corresponds with the alteration found in the concentration of the hydrogen carbonate of the plasma and the tension of carbon dioxide in the alveoli respectively. S. S. ZILVA.

Influence of meals on the rise of the hydrogen-ion concentration of the blood during hyperpnœa. E. H. LEPPER and M. MARTLAND (Biochem. J., 1927, **21**, 831—833).—In forced breathing experiments carried out 3 or more hrs. after meals the p_H of the blood rises more slowly and the maximum change is less than in similar experiments performed within 2 hrs. after food. Under the former conditions the alveolar carbon dioxide cannot be reduced to the same extent by the same rate and depth of respiration.

S. S. ZILVA.

Dispersed phase of the blood-corpuscles. R. EGE (Biochem. J., 1927, **21**, 967—970).—By means of various methods of determination, the volume of the dispersed phase of the blood-corpuscle is found to approach very nearly to the percentage of dry matter of the blood-corpuscles, which result is not in accordance with those obtained by Gough (A., 1924, i, 583).

S. S. ZILVA.

Structure of the cell membrane on the basis of a new method of surface tension determination. S. MUDD and E. B. H. MUDD (Biochem. Z., 1927, **186**, 378—390).—The methods of the authors (J. Exp. Med., 1924, **40**, 633; 1926, **43**, 127) have been used for mammalian red blood-cells, human polymorphonuclear leucocytes, rabbit's blood platelets, bacteria, and spermatozoa (human and *guinea-pig*). The influence of immune-serum on the surface of cells has been studied and it is found that the hæmolytic amboceptor attaches itself mainly to the alcohol-soluble material of the red blood-cell surface, whilst the agglutinin probably attaches itself in the first place to the protein; the binding of anti-bodies is similar to that of agglutinin. No difference can be observed between the interfacial behaviour of a denatured "immune" globulin and that of maximal sensitised acid-fast bacteria, both in sodium chloride solution, and this is regarded as support for the view that maximal sensitised bacteria are coated with a film of denatured globulin. A. WORMALL.

Sulphurous compounds of hæmoglobin. DALLA VOLTA (Arch. anthrop. crim. Lombroso, 1926, **46**, No. 4).—When a few drops of freshly-prepared ammonium sulphide solution saturated with hydroxylamine hydrochloride or sulphate are added to a dilute solution of oxidised blood, an olive-green colour is produced; the two typical absorption bands of oxyhæmoglobin fade, and a wide band appears in the orange. The compound produced is termed *chloro-hæmoglobin*. The formation of a green coloration on injection of a saturated solution of hydroxylamine into putrefying cadavers (the reaction indicating the first stages of gaseous putrefaction) shows that hydrogen sulphide and ammonia are present in putrefied tissues. If a saturated aqueous solution hydroxylamine is saturated with hydrogen sulphide and added to a blood solution, there is formed oxygenated sulphohæmoglobin, which rapidly changes hæmatin, but not to chlorohæmoglobin.

CHEMICAL ABSTRACTS.

Complex carbohydrates in blood. I. Effect of taka-diastase and of emulsin on reducing

power of blood. E. GABBE (Biochem. Z., 1927, 187, 57—71).—The reducing power of blood was increased 30—40% by the action of taka-diastase at p_H 5·3; the effect was not obtained with plasma but was obtained in still higher degree with suspensions of washed red blood-corpuscles. Similar, but somewhat less marked effects were obtained with emulsin.

C. R. HARINGTON.

Catalase content of blood at high altitudes. A. I. ALEXEEV (Biochem. Z., 1927, 187, 92—97).—The catalase content and the viscosity of the blood of inhabitants of high altitudes both undergo a reduction of about 12% between morning and evening.

C. R. HARINGTON.

Inorganic sulphates in human blood. R. F. LOEB and E. M. BENEDICT (J. Clin. Invest., 1927, 4, 33—6).—The normal sulphate content of human blood-serum varies between 0·40 and 1·00 milliequiv. per litre. In nephritis with nitrogen retention, the sulphate increases and may reach 10 milliequiv. per litre.

CHEMICAL ABSTRACTS.

Solubility and distribution of chloroform in blood. H. WINTERSTEIN and E. HIRSCHBERG (Biochem. Z., 1927, 186, 172—177).—The maximal solubility of chloroform at the ordinary temperature in distilled water is 0·55%, in physiological saline, 0·50%, in serum, 0·56—0·77%, and in whole blood, 0·75—0·86%. Near saturation, the corpuscles contain twice as much chloroform as the plasma, whereas at low concentrations the corpuscles may contain four to six times as much as the plasma.

P. W. CLUTTERBUCK.

Hydrolysis of blood pigments by alkali. H. WAELSCH (Z. physiol. Chem., 1927, 168, 188—195).—By careful hydrolysis of washed ox corpuscles with 1·5% sodium hydroxide at 85°, followed by acidification and electrodialysis, a pigment has been separated which contains the whole of the iron and probably the whole of the prosthetic portion of the original hæmoglobin, still in combination with small amounts of amino-acids derived from the globin portion of the conjugated protein. Proline and alanine have been identified as forming the greater part of these amino-acids. By boiling oxyhæmoglobin solution with 2% sodium hydroxide for 96 hrs., 26% of the globin-nitrogen is obtained as free ammonia.

H. D. KAY.

Absorption in the ultra-violet by porphyrins. H. HAUSMANN and O. KRUMPEL (Biochem. Z., 1927, 186, 203—212).—The ultra-violet absorption spectra of acid and alkaline hæmatoporphyrin, of the tetramethyl esters of hæmatoporphyrin and coproporphyrin of the octamethyl ester of uroporphyrin in chloroform are described.

P. W. CLUTTERBUCK.

Interaction of a finely-divided lead suspension in blood-serum, Ringer solution, and aqueous phosphate solution. J. BROOKS (Biochem. J., 1927, 21, 766—776).—The final values obtained for the ratio g.-atoms of phosphorus bound to g.-atoms lead present correspond with the formation of the tertiary phosphate in the aqueous phosphate solution. In Ringer solution and serum the ratio corresponds with the secondary phosphate. Using lead acetate instead suspension the secondary phosphate is formed in serum and the tertiary salt in the other two cases. From the rate of disappearance of the phosphate ions it is concluded that the lead particles are rapidly oxidised to the hydroxide, which in its turn quickly combines with the phosphate. About 90% of the combined phosphate is thus removed from the solution. The remaining 10% combines at a much slower rate with the lead carbonate in suspension. The results obtained with a suspension of lead carbonate alone show that the velocity of this latter reaction is not governed by the rate of diffusion of the phosphate ions to the reaction surface of the particles but by the slow chemical reaction at the surface. No detectable amount of ionic lead was found in the small volume of ultrafiltrates from the mixture of serum or Ringer solution and the lead suspension. The rate of settling of lead suspension at the ordinary temperature and at 37·5° is in the following order: Ringer's solution > water, serum > phosphate solution. The particles of the lead suspension are negatively charged.

S. S. ZILVA.

Physico-chemical investigation of irradiated proteins. I. Changes of serum-albumin during ultra-violet irradiation and their relationship to heat-coagulation. M. SPIEGEL-ADOLF (Biochem. Z., 1927, 186, 181—193).—Serum-albumin, free from electrolytes, coagulates under the action of ultra-violet light in the same way as by heating but the coagulum cannot be converted into a water-soluble product by treatment with sodium hydroxide and dialysing as with the heat-coagulum. Serum-albumin can be salted out after irradiation in presence of hydrochloric acid, but not after heating in presence of acid. On the other hand, serum-albumin heated or irradiated in presence of sodium hydroxide shows the same behaviour to neutral salts. The presence of larger concentrations of neutral salts does not prevent the coagulation of serum-albumin during irradiation but the presence of multivalent ions does inhibit precipitation. Potassium thiocyanate, in opposition to its effect on heat-coagulation, is able neither to inhibit the coagulation by ultra-violet light nor to bring the coagulum into solution.

P. W. CLUTTERBUCK.

Destruction of organic substances for micro-determination of phosphorus in blood. M. MACHEBŒUF and G. ZWILLING (Bull. Soc. Chim. biol., 1927, 9, 697—699).—A mixture of 2 c.c. of serum and 1 c.c. of sulphuric acid is heated for 10 min. To the cooled solution 2 c.c. of nitric acid are added and heating is continued for 15 min. until the nitrous fumes disappear. After cooling, 0·2 g. of powdered potassium permanganate is added, and the mixture heated gently after the initial reaction has subsided. If the product is not colourless a further 0·2 g. of permanganate may be added and the mixture heated to complete the destruction of the organic material. For each 0·2 g. of potassium permanganate used 0·11 c.c. of sulphuric acid must now be added before determination of the phosphorus as ammonium phosphomolybdate (cf. A., 1926, 1067).

W. O. KERMACK.

Micro-determination of phosphoric acid combined as ester in blood and serum. M. MACHEBŒUF (Bull. Soc. Chim. biol., 1927, 9, 700—702).—The proteins are precipitated by trichloroacetic acid

and the total phosphoric acid in the filtrate is determined by the application of the nitrosulphuric acid ammonium molybdate method of the author (cf. A., 1926, 1067). The inorganic phosphate in the filtrate is determined by the addition of sulphuric acid, ammonium nitrate, and, after brief heating on the water-bath, of ammonium molybdate. The phosphomolybdate which separates is determined as previously described (cf. this vol., 370). The difference between the two determinations gives the amount of the phosphoric esters present. W. O. KERMACK.

Colorimetric determination of sodium in 0·1 c.c. of serum or blood. S. YOSHIMATSU (Tohoku J. Exp. Med., 1927, **8**, 496—500).—Sodium is precipitated as pyroantimonate, which is dissolved in hydrochloric acid; the antimony is converted into the sulphide with sodium sulphide, and determined colorimetrically. The deviation from Kramers' method is ±3%. CHEMICAL ABSTRACTS.

Body-fluid of the silkworm. S. BITO (Bull. Agric. Chem. Soc. [Japan], 1926, **2**, 167).—The composition varies with the stages of metamorphosis; sugar, cholesterol, and lecithin are present. The blood of the female is higher in organic and lower in inorganic substances than that of the male. The magnesium and phosphorus contents are high, and those of potassium, sodium, calcium, silicon, and sulphate are low. The manganese content is higher than in mammals. CHEMICAL ABSTRACTS.

Behaviour of vitally important amino-acids during the incubation of the hen's egg. II. Cystine and cysteine. Changes in creatine and creatinine during the incubation of the hen's egg. Y. SENDJU (J. Biochem. [Japan], 1927, **7**, 175—180, 181—189).—The cystine content of the hen's egg diminishes during incubation, and is practically absent from the yolk after the 19th day, when the entire cystine content is in the embryo. The creatinine of the albumin and yolk disappears after the 14th day, whilst that of the embryo increases steadily. The creatine content of the embryo also increases. CHEMICAL ABSTRACTS.

Plasmalogen. II. Occurrence of plasmalogen in animals. K. IMHAUSER (Biochem. Z., 1927, **186**, 360—375).—The aldehyde, plasmal, is widely distributed as the precursor (plasmalogen) and is found in the cells of all animal organisms. The plasmalogen contents of various tissues and organs of several animals, including man, have been compared and similar results have been obtained with different animals. The white matter of the cerebellum, and the suprarenal cortex are specially rich in this substance, and, in general, a high plasmalogen content is found for organs rich in lipins. Using the colour reaction of Feulgen and Imhauser (this vol., 369), the plasmalogen content of the sera of different animals has been determined and the effect on these values of certain factors studied. Significant differences are observed, the highest values being obtained with the ox and cow, the lowest with the sheep, goat, pig, and rabbit, whilst human serum gives medium or moderately high values. No great differences are observed between the sexes, although the female animal usually gives a slightly higher value than the male. The diet has a marked influence on the serum plasmalogen, and with the dog a meat-free diet causes the value to fall to a low minimum; a vegetable diet has no influence. Age is another important factor, since calves give distinctly lower values than do the ox and cow. A. WORMALL.

Magnesium content of normal rats at different ages. G. MEDES and G. J. HUMPHREY (J. Biol. Chem., 1927, **74**, 149—151).—The absolute amount of magnesium in growing rats increased up to 90 days of age, whilst the relative amount decreased after 60 days; differences between the sexes were insignificant in comparison with the age variations. C. R. HARINGTON.

Arginine content of some proteins and of normal organs and organs showing amyloid degeneration. O. FURTH and O. DEUTSCHBERGER (Biochem. Z., 1927, **186**, 139—154).—The method of Kossel and Gross (A., 1924, ii, 211) for the determination of arginine in pure proteins is modified and made applicable to its determination in organs. The arginine contents of the following are: gelatin, 9%; hæmoglobin, 4·4%; fibrin and Witte's peptone, 7%; serum-albumin and globulin, 6·1%, caseinogen, 5·2%; egg-albumin, 6%; egg-globulin, 4·1%; legumin, 11·4%; keratin, 4·7%; fibroin, 1·5%; sericin, 4·3%; pancreatic nucleoprotein, 10%; human kidney, liver, and spleen, between 6·5 and 8·1%. Organs showing amyloid degeneration have the same arginine content as normal organs (cf. A., 1925, i, 1505; *1926, 967*). P. W. CLUTTERBUCK.

Lithium and strontium in human teeth and bones. A. DESGREZ and J. MEUNIER (Compt. rend., 1927, **185**, 160—163).—When the calcium in the ash of human bones or teeth is separated into phosphate and carbonate portions, lithium is found (spectrographically) in the phosphate and strontium in the carbonate fraction. These elements thus probably pass from the blood into the tissues without changing their chemical state (cf. A., 1923, i, 403). B. W. ANDERSON.

Crystalline lens. II. Modifications of the ultramicroscopic structure of the crystalline lens by salts, alkalis, and acids. D. CATTANEO (A i R. Accad. Lincei, 1927, [vi], **5**, 711—716).—Ultramicroscopic observations have been made of modifications produced in the crystalline lens by e action of hypertonic, isotonic, and hypotonic so u- tions of sodium hydroxide, hydrochloric acid, a sodium chloride. LUNT.

Alcohol content of normal placental tissue. W. D. MCNALLY, H. C. EMBREE, and C. A. RUST (J. Biol. Chem., 1927, **74**, 219—222).—The tissue was minced, acidified with tartaric acid, and subje to steam-distillation; the distillate was fractiona and the fraction containing volatile substances distilled in presence of silver nitrate and so m hydroxide; the alcohol in the final distillate was e mined by a modification of the method of (A., 1913, ii, 800). Normal placenta contains 0·0008—0·0052% of alcohol. C. R. HARINGTON.

Enzymes of the skin. VIII. Formation of lactic acid in the skin and thereon of various rays. J. W T. IKEBATA (IO

Z., 1927, **186**, 43—53).—Fresh skin of normal and diabetic human subjects and of normal guinea-pigs and, to a less extent, skin of the cadaver can form lactic acid from carbohydrate, most readily from lævulose. Insulin does not influence this power to form lactic acid in the case of fresh human skin, but increases it in the case of the skin of diabetics and of the cadaver. This power is reduced somewhat by irradiation with normal sunlight, the injury being greater with strong artificial sunlight and greatest with *X*-rays (cf. A., 1926, 94, 865, 1060).

P. W. Clutterbuck.

Preparation of vital neutral-red. M. Phillips and B. Cohen (Stain Tech., 1927, 2, 74—79).—Neutral-red iodide, suitable for vital staining, was prepared by condensing nitrosodimethylaniline hydrochloride with *m*-tolylenediamine. The indamine, tolylene-blue, so obtained was oxidised to neutral-red (eurhodine) by passing a current of air through a boiling aqueous 2·5% solution for 2 hrs. The neutral-red was purified by conversion into its double salt with stannous chloride, from a solution of which the iodide of the dye was precipitated by means of potassium iodide. After repetition of this precipitation it was finally recrystallised from 95% ethyl alcohol.

H. W. Dudley.

Surface activity of trypan-blue at various limiting surfaces. N. Okunev (Biochem. Z., 1927, **187**, 37—50).—Trypan-blue shows no capillary activity at a water–air surface, but shows such activity in increasing degrees at water–olive oil, water–benzene, and water–light petroleum surfaces; the bearing of these observations on the phenomenon of vital staining is discussed. C. R. Harington.

Vital staining and adsorption. H. A. Krebs and D. Nachmansohn (Biochem. Z., 1927, **186**, 478—484).—With acid dyes, mainly azo and triphenylmethane compounds, a parallelism, similar to that existing for basic dyes, has been found between adsorption on kaolin and staining of *paramœcia*. The vital staining power is not a function of the "lipoid solubility," and the main factor concerned is adsorption. A. Wormall.

Stain solubilities. II. W. C. Holmes (Stain Tech., 1927, 2, 68—70; see also this vol., 593).—The solubilities of 23 biological stains in water and in alcohol are tabulated. To obtain trustworthy figures for solubility it is essential that the dyes examined should be free from inorganic salts. H. W. Dudley.

Detection [and determination] of very small quantities of iodine [in urine and organs]. H. Eschenbrenner (Pharm. Ztg., 1927, 72, 984—986).—Solids (about 2 g.) are fused in a nickel crucible at the lowest possible temperature with sodium hydroxide and a sufficient quantity of sodium nitrate to oxidise completely the organic matter, the product is extracted with water and the solution just neutralised with sulphuric acid and treated with 1 c.c. of *N*-sulphuric acid. Liquids, such as urine, are acidified with nitric acid. In both cases the solution is treated with an excess of silver nitrate and set aside in a dark place for 24 hrs. The precipitate of silver chloride iodide is collected, washed, and suspended in water containing 1 c.c. of *N*-hydrochloric acid. The mixture is boiled with two portions of 15 c.c. each of freshly-prepared chlorine water, which converts the silver iodide into silver chloride and iodic acid. When all the chlorine is expelled the precipitate is separated, the filtrate cooled, treated with 20 c.c. of phosphoric acid, 20 drops of 10% potassium iodide solution, and 2 c.c. of a 1% starch solution, and the liberated iodine is titrated with 0·1 *N*-thiosulphate solution.

A. R. Powell.

Lactic acid content of cerebrospinal fluid. A. Wittgenstein and A. Gaedertz (Biochem. Z., 1927, **187**, 137—145).—The normal lactic acid content of the cerebrospinal fluid of man and the dog is 13—16 mg.% as compared with 15—18 mg.% for the blood-serum. The lactic acid of the serum is completely diffusible. After muscular work the lactic acid content of the cerebrospinal fluid does not rise so much as that of plasma, but takes longer to return to the normal level. Intrathecal injection of calcium lactate caused no physiological disturbances; injection of lactic acid, however, caused death of the animal with the symptoms of acidosis. C. R. Harington.

Influence of the age of the cow on the yield and quality of the milk. M. K. White and T. J. Drakeley (J. Agric. Sci., 1927, **17**, 420—427).—The yield of milk of all breeds of cows at first increases rapidly with age, reaches a maximum, and then gradually diminishes; the percentage of fat in the milk increases slightly and then decreases, and the percentage of solids-not-fat decreases continuously with age. C. T. Gimingham.

Effect of temperature on some of the properties of caseinogen. V. Pertzoff (J. Gen. Physiol., 1927, **10**, 961—984).—The solubility of caseinogen in a solution of base is approximately constant between 21° and 37°, the corresponding combining weight being 2100. The solubility varies between 37° and 60°, but is again approximately constant between 60° and 85° at a value corresponding with a combining weight of 3700. The maximum amount of caseinogen which dissolves in 1000 c.c. of water at 5° contains 7 mg. of nitrogen. W. O. Kermack.

Effect of rennin on caseinogen. I. Solubility of casein in sodium hydroxide. V. Pertzoff (J. Gen. Physiol., 1927, **10**, 987—1004).—Casein prepared by the action of rennin (or pepsin) on milk was purified by repeated dissolution in sodium hydroxide solution and reprecipitation by acid at the point of minimum solubility. The resulting product is free from active enzymes. The casein which dissolves in 1000 g. of pure water at 5° contains 7 mg. of nitrogen (cf. preceding abstract). The solubility of casein in base at 5° corresponds with a combining wt. of 810, whereas at the same temperature the solubility of caseinogen corresponds with a combining wt. of 1300. At 23° the corresponding combining wts. are respectively 1450 and 2100. These results support the view that a chemical change occurs when caseinogen is acted on by rennin. W. O. Kermack.

Formation of acid in milk by heating. E. O. Whittier and A. G. Benton (J. Dairy Sci., 1927, 10 126—138).—The rate of formation of acid in milk on heating is a direct function of the time and temper-

ature of heating and of lactose concentration, and is unchanged by coagulation of caseinogen. Lactose is the principal source of the acid. Addition of sucrose has no effect. CHEMICAL ABSTRACTS.

Micro-determination of carbamide in urine without the use of urease. W. LAUBENDER (Biochem. Z., 1927, **186**, 158—171).—A magnesium chloride method for the determination of carbamide in urine is described. The results for human, rabbit, and dog urine agree satisfactorily with those obtained by the urease method. The method determines 1·4—10·8 mg. of carbamide with an error of 1·5% and is adapted for urines containing sugar and urease poisons. P. W. CLUTTERBUCK.

Determination of oxalic acid in urine. G. M. ZU HORSTE (Z. physiol. Chem., 1927, **168**, 196—200).—Oxalic acid is precipitated from the urine by addition of calcium chloride and suitable adjustment of the reaction. The impure calcium oxalate is centrifuged off, dilute sulphuric acid is added, and the free oxalic acid distilled off direct from the centrifuge tube under reduced pressure. The sublimate is dissolved in hot water and titrated in the usual way with potassium permanganate solution. Known quantities of oxalic acid (of the order of 2—7 mg.) may thus be recovered almost quantitatively from urine.

H. D. KAY.

Oxyhæmoglobin dissociation curves of whole blood in anæmia. D. W. RICHARDS, jun., and M. L. STRAUSS (J. Clin. Invest., 1927, **4**, 105—126).—The curves were normal at p_H 7·24 and 7·44, and subnormal at p_H 7·64. CHEMICAL ABSTRACTS.

Effect of partial pancreatectomy on the sugar excretion threshold. G. EDA (J. Biochem. [Japan], 1927, **7**, 79—99).—On removal of one half to one third of the pancreas, the threshold of sugar elimination is increased simultaneously with diminution of sugar assimilation, although not necessarily immediately.

CHEMICAL ABSTRACTS.

Relation between the metabolism of dextrose and fats in diabetes. N. R. DHAR (J. Physical Chem., 1927, **31**, 1259—1262).—A theoretical paper in which the oxidation of fats, carbohydrates, and protein is discussed. L. S. THEOBALD.

Ketone excretion, D : N ratios, and glycogen contents of liver and muscles of fasting, depancreatised dogs. I. CHAIKOFF (J. Biol. Chem., 1927, **74**, 203—218).—Dogs were depancreatised and allowed to recover from the operation under the influence of insulin; the physiological response to the withdrawal of insulin and of food was then observed. The D : N ratios reached after 3 days without insulin were in some cases higher than those observed in phloridzinised dogs; the magnitude of the ratio was, however, dependent on the state of nutrition of the animal, rising with increase in weight of the dog. Following withdrawal of insulin, the glycogen content of the liver was 0·3% on the third and 0·06% on the fifth day, whilst that of the muscles was 0·45% and 0·35% respectively. Excretion of ketones ran approximately parallel to that of dextrose, and, in relation to the body-weight, was similar to the ketone excretion observed in human diabetics.

C. R. HARINGTON.

Influence of "synthalin" on the respiratory quotients of diabetics. A. LUBLIN (Arch. exp. Path. Pharm., 1927, **124**, 118—128).—Diabetics to whom "synthalin" has been given by mouth show an increase in the respiratory quotient following the administration of dextrose. W. O. KERMACK.

Protein-sugar in different pathological conditions. X. CHAHOVITCH, V. ARNOVLJEVITCH, and (MLLE.) M. VICHNJITCH (Compt. rend., 1927, **184**, 1495—1496).—An increase of both the free and protein-sugar in the blood occurs in cases of pulmonary tuberculosis, cancer of stomach, peritonitis, pleurisy, pneumonia, broncho-pneumonia, chronic nephritis, cirrhosis of the liver, malaria, typhoid fever, and dyspepsia, evidence of malnutrition occurring in all cases. Protein hyperglycæmia is thus only a general expression of disturbed metabolism.

R. BRIGHTMAN.

Iodine content of the thyroid in relation to its histological structure and activity. C. ABELIN (Arch. exp. Path. Pharm., 1927, **124**, 1—40).—The iodine contents of a large number of thyroids, normal and pathological, have been determined and the results are compared with the histological findings and with the effect of the thyroid on the rate of metamorphosis of the tadpole. W. O. KERMACK.

Deposition of lipins in the walls of the aorta in infants. N. N. KOUBLE (Arkh. Biol. Nauk, 1926, 26, 163—180). CHEMICAL ABSTRACTS.

Distribution of alkalis in the serum of infants. Z. VON BÓKAY (Magyar Orvosi Arch., 1927, **28**, 1—5).—In premature birth, rickets, and tetany combined with rickets the hydrogen carbonate in the serum is subnormal. At the carbon dioxide tension of the blood, 60% of the serum alkali is combined as sodium hydrogen carbonate and 40% as sodium albuminate; at that of the air the percentages are 44 and 56, respectively. CHEMICAL ABSTRACTS.

Calcium and phosphorus metabolism. IV. Influence of free fatty acids in the intestine on the absorption and excretion of the mineral elements. V. Infantile rickets. Excretion and absorption of the mineral elements, and influence of fat in the diet on mineral metabolism. S. TELFER (Quart. J. Med., 1926, **20**, 1—25).—Conditions permitting a consistent excess of free fatty acids in the intestine facilitate the absorption of phosphorus. In infantile rickets, the percentage of mineral acids, magnesia, lime, and phosphoric acid in the fæcal solids is increased; excess of mineral matter is excreted in the fæces chiefly as calcium phosphate. The amount of combined fatty acids is low, urinary phosphorus is less than the fæcal phosphorus. Metabolic changes accompanying healing are described; alterations in the mode of excretion in healing progresses are due to increased absorption of minerals from the intestine.

CHEMICAL ABSTRACTS.

Rickets. Calcium absorption in relation to gastric acidity. L. WILLS, P. SANDERSON, and PATERSON (Arch. Dis. Childhood, 1926, **1**, 245—[illegible]).—Calcium retention is reduced by milk containing hydrogen chloride or ammonium chloride. Lactic

acid milk causes a slight loss of calcium and rise in gastric acidity. There is no causal relation between calcium metabolism and gastric acidity.

CHEMICAL ABSTRACTS.

Distribution of oxygen in individual organs as shown by experiments with angiostomised dogs. E. S. LONDON and L. M. RABINKOVA (Biochem. Z., 1927, **186**, 155—157).—The blood of the portal, splenic, renal, and pancreatico-duodenal veins is, during digestion, poorer in nitrogen than during the fasting condition. The blood of the right and left renal veins contains different amounts of oxygen.

P. W. CLUTTERBUCK.

Mechanism of cellulose digestion in the ruminant organism. H. E. WOODMAN (J. Agric. Sci., 1927, **17**, 333—338).—To explain cellulose digestion in ruminants, it is suggested that, by the action of bacteria, dextrose, or a sugar capable of hydrolysis to dextrose, is formed from cellulose by hydrolysis. Assuming that further bacterial breakdown will be no greater than in the case of the digestible nitrogen-free extractives of the food, this explanation is in keeping with Kellner's findings as to the productive value of digested fibre. The occurrence of cellobiose and dextrose in the fermentation of cellulose by bacteria, as shown by Pringsheim (A., 1912, ii, 587), is quoted in support of this view.

C. T. GIMINGHAM.

Specific dynamic action of foodstuffs. VI. Specific dynamic action and carbohydrate exchange. I. ABELIN and B. KOBORI (Biochem. Z., 1927, **186**, 3—27).—Repeated injections of phloridzin increase considerably the specific dynamic action of meat, the increased requirement of sugar possibly inducing an increased synthesis from protein by a series of exothermic reactions (cf. A., 1925, i, 332; this vol., 276). P. W. CLUTTERBUCK.

Relation of the intestinal wall and of the liver to the formation of glycogen. A. Y. KHARIT (Arkh. Biol. Nauk, 1926, **26**, 255—258).—Glycogen is not synthesised from lower carbohydrates by the intestinal wall of dogs. The glycogen content of blood of the portal vein was equal to or less than that of the hepatic vein, or of peripheral blood.

CHEMICAL ABSTRACTS.

Dextrose metabolism of kidney tissue *in vitro*. I. J. T. IRVING (Biochem. J., 1927, **21**, o80 886).—Kidney tissue *in vitro* utilises dextrose aerobically at a rate which is probably linear. In a vacuum or in the presence of potassium cyanide the utilisation of dextrose is markedly inhibited, or stopped completely. The integrity of the kidney cell is essential for the utilisation of dextrose. It is probable that an active surface is involved. S. S. ZILVA.

Metabolism of lactose. I. Fate of intravenously administered galactose in the rabbit. Effect of dextrose and galactose on fate of galactose in the rabbit. R. C. CORLEY (J. Biol. m., 1927, **74**, 1—18, 19—31).—I. After intraven- us injection of 0·5—2·0 g. of galactose into rabbits e taken for the substance to disappear from e blood was proportional to the dose; larger doses appeared approximately the same time as the 2 g. ose. The rate of disappearance was increased by simultaneous administration of insulin, but was not affected by variations in renal excretion induced by administration of tartrates, uranium salts, or phloridzin, or by hepatic insufficiency resulting from poisoning with chloroform or phosphorus.

II. Although the rate of disappearance of galactose from the blood was increased by simultaneous administration of dextrose, the effect was probably due to increased urinary excretion rather than to increased metabolism of the galactose; the metabolism of the latter was not affected by previous treatment of the animals with dextrose or with galactose itself.

C. R. HARINGTON.

Formation of lactic acid after severe hæmorrhage. Rate of disappearance of sodium lactate injected intravenously and its effect on sugar and inorganic phosphate of the blood. C. RIEGEL (J. Biol. Chem., 1927, **74**, 123—134, 135—148).—Hæmorrhage, in dogs, resulted in an increase in the lactic acid content of the blood; the extent of the increase varied directly with the severity of the hæmorrhage; in the most severe experiments the concentration continued to increase after actual bleeding had ceased. The increased lactic acid content of the blood resulting from injection of sodium lactate decreased at first rapidly, by diffusion, and then more slowly as it was utilised by the tissues. There was simultaneously a fall in the inorganic phosphate and a rise in the sugar content of the blood, from which it is concluded that the utilisation of the lactic acid consisted in its synthesis into lactacidogen and glycogen. C. R. HARINGTON.

Production of lactic acid in frog's muscle *in vivo*. C. E. WOODROW and V. B. WIGGLESWORTH (Biochem. J., 1927, **21**, 812—814).—When placed in a bath at 38° the frog is at first violently active but becomes stiff and motionless in about 1 min. In this state the muscles of the hind legs show an average content of lactic acid of 0·125%. The muscles of a pithed frog under similar conditions contain little more lactic acid (0·043%) than the normal resting minimum (0·03%). On removal to the ordinary temperature the high lactic acid content of muscle does not regain the normal level until ½ to 1 hr. later.

S. S. ZILVA.

Digestion in the cockroach. I. Hydrogen-ion concentration in the alimentary canal. II. The digestion of carbohydrates. V. B. WIGGLESWORTH (Biochem. J., 1927, **21**, 791—796, 797—811).—I. In wild cockroaches (*Blatella germanica*) the average p_H of the saliva is 6·9, of the crop contents 5·2, and of the stomach 6·2. The acid in the crop is produced by bacterial and yeast fermentation from the carbohydrate ingested by the insect, the acid production being more intense with sucrose and dextrose than with starch, maltose, and lactose. After protein food the average p_H in the crop is 6·3; after carbohydrate food it is 4·8. A colorimetric method for the determination of p_H in about 0·002 c.c. is described. It is based on the use of waxed plates and pipettes in the manipulation of the fluid.

II. The salivary glands of the cockroach secrete an amylase and in *B. germanica* (although not in *Periplaneta americana*) an invertase. Extracts of the crop

when thoroughly freed from food contents do not contain enzymes acting on carbohydrates. The stomach and hepatic cæca secrete invertase, maltase, and small quantities of lactase. The ratio of amyloclastic to saccharogenic activity is similar to that of human ptyalin. The p_H-activity curves for these two enzymes have been compared. Under the same conditions cockroach amylase is more resistant to acid (optimum p_H 5·9). This is due in part at least to some associated factor which is not destroyed by heating at 100° for 5 min. Cockroach invertase is partly inhibited by 1% sodium chloride, 20% glycerol, or 0·0001*N*-silver nitrate, and completely inhibited by 0·001*N*-silver nitrate. The p_H-activity curve for cockroach invertase shows an optimal range from 5·0 to 6·2, which is intermediate between the ranges for yeast invertase and human jejunal invertase. Cockroach maltase is partly inhibited by 1% sodium chloride and completely inhibited by 10% glycerol. It is adsorbed by powdered sand, but can be extracted from this with phosphate buffer p_H 6·8. The p_H-activity curves show an optimal range from 5·0 to 6·2 which is more acid than the range in the maltase of either yeast or human jejunum. Cockroach lactase is completely inhibited by 10% glycerol and shows an optimal zone of p_H from 5·0 to 6·4. S. S. Zilva.

Effect of alkalosis on the excretion of chloride and on carbohydrate metabolism. M. W. Goldblatt (Biochem. J., 1927, **21**, 991—1004).—The maximum concentration of hydrogen carbonate present in the urine of a normal human subject after the ingestion of 30 g. of sodium hydrogen carbonate is 3·2%. The rise in the excretion of the carbonate is accompanied by a marked fall in chloride excretion. This fall is not recorded in the blood, the plasma, or the stomach. Alkalosis is accompanied by a definite diminution in carbohydrate tolerance and sometimes by a ketosis. This ketosis is not a "washing-out" effect, *i.e.*, elimination of the ketonic acids in association with the excreted alkali, but is due to defective carbohydrate utilisation. The ketosis of starvation is much increased in alkalosis and the maximum excretion of ketonic acids does not necessarily coincide with the maximum output of alkali in the urine. The ketolytic action of dextrose in starvation is markedly diminished by ingestion of alkali and so is also the action of insulin. From experiments in rats it is found that the deposition of glycogen in the liver and muscle is diminished by alkalosis.

S. S. Zilva.

Fat and lipin metabolism. IV. Role of the reticulo-endothelial system. V. Role of the spleen. S. Leites (Biochem. Z., 1927, **186**, 391—412, 436—450).—IV. Experiments have been carried out to determine the effect of "blocking" the reticulo-endothelial systems by intravenous injection of colloidal silver, colloidal iron, or Indian ink on the fat, cholesterol, and lipin of the blood. Simple blocking with the colloidal solution causes a conversion of the first type of lipæmia into the second type (cf. this vol., 695) and splenectomy has a similar effect. The lipæmia and cholesterolæmia, resulting from the administration *per os* of large amounts of olive oil, lecithin, oleic acid, or olive oil+cholesterol, are less intense after the "blockade" than before. It is concluded that the reticulo-endothelial systems of the spleen, liver, and bone-marrow are concerned in the removal of neutral fat and cholesterol from the blood and in the metabolic changes of these substances.

V. The administration *per os* of large amounts of olive oil or olive oil+cholesterol usually, but not always, causes a greater cholesterolæmia in splenectomised dogs than in the normal animal. Similarly the intravenous injection of an emulsion of olive oil leads to a rise in the blood neutral fat after splenectomy, whereas no increase occurs before the operation. The characteristic results obtained after splenectomy are due to the absence of the spleen, which is concerned with the elimination of neutral fat, and to a disturbance in the elimination or splitting of neutral fat in the liver. A. Wormall.

Nutritive value of fats and lipins. K. Takahashi (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1927, **5**, 103—132).—From feeding experiments with rats using a basal diet of flesh, starch, lactose, mineral salts, and oryzanin, it is concluded that 1% of cholesterol, lecithin, kephalin, or protagon does not supply the necessary growth factor. Normal growth is not procured when 5, 10, or 20% of the following synthetic fats are added to a fat-free basal diet deficient in vitamin-*A*: triacetin, tributyrin, trivalerin, tricaproin, tricaprylin, tricaprin, trilaurin, trimyristin, tripalmitin, tristearin, triarachin, tricerotin, triolein, trilinolein. The nutritive value of these synthetic fats increases from cerotin to caprin, and then decreases from caprin to acetin, with the exception of tributyrin and trivalerin, which are definitely toxic. Using a fat-free basal diet not deficient in vitamin-*A* or -*B* and 10% of a single synthetic fat (stearin, palmitin, laurin, and olein) fairly good growth is secured; the replacement of the fat by an equal amount of the corresponding acid fails to produce satisfactory growth. Good growth of rats was secured on a fat-free diet of flesh, starch, salts, and vitamins-*A* and -*B* and also on a carbohydrate-free diet of protein, butter-fat, salts, and vitamins-*A* and -*B*. E. A. Lunt.

Is the metabolism of sterols related to that of fats? E. F. Terroine, R. Bonnet, G. Kopp, and J. Vechot (Bull. Soc. Chim. biol., 1927, **9**, 678—691). When the total fat of animals has been increase by rich nutrition, there is no increase in cholestero , and in bacteria rich in fat, whether naturally or as a result of culture on media containing much dextrose, there is no parallelism between their conten of fatty acids and of sterols. Such facts sugges independence of the metabolism of fats and of stero . On the other hand the germination of certain see is accompanied by a decrease in fatty acids an increase in phytosterol, whilst *Aspergillus nige* richer in sterols when cultivated on fatty ma e than when grown on dextrose or peptone.

W. O. Kermack.

Effect of irradiation on fat metabolism. Kultjugin (Biochem. Z., 1927, **186**, 36—4.). effect of irradiation on the weight, the total n inorganic phosphorus, calcium, potassium, magnesium contents of the urine and on the o cholesterol, inorganic phosphorus, organic phosp

calcium, potassium, and magnesium of the blood of rabbits is tabulated. In blood, the total fat is greatly increased, and the cholesterol and inorganic phosphorus to a less degree. P. W. CLUTTERBUCK.

Relationship between amino-acids and bile acids in fat digestion in the intestine. R. KARASAWA (J. Biochem. [Japan], 1927, 7, 117—127). CHEMICAL ABSTRACTS.

Effect of bile acids on the protein and purine metabolism and the significance of choleic acid. R. KARASAWA (J. Biochem. [Japan], 1927, 7, 145—519).—Injection of bile acids into rabbits inhibits the protein metabolism and stimulates the purine metabolism. The effect of cholic and deoxycholic acids is much greater in this respect than that of stearincholeic acid. The degenerative changes in cells during stasis icterus are ascribed to the toxic action of the bile acids which strongly stimulate the purine metabolism. Choleic acid influences the protein and purine metabolism to a much smaller degree than deoxycholic acid in post mortem autolysis. The formation of choleic acid from the deoxycholic acid present in the liver is regarded as a process of detoxication of the latter. CHEMICAL ABSTRACTS.

Fate of heterocyclic compounds in the animal body. N. J. NOVELLO (J. Biol. Chem., 1927, **74**, 33—36).—After administration to rabbits, pyridine was excreted entirely unchanged; glyoxaline was for the most part unchanged but gave rise to a small increase in uric acid excretion; pyrrole was eliminated unchanged to the extent of 40—50%, the remainder being accounted for by an increase in the carbamide excretion. C. R. HARINGTON.

Effect of composition of diet on the urinary C : N ratio with special reference to amino-acids. A. BICKEL and I. REMESOV (Biochem. Z., 1927, **186**, 54—63).—When a portion of the normal protein of a dog's diet is replaced by an amount of amino-acids equivalent in nitrogen content, the absorption in the intestine of nitrogen and carbon is more complete and the urinary C : N ratio increases. The amount of protein metabolised is not increased and the excess of nitrogen is retained. P. W. CLUTTERBUCK.

Influence of administration of active iron oxide on metabolism with special reference to nitrogen equilibrium and the behaviour of the urinary quotient. I. REMESOV (Biochem. Z., 1927, **186**, 64—86).—Administration of "active" iron oxide to dogs usually produces a retention of nitrogen due to decreased oxidation of protein together with a better utilisation of the food in the intestine. e oxide also appears to modify the oxidation of ats and carbohydrates (cf., A., 1926, 1057). P. W. CLUTTERBUCK.

Influence of variations in the sodium : potassium ratio on the nitrogen and mineral metabolism of the growing pig. II. M. B. RICHARDS, W. and A. D. HUSBAND (Biochem. J., 1927, **21**, 971—98 addition of potassium citrate to a ration cereal grain fed to growing pigs decreases assimilation and retention of nitrogen, phosphorus, and calcium. There is an immediate increase in the ry excretion of chlorine followed at once by a decrease, after which the continued intake of potassium has little or no effect on the excretion. The converse takes place on withdrawing the salt. Observations on the sodium excretion do not support the theory of sodium impoverishment consequent on increased potassium intake put forward by Bunge as the result of experiments on himself. S. S. ZILVA.

Minimum mineral requirements in cattle. A. THEILER, H. H. GREEN, and P. J. DU TOIT (J. Agric. Sci., 1927, **17**, 291—314).—Experiments with regard to the minimum requirements of growing cattle for calcium, phosphorus, sodium, potassium, and chlorine are recorded. Special attention was given to phosphorus deficiency, and "aphosphorosis," or clinically recognisable phosphorus deficiency disease, was experimentally produced, and shown to be identical with the naturally occurring South African disease, "Styfsiekte." Minimum requirements for growth are higher for phosphorus than for calcium, and a ratio as high as $3P_2O_5 : 1CaO$ is not necessarily disadvantageous. Requirements for sodium and chlorine are low. No evidence was obtained that excess of basic over acidic constituents was necessary. The composition of the milk of animals suffering from aphosphorosis need not necessarily be abnormal, but the inorganic phosphorus of the blood may drop to a quarter of the normal, the calcium of the blood remaining unaffected. C. T. GIMINGHAM.

Influence of concentration on the loss in weight of young fasting eels in sodium chloride solution. U. D'ANCONA (Atti R. Accad. Lincei, 1927, [vi], **5**, 693—696).—Data are cited for the weight of young eels under normal conditions of growth and for the following characteristics of young fasting eels in pure water, and in 0·5, 1·0, 3·0, and 5·0% sodium chloride solutions: mean length, mean weight, mean dry weight, and mean ash. The percentage loss in mean weight diminishes from 15·61 in pure water to 11·21 in 1% sodium chloride solution, and then rises to 28·81 in 5% sodium chloride solution; the ratio of dry to total weight shows a minimum at 0·5% sodium chloride solution, a maximum at 1%; the ratio of ash to total weight shows a minimum at 6% sodium chloride solution. R. W. LUNT.

Diurnal variation of the gaseous constituents of river waters. R. W. BUTCHER, F. T. K. PENTELOW, and J. W. A. WOODLEY (Biochem. J., 1927, 21, 945—957).—In the water of the rivers Lark and Itchen the dissolved oxygen and the p_H are at maximum during the day, whilst ammoniacal nitrogen is at a minimum. The reverse is observed at night, since in the process of diurnal photosynthesis the plants liberate oxygen which removes the ammonia produced by the decay of organic matter. At night, on the other hand, not only is there a cessation in the production of oxygen, but also any residue of this gas is being utilised in the nocturnal respiration of river organisms. S. S. ZILVA.

Blood-fat and exercise. J. W. T. PATTERSON (Biochem. J., 1927, **21**, 958—966).—There is a remarkable constancy of the fasting blood-fat content for the same individual, but after severe exercise there is a definite increase. If, however, the individual receives 100 g. of dextrose *per os* prior to the muscular

exertion this increase is not observed. The blood-cholesterol content is unaffected by the exercise.
S. S. ZILVA.

Effect of cooling on muscle. I. Biochemistry of frozen fish. II. Creatine and creatinine in albino-rat muscle. H. AKATSUKA (J. Biochem. [Japan], 1927, 7, 27—39, 41—51).—I. When carp is frozen at −1° to −3°, or −10° to −13°, no change in the total or residual nitrogen content of the muscles takes place; freezing at −24° for 20 mm. decreases the creatine content by 19%.

II. Freezing at −3° to −20° for 2 hrs. causes a slight increase, and for 6 hrs. a diminution of 8% in muscle creatine. In moderate curare paralysis the diminution is 7%. Freezing curarised albino-rat muscle for 6 hrs. causes a decrease of 22—23%.
CHEMICAL ABSTRACTS.

Effect of increased calcium intake on dystrophic renal calcification in rabbits. I. REMESOV (Biochem. Z., 1927, **187**, 51—56).—Administration of calcium salts by any route caused an increase in the calcium content of the kidneys of normal rabbits. When one kidney was ligated the process of calcification was accelerated by intravenous or subcutaneous, but not by oral, administration of calcium salts.
C. R. HARINGTON.

Physico-chemical basis of the action of the phenol–camphor medicaments. F. MÜLLER, P. GÜNTHER, and M. PEISER (Arch. exp. Path. Pharm., 1927, **124**, 41—58).—The m. p., d, and n_D of mixtures of phenol and camphor in varying proportions have been determined. It is concluded that the phenol–camphor mixture used medicinally is a very loose molecular compound which is readily dissociated in contact with water, giving rise to an aqueous phase containing phenol in approximately constant (1·3%) concentration, the camphor being precipitated in a very finely-divided condition.
W. O. KERMACK.

"Sympathol," a new adrenaline-like substance. Constitution and pharmacodynamical action. F. LASCH (Arch. exp. Path. Pharm., 1927, **124**, 231—244).—"Sympathol" (methyl-α-hydroxy-β-*p*-hydroxyphenylethylamine hydrochloride), m. p. 154°, has pharmacological properties resembling those of adrenaline, although there are quantitative and qualitative differences. W. O. KERMACK.

Action of "synthalin" in the animal organism. P. E. SIMOLA (Z. physiol. Chem., 1927, **168**, 274—293).—It has been claimed (Northmann and Wagner, Deut. med. Woch., 1926, **52**, 2067) that "synthalin," a synthetic guanidine derivative, is of great value as a substitute for insulin in the treatment of diabetes, particularly since it may be effectively given by the mouth. The result of the administration of this substance on the concentration of reducing substance, lactic acid, and inorganic phosphorus in the blood of goats and of rabbits has been investigated. "Synthalin" administered either by the mouth or subcutaneously differs from insulin in its effect on the blood-sugar, hypoglycæmia being far less marked (in some cases scarcely perceptible), coming on after some hours, and lasting longer. In most, but not all cases there is a fall in the inorganic phosphorus of the blood accompanying the fall in blood-sugar. If a poisonous dose of "synthalin" is given, the inorganic phosphorus rises sharply. Lactic acid increases in the blood of sheep after "synthalin" administration. The toxic symptoms which often develop are reminiscent of guanidine poisoning. H. D. KAY.

Intoxication with commercial methyl chloride. H. M. BAKER (J. Amer. Med. Assoc., 1927, **8**, 1137—1138).—Commercial methyl chloride, which may be absorbed by respiration in toxic amounts, is cumulative in action. It may be detected in the urine as ammonium formate before symptoms of intoxication develop. A. A. ELDRIDGE.

Toxic effects of ethylene dibromide. B. G. H. THOMAS and W. P. YANT (U.S. Pub. Health Rep., 1927, **42**, 370—375).—Ethylene dibromide (0·25 c.c.) applied to the abdomen of rats or inhaled (0·8% for 30 min., 0·4% for 60 min., or 0·2% for 150 min.) causes death within 24 hrs. CHEMICAL ABSTRACTS.

Toxicity of phenylarsinic acids for *Balantidium coli*, Malm., in cultures in relation to their chemical constitution. A. S. CORBET and A. P. JAMESON (Biochem. J., 1927, **21**, 986—990).—The toxicities of the sodium salts of a number of these acids are tabulated. Amino- and hydroxy-phenylarsinates are toxic in dilutions above 1/20,000, sodium 3-hydroxy-1 : 4-benz*iso*oxazine-6-arsinate, sodium *N*-glycineamidophenylarsinate, sodium 5-acetamido-4-hydroxyphenylarsinate in dilutions below *1/10000*, whilst sodium 5-acetamido-2-hydroxyphenylarsinate and sodium 8-acetamido-3-hydroxy-1 : 4-benzisoxazine-6-arsinate are not toxic in dilutions of 1/500 and only very slightly so in 1% dilutions.
S. S. ZILVA.

Differential analysis of heart poisons. V. Action of magnesium, strontium, and barium chlorides on stimulus formation in the heart of cold-blooded animals. B. KISCH (Arch. exp. Path. Pharm., 1927, **124**, 210—230).—A pharmacological investigation of the action of the above salts on stimulus formation in the shark's heart.
W. O. KERMACK.

Purgative action of hydroxyanthraquinones. H. FÜHNER and J. DE DIOS FERNANDEZ (Arch. exp. Path. Pharm., 1927, **124**, 185—191).—The purgative action has been determined, on white mice, of seven dihydroxy- and four trihydroxy-anthraquinones as well as of 1 : 8-dihydroxy-3-methylanthraquinone (chrysophanol, chrysophanic acid) and 1 : 6 : 8-trihydroxy-3-methylanthraquinone (rheumemodin).
W. O. KERMACK.

Toxicity of zinc. V. G. HELLER and A. D. BURKE (J. Biol. Chem., 1927, **74**, 85—93).—Addition of metallic zinc, zinc oxide, or soluble zinc salts to the diet of rats in amounts up to 0·5% caused no pathological symptoms and no significant increase in zinc content of the viscera. Contamination of food with zinc from zinc containers appears, therefore, not to be a danger. C. R. HARINGTON.

Mechanism of enzyme action. F. F. NORD (Nature, 1927, **120**, 82—83).—Certain chemical compounds are capable of forming an adsorption on the surface of enzymes which acts as protec

So-called "activators" are really protectors, protecting the enzyme from the damaging effect of intermediate or final products of the reactions concerned. A. A. ELDRIDGE.

Conditions of autolytic ammonia formation in tissues. III. Relation of tissue ammonia to purine metabolism. P. GYORGY and H. ROTHLER (Biochem. Z., 1927, **187**, 194—219).—Extracts of liver, kidney, muscle, and thymus (but not blood) are able to eliminate ammonia from sodium nucleate and from adenosine; the course of the reaction is similar to the liberation of ammonia which takes place in the tissues alone as the result of autolysis. The optimum p_H for the reaction is 5·2—5·5 except in the case of muscle, for which it is 7·0—8·0. The experiments indicate a relationship between formation of ammonia in tissues and purine metabolism. C. R. HARINGTON.

Nucleosidases. I. H. VON EULER and E. BRUNIUS (Ber., 1927, **60**, [*B*], 1584—1591).—Nucleosidase is obtained by extraction of pig kidney with water and purified to some extent by dialysis or, preferably, by isoelectric precipitation combined with dialysis. Kaolin is unsuitable as adsorbent, whereas aluminium hydroxide *B* at p_H 5—6 effects 75% adsorption; subsequent elution is difficult. Precipitation with alcohol and colloidal ferric hydroxide effects adsorption of the enzyme, which is not recovered by means of phosphate or alkali. The best purification is effected by combination of precipitation with acetone and isoelectric precipitation. Activity is measured by using adenosine as substrate, the liberated ribose being determined. The enzymic action of nucleosidase is restricted by nucleic and uric acids but appears to be unaffected by arabinose. Apparently the amino-group of adenosine and the primary alcoholic group of ribose are not essential for the specific union of adenosine and the nucleosidase. H. WREN.

Phosphoric and lactic acid production in pulped glands. F. KRAUSE (Z. physiol. Chem., 1927, **168**, 216—232).—If pulped glands (liver, pancreas, salivary gland) are incubated in sodium hydrogen carbonate solutions at 42°, phosphoric and lactic acids are produced. As a rule there is a greater molecular quantity of the former acid. In presence of sodium fluoride, although acid production is checked, there is no synthesis of phosphoric ester, and it is concluded that a substance similar to lactacidogen is not present in these glands. Nucleic acid, present in considerable quantities in the fresh tissues, is believed to be the source of both the phosphoric and the lactic acid. H. D. KAY.

Behaviour of bile acids in the digestion of protein. R. KARASAWA and M. SHODA (J. Biochem. [Japan], 1927, **7**, 129—143).—Bile acids exert no noticeable effect on protein hydrolysis. They have a depressing effect on the tryptic digestion of protein, which, however, is lessened when the bile acids are in the colloidal state. The protein digestion by erepsin is also depressed to a variable degree by different bile acids. Thus, cholic acid has the strongest depressing effect on the peptide cleavage, whilst the other acids exert a diminishing effect in the order: gallodeoxycholic, deoxycholic, and hyodeoxycholic acids. CHEMICAL ABSTRACTS.

Enzyme action. XLV. Lipase action of the whole trout at different ages. K. G. FALK, H. M. NOYES, and I. LORBERBLATT. **XLVI. Ester-hydrolysing actions of whole trout preparations under various conditions.** H. M. NOYES, I. LORBERBLATT, and K. G. FALK (J. Gen. Physiol., 1927, **10**, 837—844, 845—851; cf. A., 1925, i, 1360; this vol., 227).—The ester-hydrolysing actions of extracts and total solids of trout eggs and whole trout of various ages have been ascertained, ten different esters being used as substrates. The type of diagram which represented the relative ester-hydrolysing powers varied from that characteristic of immature eggs to that given by the adult fish after they had eaten for a few weeks, and henceforward it remained constant for 4—5 years. The influence of the hydrogen-ion concentration on the activity of the enzymes has been investigated, and also the effect of using various solvents such as glycerol or sodium chloride solutions instead of water for the preparation of the extracts. W. O. KERMACK.

Amount of light emitted by mixtures of *Cypridina* luciferin and luciferase. K. P. STEVENS (J. Gen. Physiol., 1927, **10**, 859—873).—A photometric method is described for the determination of the amount of light produced per c.c. of the luciferin solution containing luciferase and from the results the amount of light emitted by 1 g. of dried *Cypridina* powder has been calculated. This amount varies slightly with the concentration of luciferin and also markedly with the nature of the medium, being maximal in neutral sea-water and minimal in distilled water saturated with hydrogen. It also decreases slightly as the concentration of luciferase is increased. W. O. KERMACK.

Quanta of light produced and the molecules of oxygen utilised during *Cypridina* luminescence. E. N. HARVEY (J. Gen. Physiol., 1927, **10**, 875—881).—From measurements of the oxygen absorbed during the oxidation of luciferin with production of light, it is found that $11{\cdot}4\times10^{-5}$ g. of oxygen is utilised for each lumen of light produced or that 88 mols. of oxygen correspond with the emission of one quantum of light of 4800 Å. (the wave-length of maximum intensity). This result may be too high, and it is probable that for each quantum of light produced about 50 mols. of oxygen are absorbed and 100 mols. of luciferin oxidised. Of the energy produced, 1% is converted into light. W. O. KERMACK.

Effect of cyanide on the Schardinger enzyme. M. DIXON (Biochem. J., 1927, 840—843).—Inhibition of the aerobic oxidation of aldehyde by the Schardinger enzyme is produced only by concentrations of cyanide greater than $M/200$. It is due to an actual destruction of the enzyme itself, and not to the inactivation of the iron, which acts catalytically on molecular oxygen in accordance with Warburg's theory (cf. Szent-Gyorgyi, A., 1926, 867). S. S. ZILVA.

Hydrolysis of sucrose by invertase in very concentrated solutions. C. D. INGERSOLL (Bull.

Soc. Chim. biol., 1927, 9, 838—840).—Polemical against Achalme (A., 1926, 977). W. O. KERMACK.

Alcoholic fermentation. XIII. Non-existence of cell-free fermentation. S. KOSTYTSCHEV, G. MEDVEDEV, and H. KARDO-SYSOJEVA (Z. physiol. Chem., 1927, **168**, 244—266).—Alcoholic fermentation by dried yeast or by extracts of dried yeast is due, not to so-called "cell-free fermentation" but to the presence of relatively small numbers of surviving cells, the activity of which is extraordinarily stimulated by unknown substances derived from the killed cells. The fermentative activity of such preparations is a function of the number of living cells present. These findings explain many anomalies in current views on "cell-free fermentation." H. D. KAY.

Fermentation of glycogen and starch by maltase-free yeast. A. GOTTSCHALK (Z. physiol. Chem., 1927, **168**, 267—273).—Dried, washed *S. Ludwigii*, which does not attack maltose, will nevertheless ferment glycogen readily, and soluble starch less readily, if relatively large amounts of co-zymase are present (boiled extract of fresh bottom yeast used). Dextrose appears to be produced by such yeast preparations from both these substances without the intermediate formation of maltose. The production of phosphoric esters, which is dependent on the presence of co-zymase, is an essential step in the fermentation of glycogen by *S. Ludwigii*.
H. D. KAY.

Influence of different carbohydrate phosphoric esters on the fermentation of dextrose. P. MAYER (Biochem. Z., 1927, **186**, 313—316).—All the known carbohydrate monophosphoric esters accelerate the commencement of fermentation, those of Neuberg and of Robison having the greatest effect.
P. W. CLUTTERBUCK.

Graded phytochemical reduction. G. NAGELSCHMIDT (Biochem. Z., 1927, **186**, 317—321).—Diacetyl added to a fermenting sugar solution is converted fairly rapidly into acetylmethylcarbinol, which is then much more slowly reduced to $\beta\gamma$-butylene glycol.
P. W. CLUTTERBUCK.

Fermentation of α-ketobutyric and oxalacetic acids. VII. Dependence of alcoholic fermentation on p_H. E. HAGGLUND and A. RINGBOM (Biochem. Z., 1927, **187**, 117—119).—The velocity of fermentation of α-ketobutyric acid by yeast is greatest at p_H 4·3, and that of oxalacetic acid at p_H 4·6; neither acid is fermented at all below p_H 3·0 or above p_H 8·0. The p_H range of activity of carboxylase appears therefore not to be dependent on the substrate.
C. R. HARINGTON.

Yeast fermentation. III. Pyruvic acid. H. HAEHN and M. GLAUBITZ (Z. physiol. Chem., 1927, **168**, 233—243).—Sodium pyruvate in presence of excess of yeast only gives rise to minimal quantities of carbon dioxide. 1% pyruvic acid rapidly kills yeast-cells. If, however, disodium hydrogen phosphate is added in increasing quantities to 1% pyruvic acid, increasing speeds of fermentation are observed when yeast is added. The proportion of yeast-cells which survive the process rises with increase in the added phosphate. Lysine hydrochloride+sodium hydroxide, and glycine both act as good buffers for this system, the fermentation of pyruvic acid in their presence proceeding almost as rapidly as in the (unbuffered) dextrose controls. H. D. KAY.

Fermentation of sugar and pyruvic acid. A. LEBEDEV (Biochem. Z., 1927, **186**, 376—377).—Mainly deals with priority questions. The author cannot support the statement (Hagglund and Augustson, A., 1926, 543; Hagglund and Ahlbom, this vol., 379) that on occasions the zymase may still be active, even when the carboxylase is inactive.
A. WORMALL.

Fermentation of pyruvic acid. C. NEUBERG and E. SIMON (Biochem. Z., 1927, **187**, 220—253).—The theory of the intermediary part played by pyruvic acid in alcoholic fermentation is supported by the fact that, under the appropriate conditions, all preparations of yeast can ferment pyruvic acid more rapidly than dextrose. The failure of other workers to secure this result is due to neglect of such considerations as the effect of p_H, the difference of permeability of the yeast-cell towards dextrose and pyruvic acid, and the toxicity of high concentrations of the latter towards yeast. C. R. HARINGTON.

Purification of co-zymase. A. L. RAYMOND and H. M. WINEGARDEN (J. Biol. Chem., 1927, 74, 175—188).—Solutions of co-zymase were prepared by extracting yeast with hot water; electrodialysis, precipitation with alcohol, cadmium hydroxide, or ferric hydroxide, caused no purification. Treatment with lead acetate gave variable results and the experiments of von Euler and Myrback (A., 1924, i, 918) could not be repeated. By precipitation of the co-zymase with excess of mercuric chloride or nitrate or silver nitrate and recovery by decomposition of the precipitates with hydrogen sulphide, a 4- or 5-fold increase in activity was obtained, which was, however, accompanied by considerable loss of material. Preliminary treatment of the crude extract with lead acetate, followed by adsorption of the co-zymase in the filtrate on aluminium hydroxide at p_H 10, and recovery from the adsorbate with hydrochloric acid at p_H 6·0, gave a 9-fold purification and better yields.
C. R. HARINGTON.

Co-zymase. XII. Molecular weight of co-zymase. H. VON EULER, K. MYRBACK, and R. NILSSON (Z. physiol. Chem., 1927, **168**, 177—187).—From observations on the rate of free diffusion of co-zymase in an apparatus adapted by Euler (Wied. Ann., 1897, **63**, 273) and by Oholm (A., 1910, ii, 273) for the determinations of the mol. wt. of dissolved substances, that of co-zymase has been found to be 486±6. This mol. wt. is constant for very different degrees of purity of co-zymase, and does not change with the acidity of the diffusing solution. The concentration of co-zymase was determined by its effect on carbon dioxide production in co-zymase-free yeast under standard conditions. In the same apparatus sucrose gave a mol. wt. of 336±8. H. D. KAY.

Extraction of maltase from yeast. V. K. KRIEBLE, E. L. SKAU, and E. W. LOVERING (J. Amer. Chem. Soc., 1927, **49**, 1728—1735).—The rate of extraction of maltase from dried yeast increases with rise in temperature, but stronger extracts can be obtained at lower temperatures (15°) as the rate

destruction of the maltase is less. The maximum activity is obtained when the extracting medium is neutral, but this effect is less marked with fresh than with dried yeast. The rate of extraction of maltase from fresh yeast is less than that from dried yeast, but maltase is best extracted from fresh yeast at 30°.

F. G. Willson.

Unsaponifiable matter of yeast-fat. C. G. Daubney and I. S. Maclean (Biochem. J., 1927, **21**, 869; cf. this vol., 373).—The iodine values of the unsaponifiable matter vary widely according to the particular sample of yeast and according to the method used for the preparation of the fraction. After removal of the sterol precipitable by digitonin an oil may be obtained giving a very high iodine value, the degree of unsaturation being very largely influenced by the method of saponification and by the subsequent treatment of the material. S. S. Zilva.

Iodine as a biogenic element. XI. Action of iodine on yeast. K. Scharrer and W. Schwartz (Biochem. Z., 1927, **187**, 159—179).—Iodine in small concentrations has a slight stimulating effect on the growth of yeast, the iodine being taken up to some extent by the yeast-cells; it does not appear, however, to be of great significance in yeast metabolism.

C. R. Harington.

Necessity of carbon dioxide for the growth of bacteria, yeasts, and moulds. G. E. Rockwell and J. H. Highberger (J. Infect. Dis., 1927, **40**, 438).—Experiments indicate that bacteria, yeasts, and moulds require carbon dioxide as a source of carbon.

Chemical Abstracts.

Physico-chemical antagonisms of bacteria. C. Arnaudi, W. Kopaczewski, and M. Rosnowski (Compt. rend., 1927, **185**, 153—156).—The antagonism between different species of bacteria present together in a culture medium is explainable by variations in certain physical properties of the medium.

T. H. Pope.

Relation of the growth of certain micro-organisms to the composition of the medium. I. The synthetic culture medium. II. The effect of changes of surface-tension on growth. V. Reader (Biochem. J., 1927, **21**, 901—907, 908—912).—I. Traces of manganese or iron do not increase the rate or amount of growth of *Streptothrix corallinus*, a white *Streptothrix*, and *Sarcina aurantiaca*. No appreciable variation in the growth of these organisms takes place when the medium contains dextrose within the range 0·06—2%. Glycerol, mannitol, arabinose, sodium lactate, sodium citrate, sodium pyruvate, or glycogen may replace dextrose as a source of carbon without loss of efficiency in the medium. The substitution by lævulose, rhamnose, sodium acetate, propionate diminishes the growth, whilst the butyrate, oxalate, succinate, or tartrate cannot be used as a source of carbon at all. Of the amino-acids glycine, asparagine, alanine, and possibly cystine can supply the carbon requirements of the medium but none of the amino-acids tried acted as efficiently as ammonium salts in providing nitrogen.

The amount of growth of *Streptothrix* in synthetic medium containing additions of broth or antineuritic concentrates (torulin) is not related to the change of surface tension between the medium and air or the medium and benzene. The type of growth (film or deposit) is correlated with change in interfacial tension of the medium against benzene.

S. S. Zilva.

Mechanism of the action of fatty acids and particularly of the unsaturated acids and of their soaps on bacteria and toxins. P. Sedallian and L. Velluz (Bull. Soc. Chim. biol., 1927, **9**, 825—837).—From experiments on the neutralisation of tetanus toxin by various fatty acids and soaps, it is concluded that the formation of cryptotoxins is dependent on the adsorption of these acids on the toxin-micelles in such a way as to inhibit their action on the animal organism.

W. O. Kermack.

Quantitative dismutation of methylglyoxal to lactic acid by *Bacillus Delbrücki* and by *Bacterium lactis aërogenes*. Irregular behaviour of phenylglyoxal in this reaction. C. Neuberg and E. Simon (Biochem. Z., 1927, **186**, 331—336).—*B. Delbrücki* and *B. lactis aerogenes* convert methylglyoxal quantitatively into *r*-lactic acid but, although both convert phenylglyoxal quantitatively into mandelic acid, the former gives rise to a product containing 82% of the *d*-acid whilst the latter gives a product containing 10% excess of the *l*-acid.

P. W. Clutterbuck.

Vitamins and tubercle bacilli. I, II. N. Uyei (J. Infect. Dis., 1927, **40**, 425, 433).—Growth-stimulating substances could not be found in tubercle bacilli or their metabolic products. Substances rich in vitamin-*B* stimulate the growth of tubercle bacilli in Long's medium.

Chemical Abstracts.

Influence of thyroid on the stimulation of autonomic nerves and on the action of adrenaline. W. Feldberg and E. Schlif (Arch. exp. Path. Pharm., 1927, **124**, 94—101).—Thyroxine and other thyroid preparations have no immediate action in increasing the effect of adrenaline in raising the blood-pressure. Likewise they do not intensify the action of vagus stimulation in lowering the blood-pressure nor the effect of stimulating the cervical-sympathetic in dilating the pupil.

W. O. Kermack.

Fat metabolism. I. A. Low and R. Pfeiler (Biochem. Z., 1927, **187**, 114—116).—Injection of 0·4 mg. of adrenaline into rabbits causes a slight decrease in the light petroleum-soluble and a marked increase in the alcohol-soluble fraction of the blood-lipins.

C. R. Harington.

Determination of adrenaline. L. C. Baker and G. F. Marrian (Biochem. J., 1927, **21**, 1005—1009).—A modification of Folin, Cannon, and Denis' method (A., 1913, ii, 163). Comparisons are made in a Lovibond colorimeter and a calibration curve is utilised, the working temperature being 20°. In the extraction by the Folin, Cannon, and Denis method there is small but definite oxidation of adrenaline. This can be avoided by using trichloroacetic acid as the extracting agent.

S. S. Zilva.

Effect of insulin on the sugar excretion threshold and its after-effect on sugar assimilation. G. Eda (J. Biochem. [Japan], 1927, **7**, 53—77).—After the first insulin injection the threshold of sugar

excretion is often lowered; after several consecutive days' injections it usually rises (*e.g.* 0·04%), but the effect is variable. Long-continued insulin injections diminish the assimilability of sugar, but the effect rapidly disappears when the injections are discontinued. CHEMICAL ABSTRACTS.

Insulin and glycogen formation. K. POGANY (Biochem. Z., 1927, **187**, 72—77).—In mice weighing 17—25 g., doses of 0·004—0·006 unit of insulin have no effect on the total glycogen content; 0·01—0·02 unit causes an increase, whilst larger doses cause more or less complete disappearance of the glycogen. C. R. HARINGTON.

Variations in the serum-calcium of rabbits. K. CULHANE (Biochem. J., 1927, **21**, 1015—1023).—The administration of insulin whether pure or crude causes no rise in the serum-calcium of rabbits, nor can such a rise be recorded during insulin convulsions (cf. Davies, Dickens, and Dodds, A., 1926, 980). An immediate rise in the serum-calcium occurs independent of insulin administration in rabbits fed with cabbage except when the initial value is exceptionally high. S. S. ZILVA.

Vitamin-*A* formation in the etiolated wheat shoot. T. MOORE (Biochem. J., 1927, **21**, 870—874).—Fresh etiolated wheat shoots, 10 days old, fed to rats receiving a diet deficient in vitamin-*A* but adequate in vitamin-*D* at the rate of thirty shoots per day, prevent death and restore growth. Seeds fed at the same rate are ineffective. The condition of the animals after a few months is, however, not as good as that of animals subsisting on a liberal diet (cf. Wilson, J. Biol. Chem., 1922, **51**, 455; Coward, this vol., 595). S. S. ZILVA.

Vitamin-*A* and greenness in plant tissue. I. Relative vitamin-*A* content of head and leaf lettuce. M. DYE, O. C. MEDLOCK, and J. W. CRIST (J. Biol. Chem., 1927, **74**, 95—106).—The vitamin-*A* content of the leaves of lettuces of various modes of cultivation was approximately proportional to their chlorophyll content. C. R. HARINGTON.

Detection of the antirachitic factor in grasses grown in the dark and under glass. W. VOLTZ and W. KIRSCH (Biochem. Z., 1927, **186**, 255—263).—Grass seeds (*Lolium perenne*) do not contain the antirachitic factor, but the germinating plants do, even when grown under glass or in complete darkness. This is opposed to the view that the antirachitic vitamin is formed only by irradiation of a provitamin. P. W. CLUTTERBUCK.

Vitamins-*A* and -*D* of spinach. S. G. WILLIMOTT and F. WOKES (Biochem. J., 1927, 21, 887—894).—A stable acetone–ether extract of dried spring spinach was prepared which in daily doses of 25 mg. secured complete freedom from xerophthalmia and induced satisfactory although slightly subnormal growth in rats. A dose of this order, however, did not show any significant antirachitic protection. The extract is practically free from mineral matter and oxidising enzymes. S. S. ZILVA.

Nutrition. VII. Fat-soluble vitamin requirements of chickens. R. H. A. PLIMMER, J. L. ROSEDALE, and W. H. RAYMOND (Biochem. J., 1927, **21**, 940—944).—The minimum quantity of cod-liver oil required for rearing chicks is 0·5% of the diet. There are indications that a higher percentage is necessary for hens in order to ensure the production of fertile and hatching eggs. S. S. ZILVA.

Antineuritic yeast concentrates. II. Use of norite charcoal in the concentration of torulin. H. W. KINNERSLEY and R. A. PETERS (Biochem. J., 1927, **21**, 777—790).—The aqueous extract from yeast is precipitated with neutral lead acetate. By treating the filtrate with baryta gum impurities are further removed. After removing the baryta from the solution with sulphuric acid more impurities are precipitated with mercuric sulphate. The solution is then adsorbed with norite at p_H 7·0 twice and the active principle extracted from the adsorbent by extraction with 0·1*N*-hydrochloric acid and with 50% alcohol. The highest yield obtained by this method from 14 lb. of yeast was 4400 doses of about 1 mg. The treatment with mercuric sulphate can be avoided if the solution is brought to p_H 2·5 after treatment with baryta, and after removal of the reagent the solution is adsorbed with norite. At this p_H the adsorbent removes impurities. By bringing the solution to p_H 7 after this purification, the fractionation can be continued as before; the yield, however, is not as good as that obtained by the first method. Adsorption on norite charcoal is not a property of torulin of activity 1·0 mg. per daily dose and is therefore due to to a co-adsorbent in the earlier stages. S. S. ZILVA.

Temporary spontaneous disappearance of typical "beri-beri" symptoms in pigeons fed on diets deficient in vitamin-*B*. S. K. KON (Biochem J., 1927, 834—836).—The occurrence of temporary spontaneous cures in a large percentage of pigeons fed on a vitamin-*B*-deficient but otherwise complete synthetic ration is fully confirmed (cf. Kon and Drummond, this vol., 702). S. S. ZILVA.

Effect of administration of glycine to pigeons on a diet deficient in vitamin-*B*. S. K. KON (Biochem. J., 1927, **21**, 837—839).—Administration of glycine has no beneficial effects on pigeons fed on diets deficient in vitamin-*B*. Bad effects were observed on the administration of the amino-acid an these are attributed to the high molecular concentration of the solution given. Collazo's opinion (*J.*, 1923, i, 506) that carbohydrates when administered to vitamin-*B*-deficient pigeons are toxic *per se* is no corroborated. S. S. ZILVA.

Different behaviour of pigeons and hens on supplying their vitamin-*B* requirements y fresh green plants. A. SCHEUNERT and SCHIEBLICH (Biochem. Z., 1927, **186**, 222—228). Pigeons require a much greater amount of gree material *e.g.*, sugar-beet leaves, grass, lucerne, certain acid fodders, than do hens, in order to sa their requirements of the antineuritic factor. this large amount cannot be administered satisfac or y, pigeons are unsuitable for testing plant materia an must not be concluded from negative experimen s pigeons that such material is lacking in the antineu factor. P. W. CLUTTERBUCK.

Nutrition. VI. Balance of food by vitamin-*B*. R. H. A. PLIMMER, J. L. ROSEDALE, and W. H. RAYMOND (Biochem. J., 1927, 21, 913—939).—Protein, fat, and carbohydrate in the diet need balancing by vitamin-*B*, which must not fall below a certain ratio to the calorie content. Chickens require more of the vitamin than pigeons, and pigeons more than rats, per unit calorie, the requirement of young animals being higher than that of adults. As tested on pigeons "marmite" is about half as potent as dried yeast; samples of yeast extract vary considerably in potency. Various pathological changes are produced by the consumption of diets containing too little vitamin-*B*. The composite nature of vitamin-*B* has not been taken into consideration in this research.

S. S. ZILVA.

Relation of protein intake to requirement and determination of vitamin-*B*. H. C. SHERMAN and O. H. M. GLOY (J. Biol. Chem., 1927, 74, 117—122).—Neither the time of survival of rats after deprivation of vitamin-*B* nor their maintenance requirements of this vitamin were altered by changing the protein content of the basal diet from 12 to 54%.

C. R. HARINGTON.

Determination of vitamin-*B*. H. C. SHERMAN and E. H. MACARTHUR (J. Biol. Chem., 1927, 74, 107—115).—In quantitative tests for vitamin-*B* carried out on young rats, the amount of vitamin-containing food should be adjusted until, in combination with the basal diet, it induces a preliminary gain in weight followed by a slight fall and subsequently a steady period of some weeks. Preliminary removal of vitamin-*B* from the diet is of no advantage in testing for this factor. At the same age, larger animals respond less readily than smaller ones to vitamin-*B*, whilst, under the same conditions of age and weight, females require larger amounts of the vitamin than males. C. R. HARINGTON.

Content of glutathione in certain tissues, and in the blood of the pigeon under normal conditions, when underfed, and when deprived of vitamin-*B*. L. RANDOIN and R. FABRE (Compt. rend., 1927, 185, 151—153).—With the normal adult pigeon, the skeletal muscles contain, per 100 g. of fresh tissue, 0·017—0·032 g. (average 0·026 g.) of glutathione; the heart, 0·030 g.; the liver, 0·140 g.; and the blood, 0·061 g., with comparatively large individual variations. Malnutrition causes a general lowering of the content of glutathione, the average for the skeletal muscles being 0·0143 g. Deprivation of vitamin-*B* produces no marked change at first, but [illegible] a lowering of the proportion of glutathione to 0·0134 g. and, at the critical period, to 0·0139—0·0099 g. per 100 g. of skeletal muscle; with the heart and the blood, the diminution is far less, and [illegible] the liver there is a tendency to increase. Increase in [illegible] value the ratio $n' : n$ in the case of skeletal muscle is pronounced when vitamin-*B* is withheld and indicates an increase in reducing substances other than those containing the sulphydryl group.

T. H. POPE.

[illegible] content of green grass; weight of [illegible] in curvy. BROUWER (Biochem. Z., 1927, 187, 183—193).—At all seasons *Lolium perenne*, in the fresh condition, is rich in vitamin-*C*, 1 g. *per diem* being sufficient to protect guinea-pigs against scurvy. In scurvy there was observed a decrease in the weight of the thymus and an increase in that of the adrenals. C. R. HARINGTON.

Dietary requirements for reproduction. VIII. Reproduction-deficient diet. IX. Cod-liver oil *versus* wheat oil as sources of vitamin-*E*. X. Vitamin-*B* requirements for lactation. XI. Potency of butter-fat in vitamin-*E*. B. SURE (J. Biol. Chem., 1927, 74, 37—44, 45—53, 55—69, 71—84).—VIII. In contradiction to the results of Anderegg and Nelson (B., 1925, 520), the fact is confirmed that on a diet of dried skimmed milk, cod-liver oil, and yeast, rats are sterile; addition to such a diet of 0·035% of the unsaponifiable matter from cotton-seed oil secures a normal reproductive cycle.

IX. Normal reproduction could not be obtained by increasing the proportion of cod-liver oil in the above-mentioned basal diet, although the oil was rich in vitamins-*A* and -*D*; large increases in the amount of oil caused toxic effects.

X. The vitamin-*B* requirements of rats are much increased during lactation. Preparations rich in vitamin-*B* were made by extracting wheat embryo with 25% alcohol in the cold; such an extract prepared from 6 g. of wheat embryo formed a sufficient daily supply of vitamin-*B* for the lactating rat. Wheat-germ oil in amounts up to 5% of the diet was non-toxic.

XI. Addition of 10% of butter-fat is required to convert the basal diet into one sufficient for normal reproduction; butter-fat therefore contains much less vitamin-*E* than does wheat oil.

C. R. HARINGTON.

Liberation of oxygen from fleshy-leaved plants in the absence of carbon dioxide. A. MAYER (Landw. Versuchs-Stat., 1927, 105, 261—266).—A discussion of the trend of modern research in this connexion, in comparison with the author's earlier views. A. G. POLLARD.

Special form of biological oxidation [of oxalic acid in presence of a moss]. J. HOUGET, A. MAYER, and L. PLANTEFOL (Compt. rend., 1927, 185, 304—306).—*Hypnum triquetrum* suspended in dilute oxalic acid solution through which oxygen is passed causes at 25° complete oxidation in a few hours. The action is not influenced by rise of temperature; it proceeds best at an acid concentration of 0·04—0·02*N*, and ceases if the acid is neutralised. The activity of the moss is destroyed only by vigorous treatment; *e.g.*, with water at a temperature above 96°, chlorine, osmic acid, picric acid, hydrogen peroxide, hypo-sulphites, acid sulphites, iodides, ferro- and ferri-cyanides, and phenylhydrazine hydrochloride. Urethane, phenylurethane, and hydrocyanic acid have no action.

E. W. WIGNALL.

Respiration and fermentation in green plants. L. GENEVOIS (Biochem. Z., 1927, 186, 461—473).—The respiratory and fermentative activities of six different types of algæ—*Chlorella pyrenoidea* (Chick), *Scenedesmus Basiliensis* (Chodat), *Cœlastrum Proboscideum*, *Hæmatococcus pluvialis*, *Stichococcus bacillaris*, *Pseudendoclonium Basiliense* (Visch)—have

been studied and compared with fermentation by yeast (cf. Meyerhof, A., 1926, 95). Respiration of *Chlorella*, in the presence of air, is increased by the addition of dextrose, lævulose, mannose, or galactose, the respiratory quotients in all cases being unity. Lactic acid and pyruvic acid have no influence, but acetaldehyde increases respiration up to threefold, with R.Q. 1·26; the acetaldehyde is probably synthesised to fatty acids. Propaldehyde and valeraldehyde have less effect than acetaldehyde, whilst formaldehyde completely inhibits respiration. Sodium butyrate, and to a less extent the acetate and valerate, increase respiration and cause a fall in R.Q. to 0·8, indicating that the acid is oxidised. Soluble amino-acids give a smaller but still definite increase in respiration. Lactose and sucrose have no effect but two hexosemonophosphoric acid preparations caused an increase in respiration up to threefold. The other algæ give results agreeing in general with those for *Chlorella*. No fermentation by *Chlorella* occurs in a sodium hydrogen carbonate–Ringer solution in the absence of oxygen, but fermentation is induced by the addition of dextrose, lævulose, mannose, or galactose. The other algæ behave like *Chlorella* in the fermentation experiments. Algæ differ from yeast-cells to some extent in their sensitivity to potassium cyanide, for respiration in the salt solution is inhibited by small amounts of cyanide only in the case of *Scenedesmus*. In all cases, respiration in the presence of dextrose, sodium butyrate, acetaldehyde, etc. is inhibited by cyanide. Similar amounts of cyanide cause no inhibition of fermentation, but respiration and fermentation are equally sensitive to narcotics such as phenylurethane. It is concluded that the "intramolecular" respiration of algæ is essentially similar to yeast fermentation and fission processes in animal cells. One difference, however, is that in a sugar solution part of the respiratory process is insensitive to cyanide and this respiration is approximately equal to that in a salt solution, which is itself insensitive to cyanide. A. WORMALL.

Growth of moulds on cobaltammine salts. K. KINOSHITA (Acta Phytochim., 1927, 3, 31—50).—Cultures of *Aspergillus niger*, *A. oryzæ*, and *Penicillium glaucum* have been made using various cobaltammine salts as the source of nitrogen; the nitrogen content in each case was adjusted to a constant value. In all cases growth was very much less than for the control experiments in which ammonium and potassium nitrates were used. In the few salts which produced appreciable growth the mycelium contained a high percentage of cobalt. During growth under these conditions *A. oryzæ* converts 33% of the sucrose of the culture solution into kojic acid; *A. niger* under the same conditions produces large amounts of acid. It is concluded that these effects are due to the lack of easily assimilated nitrogen, since *A. niger* when grown in a culture solution with only small amounts of ammonium nitrate produces citric, malic, succinic, tartaric, and oxalic acids.

E. A. LUNT.

Metabolism of *Aspergillus oryzæ*. I. H. TAMIYA (Acta Phytochim., 1927, 3, 51—173).—The conditions for the growth of *A. oryzæ* have been investigated with regard to the hydrogen-ion concentration of the culture medium, and to the rate of acid formation by the mould. The accumulation of kojic acid in the culture medium (determined by colorimetric titration with ferric chloride) increased the p_H but slightly; the observed increase is therefore due to the removal of the cations of the medium by the mould. When ammonium nitrate is used as the source of nitrogen the ammonium ions are consumed more rapidly than the nitrate ions; at a certain p_H (3·4) the latter begin to be consumed with a corresponding reduction in acidity. Growth can take place in cultures of this mould between the limits of p_H 2·1 and 8·6, and is a maximum at 3·5 and 7·0. At the minimum, p_H 5·5, the formation of kojic acid is maximal. Free organic acids inhibit the growth of the organism, although their salts accelerate growth: oxalic, citric, and kojic acids are most active, then follow tartaric, lactic, acetic, and formic acids. The kojic acid formation is rapidly diminished by the addition of oxalic, citric, formic, hydrochloric, and nitric acids, whilst sulphuric acid produces a slight increase; the production is also increased by the addition of tartaric acid at a low p_H, and by the addition of phosphoric, lactic, and pyruvic acids in a medium with a p_H corresponding with the so-called isoelectric point of plasma protein, 5—6.

E. A. LUNT.

Influence of temperature on the nature of the fat formed by living organisms. L. K. PEARSON and H. S. RAPER (Biochem. J., 1927, 21, 875—879). The iodine value of the fatty acids produced by *Aspergillus niger* and *Rhizopus nigricans* varies with the temperature at which these organisms are grown. At higher temperatures the fatty acids produced are more saturated. S. S. ZILVA.

Influence of Turkestan climate on the chemical processes of plants. S. L. IVANOV (Bull. Univ. Asie Centrale, 1926, No. 12, 21—25).—A warm climate lowers, and a cold climate raises, the quantity of unsaturated acid (particularly linolenic) in the oil of seeds. CHEMICAL ABSTRACTS.

Nitrogen content of aspergillin. A. RIPPEL and K. WALTER (Biochem. Z., 1927, 186, 474—477). The fractions of the black spore pigment of *Aspergillus niger* contain different amounts of nitrogen, the alcohol-soluble fraction giving a value of 3·3% and the alkali-soluble fraction about 4·6%. No conclusions can be reached as to whether these differences are due to chemical changes or to the presence of impurities. Large variations in the nitrogen supply in the medium do not, however, appreciably alter the amounts of these fractions or their nitrogen content, and it is concluded that the formation of aspergillin is due to uniform chemical processes.

A. WORMALL.

Soluble enzymes secreted by hymenomycetes. Tannin as antioxidant. L. LUTZ (Compt. rend., 1927, 184, 1493—1494).—Tannin possesses strongly antioxygenic properties in the presence of the living mycelium of hymenomycetes; in the presence of 5 drops of a 1% ethereal aqueous solution of tannin reduction of methylene-blue is apparent after 4 hrs. with cultures of *Stereum hirsutum*, *S. purpureum*,

Polyporus versicolor, whilst in tannin-free controls reduction is not perceptible until 8—15 days have passed. The coloration of guaiacol, α-naphthol, and α-naphthylamine hydrochloride in presence of the same fungus is considerably retarded in the presence of tannin. A parallel series of experiments with gallic acid gave similar results. R. BRIGHTMAN.

Nature of the dye penetrating the vacuole of *Valonia* from solutions of methylene-blue. M. IRWIN (J. Gen. Physiol., 1927, **10**, 927—947).—Spectrophotometric observations demonstrate that the dye which penetrates into the vacuoles of uninjured cells of *Valonia macrophysa*, immersed in methylene-blue solutions, is in reality the lower homologue, trimethylthionine (azure-*B*). Since this dye is a weaker base than methylene-blue, and therefore may exist as free base under the conditions of the experiment, the staining of cells by methylene-blue solutions is not necessarily a contradiction of the view that the dye ions are unable to penetrate into the cells. If the cells are injured methylene-blue itself may be detected in the vacuoles. W. O. KERMACK.

Subsidiary dyes in methylene-blue. W. C. HOLMES (Stain Tech., 1927, **2**, 71—73).—All samples of methylene-blue examined have been found to contain azure-*B* (trimethylthionine). Since the latter, and not the former, is the dye which normally enters the living cell, it is important to be able to detect it in samples of methylene-blue. The following qualitative test has been devised: 0·1 g. of methylene-blue is dissolved in 25 c.c. of *M*/15-borate buffer solution (Clark). An equal volume of water is added and the solution is shaken with 25 c.c. of chloroform. The chloroform solution is then filtered twice through paper. If azure-*B* is present the solution will appear violet in colour. The chloroform is then shaken with water (or water containing a trace of acetic acid) when the azure-*B* enters the water and may be identified spectrophotometrically. If methylene-violet is present (only traces are usually found in methylene-blue) the chloroform will remain pink after repeated extraction with water. On shaking with hydrochloric acid (p_H 1) methylene-violet is removed from the chloroform quantitatively, giving a reddish-violet solution. H. W. DUDLEY.

Ketone-aldehyde mutase in wheat, rye, and soya beans. L. KLAR (Biochem. Z., 1927, **186**, —330).—Wheat, rye, and soya beans contain the enzyme. P. W. CLUTTERBUCK.

Enzymic production of volatile products from cotine under the influence of tobacco-leaf ac s. FODOR and A. REIFENBERG (Biochem. J. 1927- vol, 765).—Polemical against Faitelowtz (this . Nicotine is decomposed in tobacco fer entation even when sterility is observed. There a sm between the decomposition of nicotine and the amount of oxygen absorbed by moistened tobacco ves, even when the macerates are filtered through porous candle or in presence of germicides. S. S. ZILVA.

ymic deamidation of asparagine in the higher plant. GROVER and A. C. CHIBNALL (Biochem. J., 1927, **21**, 857—868).—There is an enzyme present in the rootlets of germinating barley which is capable of deamidating asparagine. An active preparation of this enzyme can be obtained from the aqueous extract. It appears to be specific for the naturally occurring *l*-asparagine. The simple amides acetamide and propionamide are entirely resistant to its action but *d*-glutamine is hydrolysed by it. The optimum p_H is about 7 and the optimum temperature about 37°. Pig erepsin also deamidates asparagine. On the other hand the barley preparation hydrolyses glycylglycine. The enzyme is therefore considered to be a plant erepsin (peptidase). S. S. ZILVA.

Volatile fatty acids formed by the acid fermentation of foodstuffs. II. C. BRAHM, G. ANDRESSEN, and R. PRILLWITZ (Biochem. Z., 1927, **186**, 232—242).—The separation and determination of the volatile acids formed during acid fermentation of green maize (A., 1925, i, 623) are described. P. W. CLUTTERBUCK.

Early stages of microbiological decay and humification of vegetable tissues. A. C. THAYSEN and W. E. BAKES (Biochem. J., 1927, **21**, 895—900).—The humification of oat straw proceeds most rapidly between the first and sixty-fourth day of fermentation. The hemicelluloses (pentosans) of the raw material are at least partly responsible for the appearance of the carbohydrate fraction of the humus. The proportions of the carbohydrate and lignin fractions (B., 1926, 305) vary appreciably with the progress of the humification. In three samples of bituminous coal no definite proof could be obtained of the presence of a carbohydrate fraction in the regenerated humus, although the percentage of halogen in the chlorine derivatives of these humus samples was of the order characteristic of a mixture of carbohydrate and lignin humus. The muscular tissues adhering to a mummified human vertebra of 200 B.C. had been converted into a humus with the properties of a typical carbohydrate humus. S. S. ZILVA.

Nutrient solutions having stable p_H values throughout the growing period of plants. R. ZINZADZE (Landw. Versuchs-Stat., 1927, **105**, 267—332).—The preparation is described of a series of solutions which can be used in water culture work, without repeated changing, the p_H value remaining constant within narrow limits during plant growth. The basis of these solutions is the use of ammonium nitrate (physiologically acid), ferric sulphate (hydrolytically acid), and sparingly soluble phosphates with which the solutions are buffered. A. G. POLLARD.

Absorption of ions by citrus and walnut seedlings. A. R. C. HAAS and H. S. REED (Hilgardia, 1926, **2**, 67—106).—Rough-lemon and grapefruit seedlings remove more potassium than calcium from solutions containing equivalent amounts of the ions; with small potassium concentrations more calcium, magnesium, and phosphorus are absorbed, and potassium is excreted from the roots. Citrus seedlings absorb more cation than anion from solutions of calcium salts. Chloride is most readily absorbed from calcium chloride solution; the presence of chloride reduces the absorption of nitrate. The

nature of the growth of citrus seedlings in water cultures depends on the original p_H, maintained p_H, and the nature of the acid or alkali employed.

Walnut seedlings (ash of kernel contains 60% P) rapidly absorb all the phosphorus from a complete nutrient solution. The amount of magnesium absorbed is independent of the potassium concentration. Except with the nitrate, walnut seedlings removed more cation than anion from solutions of calcium salts. CHEMICAL ABSTRACTS.

Influence of sodium carbonate and of calcium chloride on the acidity of the sap of the maize plant (*Zea Mais*). S. KARASIEWICZ (Bull. Soc. Chim. biol., 1927, 9, 841—850).—Details are given of the procedure and methods of analysis used in experiments on the effect of calcium and of the reaction of the medium on the acidity of the sap of *Zea Maïs*. W. O. KERMACK.

Physical and chemical changes during the ripening of grapes. P. R. v.d. R. COPEMAN and G. FRATER (Dep. Agric. Union S. Afr. Sci. Bull., 1926, 50, 1—54).—The sugar content of the berries increases rapidly during ripening, but only slowly or not at all at maturity; changes in the total solids other than sugar after the commencement of ripening are small. At maturity there is a definite relation between the total solids and the sugar, the value being 0·6—0·7, according to the variety. The percentage of acid decreased to 0·45—0·63 at maturity, and the ratio of acid to sugar decreased to 0·35—0·50. A connexion between the nitrogen content and the texture, but not the ripening, of the berries was indicated. The mineral content increased during ripening and was constant at maturity. The percentage of total solids in the seed continued to increase after maturity; the ash content of the seed was maximal at the period of rapid absorption of inorganic salts, and thereafter decreased on account of the increase in ligneous and cellulose constituents as the seed set and hardened. CHEMICAL ABSTRACTS.

Nitrogen and carbohydrate composition of the developing flowers and young fruits of the apple. F. S. HOWLETT (Cornell Univ. Agric. Exp. Sta. Mem., 1926, 99, 1—79).—At the opening of the fruit-buds the flowers are low in free reducing substances, total sugars, and acid-hydrolysable fraction, but all types of carbohydrate material increase as the flowers progress towards full bloom. The nitrogen content of the flowers decreases up to full bloom. The limiting factor in normal flower development is lack of a suitable, adequate supply of nitrogen. The nitrogen content of the fruit is nearly constant. CHEMICAL ABSTRACTS.

Plant colloids. XVIII. Wheat starch. M. SAMEC [with L. GUZELJ, J. KAVCIC, and L. KLINC] (Biochem. Z., 1927, 186, 337—359).—The ash of potato starch contains a distinct excess of acid constituents over bases and the silica is sufficient to neutralise all the calcium and magnesium, thus allowing the phosphoric acid to exert its acidic effect. The ash of wheat starch, however, has a much smaller excess of acid over base, and since the silica content is relatively low, the calcium and magnesium are partly available for combination with phosphoric acid. There is a pronounced retention of phosphorus by wheat starch when the latter is washed repeatedly with dilute acids, leading to the conclusion that this firmly-bound phosphorus is not combined with metals. The comparison of mineral constituents of wheat and potato starch and experiments involving electro-dialysis, heating of the starch with water under pressure, and peptisation with ultra-violet light fail to account for the peculiar electro-chemical and other properties of wheat starch. The nitrogen present in this starch, however, shows a resistance similar to that of the phosphorus in all these processes, and it is concluded that a salt-like compound of protein and amylophosphoric acid is present. On this assumption many of the peculiarities of wheat starch can be explained. A. WORMALL.

Colloidal properties of peat. A. V. DUMANSKI (Zapiski Voronezhskii sel'skokhozyaist. Inst. [Russia], 1926, 5, 61—80).—A peat of high lime content (46% of the ash), but not one of low lime content (10% of the ash), readily formed a suspension with water. The particles are charged electronegatively and move in an electric field with a velocity of 0·000024 cm. (per sec.?) for a *P.D.* of 1 volt between electrodes 1 cm. apart. Neutral and acid salts and acids coagulate peat hydrosol; alkali hydroxides and carbonates peptise it. The coagulating power of salts is in the order sodium (1), magnesium (14), aluminium (2700). Coagulation is also effected by freezing. CHEMICAL ABSTRACTS.

Determination of carbamide by gasometric measurement of the carbon dioxide formed by action of urease. D. D. VAN SLYKE (J. Biol. Chem., 1927, 73, 695—723).—Preformed carbon dioxide and hydrogen carbonate are removed from the solution containing carbamide by acidification and agitation under diminished pressure; the solution is neutralised and treated with urease, and the ammonium carbonate formed is determined in the apparatus o Van Slyke and Neill (A., 1924, ii, 872). Details are given of the application of the method to the determination of carbamide in quantities of material varying from 0·2 c.c. of blood to 2 c.c. of urine. C. R. HARINGTON.

Cobalt thiocyanate as a microchemical reagent. J. GREGER (Biochem. Z., 1927, 185, 43 441).—A concentrated aqueous solution of co a thiocyanate has the property of dissolving s arc granules and of staining variously other consti uen s of plant-tissue; it is therefore a valuable reagen the microscopical examination of vegetable o products. C. R. HARINGTON.

Pentose metabolism. II. Micro-determination of pentoses and pentosans. G. E. Y BURG (J. Biol. Chem., 1927, 73, 599—606). termination of pentoses by the furfuraldehyde metnou is accelerated by the use of phosphoric acid ins ea the hydrochloric acid formerly employed. Wit of the colorimetric determination of furfuraldeny , its reaction with aniline in presence of acetic aci , method is applicable to quantities of pentose 0·1 to 1 mg C. R. HARINGTON.

BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

OCTOBER, 1927.

General, Physical, and Inorganic Chemistry.

Hot-cathode vacuum discharges in gases and the vapours of metals, particularly iron, and their application to spectroscopy. K. L. Wolf (Z. Physik, 1927, 44, 170—189).—A vacuum furnace is described in which a pure graphite cylinder heated electrically serves both as the hot cathode and the container for the material of which the spectrum is to be examined; the power consumption increases from 2·6 kilowatts at 1225° to 10·2 at 2155°. A variable *D.C.* potential (maximum 110 volts) is applied between the hot cylindrical cathode and a graphite anode placed near to one end of the cathode. No appreciable emission was detected below 1750°; currents of the order of 20 amp. at 30 volts are readily obtained at a temperature of 2000° when a small amount of pure iron is placed in the centre of the cathode. A number of photographs are given which illustrate the character of the iron spectrum so produced; in particular the lines are very clear and narrow and the method is therefore especially suitable for accurate measurements. Very satisfactory argon spectrograms are obtained when argon is streamed through the apparatus. It is also shown that the apparatus is readily adaptable for the determination of the influence of gas pressure on the nature of the spectrum of the vapour of a metal such as iron. R. W. Lunt.

Quartz double monochromators and a simple new fluorite vacuum spectrograph for the Schumann region. C. Leiss (Z. Physik, 1927, 44, 133—138).—A spectrograph suitable for the range 1850—1000 Å. is described. R. W. Lunt.

Quantitative sensitivity of spectral lines. T. Negresco (Compt. rend., 1927, 185, 453—455).—The relations between the concentrations of metals in alloys and the intensities of their spectral lines have been investigated for arc, flame, and oscillating spark spectra. With diminishing concentration of the metal the intensities of all its lines diminish continuously, and disappear in the same order as with the pure metal itself under the same conditions. Diminution of the quantity of an element in a source of light diminishes the intensities of all the lines, independently of the potential necessary for their production. C. W. Gibby.

True and apparent width of spectral lines. H. C. Burger and P. H. van Cittert (Z. Physik, 1927, 44, 58—69).—Following a mathematical analysis, the use of a Fabry–Perot interferometer for the measurement of the true width of spectral lines is described. The width of the cadmium line 6439 Å. so determined at approximately 390° is 0·0114 0·0008 Å., whilst the calculated width due to Doppler effect produced by thermal agitation is 0·0107 Å.; the width is thus due almost solely to Doppler effect. R. W. Lunt.

New regularities in atomic spectra. J. C. McLennan and A. B. McLay (Phil. Mag., 1927, [vii], 4, 407—413).—From an examination of the arc spectra of the elements the authors have observed a well-defined periodicity in the progression of frequency with atomic number in each period of the periodic classification, and also a similarity in the periodicities of each of the periods. A. E. Mitchell.

Absorption lines of the solar spectrum. H. von Kluber (Z. Physik, 1927, 44, 481—516).—An elaborate analysis of the optics of the absorption of lines in the solar spectrum is given, and data referring to the intensity distribution and half width of the following lines are tabulated: H_α, sodium 6154·438, 6160·596; calcium 6102·937, 6161·503, 6162·390, 6163·968, 6166·651, 6169·249, 6169·778; iron 6200·527, 6219·494. R. W. Lunt.

Nuclear vibration in the band spectrum of helium. W. Weizel and C. Fuchtbauer (Z. Physik, 1927, 44, 431—454).—The spectrum produced by damped wave-train discharges in a stream of helium has been examined; a number of new bands characteristic of the He_2 molecule have been observed associated with the vibration transitions 0—1 and 1—1. R. W. Lunt.

Numerical evaluation by wave mechanics of the mean values of the *ortho*- and *para*-terms of He and Li^+ from polarisation terms. Y. Sugiura (Z. Physik, 1927, 44, 190—206).—The mean value of the *ortho*- and *para*-terms has been evaluated numerically by solving Schrodinger's equation for the central field. This analysis leads to the following values for the distance between the outermost components of the fine structure lines: He, $\Delta\nu_{2p}=0{\cdot}86$ cm.$^{-1}$ (observed 1·07); Li^+, $\Delta\nu_{2p}=4{\cdot}25$ cm.$^{-1}$ (observed 4·4); the agreement is considered to be satisfactory. R. W. Lunt.

Transition of glow into arc discharge in nitrogen. M. Wehrli (Z. Physik, 1927, 44, 301—318).—The current–potential, arc length–potential, and pressure–potential characteristics have been determined for the direct-current discharge between tungsten electrodes (diameter 1·7 mm.) in pure nitrogen. Neither chemical action nor melting of the electrodes was observed; at pressures above 181 mm. the transition from glow to arc discharge

is continuous and independent of the distance between the electrodes; below 104 mm. regions of instability are observed in which both glow and arc discharge can exist at a given value of the current; below 20 mm. increase in the current strength fails to effect the transition. Reproducible results cannot be obtained if nitrogen is contaminated with oxygen or water vapour, the discharge becoming unstable.

R. W. Lunt.

Wave-length of the green auroral line in the oxygen spectrum. J. C. McLennan and J. H. McLeod (Proc. Roy. Soc., 1927, **A**, **115**, 515—527).—The wave-length of the oxygen green line, determined by means of a Fabry–Perot interferometer, is found to be 5577·341±0·004 Å. This is in excellent agreement with Babcock's value for the wave-length of the auroral green line, 5577·350±0·005 Å. (Astrophys. J., 1923, **57**, 209), and confirms the view advanced by McLennan and Shrum that the green auroral line has its origin in oxygen in the upper atmosphere (cf. A., 1924, ii, 642).

L. L. Bircumshaw.

Regularities in the spectrum of ionised neon. P. K. Kichlu (Proc. Physical Soc., 1927, **39**, 424—428).—Numerous lines in the spectrum obtained by passing a condensed discharge through the more volatile gases of air have been attributed to singly-ionised neon. An analysis is made which confirms the identification for the lines within the limits 7282 and 3142 Å., and is in strict accord with Hund's theory.

R. A. Morton.

Spark spectrum of neon, Ne II. I. T. L. de Bruin (Z. Physik, 1927, **44**, 157—161).—A scheme of energy levels for ionised neon is advanced whereby some 200 lines of the spark spectrum have been co-ordinated; it is in complete agreement with Hund's theory. The quadruplet terms associated with the lower energy levels and the analogies to be traced with the arc spectrum of fluorine are dealt with in detail.

R. W. Lunt.

Spectra of metallic arcs started in chlorine. M. Miyanishi (Mem. Coll. Sci. Kyoto, 1927, **10**, 273—277).—The spectra of metallic arcs and of flames from an electric furnace have been studied when the arc and furnace chambers contained an atmosphere of chlorine. The presence of chlorine causes the appearance of some super-spark lines and the enhancement of spark lines in the arc. The flames from the furnace also exhibit spark lines in an atmosphere of chlorine.

R. A. Morton.

Spectrum of argon in the extreme ultra-violet. F. A. Saunders (Proc. Nat. Acad. Sci., 1927, **13**, 596—600).—A number of lines in the portion of the argon spectrum from 894 to 797 Å. still require explanation. The possibility that some of the lines are due to collisions between metastable neon atoms and neutral argon atoms is considered, but the balance of evidence seems to indicate that some members of the argon series are present although certain variations in intensity must be left for further study. The four lines 887, 883, 875, and 871 Å. are due to a pp' group in the spectrum of A III. The neon spectrum shows a group of lines between 661 and 680 Å. which include the three neon pp' combinations, whilst the rest of the group is probably part of the A III spectrum. The inclusion of 932 and 919 in the A I spectrum is of doubtful validity.

R. A. Morton.

Displacement of certain multiplets and multiple levels for elements in the first long period. R. C. Gibbs and H. E. White (Proc. Nat. Acad. Sci., 1927, **13**, 525—531).—The irregular doublet law, together with the regular displacement law of multiplets, has enabled the approximate spectral position of multiplets of Cr III and Mn III arising from the electron transitions $3d^34p$ to $3d^34s$ and $3d^44p$ to $3d^44s$ to be located. Lande's interval rule in conjunction with the regular doublet law has enabled certain frequency differences to be picked out. The analysis has been extended through successively increasing iso-electronic systems as far as those of the Cu I, Zn II type. The regular displacement of multiplets and the displacement of multiple levels are shown diagrammatically for the entire group. On the Moseley diagram any term (taken with respect to its limit) in a sequence of iso-electronic systems should reveal a relation very nearly linear (cf. this vol., 601).

R. A. Morton.

Absorption spectra of iron, nickel, and cobalt. W. F. Meggers and F. M. Walters, jun. (U.S. Bur. Standards Sci. Paper 551, 1927, **22**, 205—226).—The high-potential under-water spark spectra of iron, nickel, and cobalt has been re-examined using a grating spectrograph; 265 iron lines (2166—4404 Å.), 225 nickel lines (2124—3858 Å.), and 340 cobalt lines (2137—4120 Å.) which are absorbed in the source have been recorded and classified. The majority of these lines are identical with the stronger lines of the arc emission spectra, and involve the normal state, or some low metastable state of the neutral atom. The results confirm an earlier conclusion that the normal state of the iron atom is represented by a quintuplet-D term, that of cobalt by a quadruplet-F term, and that of nickel by a triplet-F term.

R. W. Lunt.

Arc spectrum of copper. P. K. Kichlu (Indian J. Physics, 1927, **1**, 401—412).—The arc spectrum of copper, recently analysed by a number of investigators, is discussed. Several new lines, obtained with an arc of current 20—30 amp., are also described.

M. S. Burr.

Lengths of enhanced lines of metals excited in various media and lines of constant wave-number differences among enhanced lines of bismuth and lead. M. Miyanishi (Mem. Coll. Sci. Kyoto, 1927, **10**, 263—272).—The spark spectra of copper, zinc, aluminium, lead, bismuth, chromium, manganese, and nickel have been produced in atmospheres of hydrogen, water vapour, nitrogen, oxygen, chlorine, bromine, and iodine. The changes which occur in the appearance of enhanced lines provide a method for classifying lines into spark, super-spark, and arc spectra. In hydrogen, the lengths of super-spark and super-super-spark lines were much greater than in the air spark; in water vapour the increase in length was small; in nitrogen and oxygen no change was observed. In an atmosphere of halogen spark lines were enhanced but super-spark lines de-

creased in length and intensity. The shortening of super-spark lines with change in medium occurred in the order hydrogen (longest lines), water vapour, nitrogen, oxygen, halogen. Lines having constant wave-number differences are recorded among the enhanced lines of lead and bismuth.

R. A. MORTON.

Instantaneous spectrograms of copper, silver, and gold. H. NAGAOKA, D. NUKIYAMA, and T. FUTAGAMI (Proc. Imp. Acad. Tokyo, 1927, **3**, 319—323; cf. this vol., 809).—The spectral lines produced by the passage of a heavy disruptive discharge through electrodes of the above metals are recorded. The general character of the lines is similar in each case, and is not greatly influenced by the nature of the gas in which the electrodes are. R. CUTHILL.

Instantaneous spectrograms of zinc, cadmium, and mercury. H. NAGAOKA, D. NUKIYAMA, and T. FUTAGAMI (Proc. Imp. Acad. Tokyo, 1927, **3**, 324—329).—The spectral lines produced by the passage of a heavy discharge through electrodes of the above metals are recorded. With mercury there are two distinct stages of emission, and there are some indications of a similar phenomenon with the two other metals also. R. CUTHILL.

Instantaneous spectrograms of boron, aluminium, and thallium. H. NAGAOKA, D. NUKIYAMA, and T. FUTAGAMI (Proc. Imp. Acad. Tokyo, 1927, **3**, 330—333).—The spectral lines observed when a disruptive discharge is passed through specimens of the above metals are recorded. With thallium, the nature of the gas surrounding the electrodes influences reversal, particularly in respect of divergence.

R. CUTHILL.

Structure of the spectra of krypton and xenon. J. C. MCLENNAN and R. RUEDY (Nature, 1927, **120**, 333).—There is selective absorption of spectral lines of krypton and xenon when a weak electrical discharge is passed through the gas, examples of lines absorbed being 7601, 7854, 8104, 8112 Å., and 8231, 8819 Å., respectively. Analysis of the xenon spectrum also indicates that the structure of the spectra of krypton and xenon corresponds with that of the spectra of neon and argon. A. A. ELDRIDGE.

Electric furnace spectra of yttrium, zirconium, and lanthanum. A. S. KING and E. CARTER (Astrophys. J., 1927, **65**, 86—107).—The temperature classifications of 451 yttrium, 858 zirconium, and 695 lanthanum lines between 2808 and 7882, 2792 and 8305, and 2799 and 8347 Å., respectively, are tabulated, temperatures of 2000—2800° being employed. The lanthanum spectrum contains a large number of close doublets, and some triplets, previously regarded as single lines. A. A. ELDRIDGE.

Series spectra of silver-like atoms. R. J. LANG (Proc. Nat. Acad. Sci., 1927, **13**, 341—346).—The identification of the first members of the four ordinary series for In III and Sn IV has been completed (cf. Carroll, A., 1926, 214) and the members for Sb V have been identified. The term values of these and other series were determined. The first principal pair of lines in Te VI were also located.

S. K. TWEEDY.

Series in the spectrum of trebly-ionised tin (Sn IV). K. R. RAO (Proc. Physical Soc., 1927, **39**, 408—416).—The spectrum of tin exhibits regularities ascribed to Sn IV, and pairs of sharp and diffuse series are shown to converge to a common limit with a sixteen-fold value of the Rydberg constant. The fundamental and super-fundamental series doublets are also indicated, and term values are obtained from the related system of members by assuming a value for the G term. The lines in the tin spark spectrum have been measured with an accuracy of about 0·05 Å.

R. A. MORTON.

Spark spectrum of cæsium. G. BALASSE (J. Phys. Radium, 1927, [vi], **8**, 311—320).—The spark spectrum of cæsium produced by the electrodeless discharge has been studied. According to the method of E. and L. Bloch (A., 1923, ii, 350), the lines of the spark spectrum can be divided into two groups depending on the conditions of excitation. Arc lines belonging to the series $1s—md$ have been recognised for the first time, and can be definitely distinguished by their general aspect and by their relation to a continuous spectrum which is also formed at temperatures above 200°. As a part of the spark spectrum of the lower order, lines forming multiplets and extending from the ultra-violet region to 3200 Å., establish, in confirmation of the work of Sommer (A., 1925, ii, 4), an analogy between the spark spectrum of cæsium and those of neon and xenon. The lines observed are tabulated. L. S. THEOBALD.

Forbidden line of mercury at 2270 Å. in absorption. (LORD) RAYLEIGH (Nature, 1927, **120**, 295).—The forbidden line 2270 Å. has been observed in absorption, although the range of conditions for observation is very limited. Hence direct transition from the normal to the metastable excited state of the mercury atom can sometimes occur (cf. this vol., 607). A. A. ELDRIDGE.

Explanation of the incomplete polarisation of mercury resonance radiation. W. A. MACNAIR and A. ELLETT (Proc. Nat. Acad. Sci., 1927, **13**, 583—584).—Whenever the theories of Breit and Heisenberg predict 100% polarisation of resonance radiation, $1^1S_0—2^3P_1$, and smaller values are observed, the depolarisation is shown to be due to the peculiar behaviour of the −0·0256 Å. component.

R. A. MORTON.

Production of characteristic X-rays by electronic impact. L. H. THOMAS (Proc. Camb. Phil. Soc., 1927, **23**, 829—831).—Theoretical. The expression obtained by Rosseland (Phil. Mag., 1923, [vi], **45**, 65) connecting the ionisation energy of an electron in an atom and kinetic energy of an electron which removes it, is modified by taking into account the velocity of the core electron in its orbit and the increased velocity of the impinging electron due to the atomic field. The modified formula gives better agreement with experimental results.

W. E. DOWNEY.

Discontinuities in the absorption of X-rays by aluminium (the so-called J-phenomenon). O. GAERTNER (Physikal. Z., 1927, **28**, 493—502).—Both the experimental data regarding Barkla's J-phenomenon and the theories put forward to interpret it

are discussed critically (cf. A., 1926, 217, 447, 987). An attempt has been made to repeat the experiments of Barkla and Watson (this vol., 3) but similar results could not be obtained. R. A. MORTON.

Absorption of *X*-rays of long wave-length. L. H. MARTIN (Proc. Camb. Phil. Soc., 1927, **23**, 783—793).—The mass absorption coefficients of iron, nickel, copper, and aluminium over a wave-length range 0·705—1·932 Å. have been measured. Homogeneous beams were obtained by crystal reflexion and the absorption coefficients measured by the direct method. For iron, nickel, and copper, when the *X*-rays absorbed lie in the range on the short wave-length side of the respective *K*-absorption discontinuities, the mass absorption coefficients are represented by a relation of the form $\mu/\rho=k_1\lambda^{2\cdot8}$ (k_1 a constant). On the long wave-length side of the *K*-discontinuities, and for aluminium throughout the entire wave-length range, the absorption coefficients are given by $\mu/\rho=k_2\lambda^3$ (k_2 a constant). W. E. DOWNEY.

Simple radioactive method for the photographic measurement of the integrated intensity of *X*-ray spectra. W. T. ASTBURY (Proc. Roy. Soc., 1927, **A**, **115**, 640—657).—Details are given of an easily constructed photometric arrangement, in which the photographic plate is replaced by a carbon print, the light by α-rays, and the light-sensitive cell by a simple α-ray electroscope. This radioactivity photometer has been applied to the determination of the intensity distribution in *X*-ray crystal photographs, and, with suitable adjustment, it may possibly be made to integrate the *X*-ray intensity of a crystal reflexion after the manner of the Bragg ionisation-spectrometer. The apparatus has been used to find the intensity ratio Cu$K\alpha/K\beta$. In *X*-ray photographs of the muscovite mica cleavage plane, 1st order : 2nd order : 3rd order=66 : 31 : 100, and the ratio Cu$K\alpha$/Aβ is 6·2 (corrected for absorption). A further test with a double-wedge photograph of the 3rd order $K\alpha$ mica line gave very satisfactory intensity values for the seven steps of the wedge. The apparatus may be made to give a curve showing a relation between *X*-ray intensity and α-ray intensity which is approximately linear through the origin, and the application of this property to the determination of the integrated intensity of *X*-ray spectra is discussed. The method of preparing the carbon tissues for the radioactivity photometer is described.

L. L. BIRCUMSHAW.

Critical *L*-absorption of silver. G. KELLSTROM (Z. Physik, 1927, **44**, 269—278).—The δ values characterising the critical *L*-absorption of silver have been determined using the technique of Molin and Jonsson (this vol., 286). The δ values have been obtained from the ratio of values of the constant *A* in the equation for the true absorption coefficient τ, $\tau=A\lambda^c$; thus $\delta_{L_3}-A_{L_2}/A_{L_1}$. The following values have been obtained : $\delta_{L_1}=3\cdot17$, $\delta_{L_2}=1\cdot47$, $\delta_{L_3}=1\cdot25$.

R. W. LUNT.

Term structure and Zeeman effect of the arc spectrum of tin. J. B. GREEN and R. A. LORING (Proc. Nat. Acad. Sci., 1927, **13**, 347—350).—A preliminary paper in which the term structure of the arc spectrum of tin is analysed. The lowest set of energy levels is ^3P. The Zeeman effect is determined for several lines and discussed briefly.

S. K. TWEEDY.

Zeeman effect and structure in the spark spectra of tin. J. B. GREEN and R. A. LORING (Proc. Nat. Acad. Sci., 1927, **13**, 492—495).—Certain Zeeman patterns of tin are found to arise from combinations of doublet terms, and from combinations either between triplet terms or between triplet and singlet terms, the two types belonging respectively to the spectra of singly-ionised and doubly-ionised tin. The following lines are classified: $^2P_1{}^2S_1$, 6843·81; $^2P_1{}^2D_2$, 5332·91; $^2P_2{}^2S_1$, 6453·15; $^2P_2{}^2D_2$, 5596·69; $^2P_2{}^2D_3$, 5562·74.

Several lines in the spectrum of doubly-ionised tin have been arranged into a $^3P^3D$ multiplet and a $^3P^3S$ multiplet. The 4618 line is designated $^3P_0{}^3S_1$. The lines 3765, 3860, 3963, and 4216 have Zeeman effects like those due to combinations between ^2P and ^2S terms and are probably due to trebly-ionised tin. R. A. MORTON.

Compton effect with bound electrons. Observations with cloud-chamber photographs in argon. F. KIRCHNER (Ann. Physik, 1927, [iv], **83**, 969—976).—Wilson cloud-chamber photographs indicate that Compton recoil electrons in argon exhibit photo-emission of the second kind. When a sufficiently strongly bound electron is emitted as a scattering electron, an emission similar to the photo-emission along electron tracks recorded by Auger (A., 1925, ii, 175, 618, 730) is observed. The frequency with which the emission of two electrons which leads to scattering occurs is much smaller (about 8%) than that in the analogous absorption process (83%); this follows naturally from the fact that the scattering intensity varies as the number of electrons, whereas the influence of the most strongly bound *K*-electrons predominates greatly in the absorption process. The *K*-fluorescence for argon is the same for the hard (0·13 Å.) *X*-rays used as for the soft rays used by Auger. The photo-emission is quite unsymmetrical at the wave-length used, the mean emission angle being 73° from the ray direction. The ranges and direction-distributions for 0·13 Å. are given for recoil electrons in argon. R. A. MORTON.

Schrodinger's theory and the ionisation potential of helium. G. W. KELLNER (Z. Physik, 1927, **44**, 91—112).—The ionisation potential of helium in volts has been calculated as the difference between the energy content in volts of the normal state (1*S*) as given by Schrodinger's differential equation and the ionisation potential of singly-ionised helium, 54·9 volts. The value so obtained, 20·3 volts, is in good agreement with that computed by Unsöld by a different method. R. W. LUNT.

Energy relationships and ionisation potentials of atoms of the first row of the periodic table in all stages of ionisation. R. A. MILLIKAN and I. S. BOWEN (Proc. Nat. Acad. Sci., 1927, **13**, 531—535).—All lines between 2000 and 200 Å. emitted by atoms in the first row of the periodic table, in all stages of stripping, are now identified, even the structure of the spectra being accounted for by the Russell–Pauli–Heisenberg–Hund rules. This makes it pos-

sible to extend the Moseley diagrams into the region of low atomic numbers. Instead of following Moseley's procedure of plotting the square root of emitted frequencies against atomic number, it is better to present the diagram as the relation between atomic number and the square root of the frequencies of energy levels, *e.g.*, for stripped atoms (one-electron systems) the energies, spectroscopically determined, necessary to remove an electron from the $2p$ orbit of the stripped atoms from lithium through carbon. Similar lines are obtained by plotting the observed energies necessary to remove an electron from the $2p$ orbit of a two-electron system, a three-electron system, etc. The best way of considering the extension of the Moseley diagram from neon down to lithium is the somewhat irregular line connecting points denoting the energy necessary to detach a p electron from a neutral atom, *i.e.*, a sequence of corresponding energy levels in neutral atoms. It is pointed out that the normal oxygen atom can be ionised in twenty-five different ways each representing an ionisation potential different from all the others. The term is therefore without exact meaning unless defined, *e.g.*, as the energy corresponding with the passage from the most stable state of the atom to the most stable state of the ion. The above definition leads to the following values in volts: lithium 5·371, beryllium 9·50, 18·141; boron 8·34, 24·2, 37·786; carbon 11·3, 24·289, 45·5, 64·23; nitrogen 14·494, 29·56, 47·2; oxygen 13·565, 34·999, 54·8, 77·0; fluorine 16·9, 82·3; neon 21·482.

R. A. Morton.

Precision measurement of e/m_0 by the method of H. Busch. F. Wolf (Ann. Physik, 1927, [iv], **83**, 849—883; cf. Busch, Physikal. Z., 1922, **23**, 438).—Busch's method has been improved. The mean of 70 determinations of e/m_0 is $(1{\cdot}767_9 \pm 0{\cdot}0018) \times 10^7$ e.m.u. The maximum error is $\pm 0{\cdot}2\%$ and the mean error about 0·07%. W. E. Downey.

Excitation of high-velocity electrons. E. G. Dymond (Proc. Camb. Phil. Soc., 1927, **23**, 804—810).—The visible helium spectrum has been excited by means of high-velocity electrons. The variation in intensity of the various lines due to excitation by electrons of different velocities was measured. The bearing of these results on the various theoretical views of excitation is discussed. W. E. Downey.

Electron velocities in the normal and selective photo-electric effect. F. Wolf (Ann. Physik, 1927, [iv], **83**, 1001—1053).—The velocity of electrons liberated in the selective photo-electric effect, using wave-lengths from 365 to 546 μμ on potassium–sodium alloy, is substantially the same as the velocity for the normal effect, although the numbers of electrons liberated in the two cases differ enormously. The electron velocity varies with the frequency of the light in exactly the same way for the selective as for the normal effect, a conclusion valid for a large range of angles given on the one hand by the normal to the irradiated surface and the direction of electron release, and on the other hand by the emergence-direction and the electric vector of the light for the selective effect. Although the electron velocity is substantially the same for the two effects, the values for the selective effect are very slightly (0·02—0·03 volt) higher than those for the normal effect. The difference appears to be real. The breadth of the velocity-range increases steadily with the period of the light for the selective effect, but a maximum is shown at 400 μμ for the normal effect. The gradual decrease in photo-electric sensitivity which occurs with time progresses more rapidly for the selective than for the normal effect. The contact *P.D.* between the potassium–sodium alloy and brass has been specially investigated and has been shown to rise at first rapidly from 1·7 to 2·1 and then more slowly to about 2·6 volts. Approximate values for the velocities of electrons leaving the surface have been calculated in absolute units. Electron velocities and frequencies are linearly related for both effects as investigated. R. A. Morton.

Variation in the velocity distribution of photo-electric electrons with outgassing and gassing processes with palladium and platinum. W. Bennewitz (Ann. Physik, 1927, [iv], **83**, 913—940).—The photo-electric properties of palladium and platinum have been determined for a considerable number of samples of pure metal foil differing only in respect of gas content. The outgassing process was interrupted at various stages and finally carried as near to completion as possible and at the other end of the scale the metal was left in contact with oxygen, hydrogen, or air for one night. Values for the following magnitudes were obtained in each case: photo-electric sensitivity, maximal volt velocity (voltage necessary to reduce the velocity of the fastest electrons to zero), mean volt velocity (a magnitude taking into account the velocity distribution), contact *P.D.*, and the long-wave limit (threshold). If the values were plotted in the same order of samples the variation of each magnitude followed a qualitatively similar course; the results were throughout in agreement with Einstein's equation. In three sets of experiments the electron velocity when the number of electrons liberated reached a maximum differed by about the same amount from the maximal velocity. With palladium there are two maxima in the velocity distribution curves, one predominating at small sensitivity values and the other steadily increasing in importance as the sensitivity increases. Platinum, on the other hand, exhibits only a small shift in the maximum (towards the side of maximal velocity) with increasing sensitivity. R. A. Morton.

Space distribution of the photo-electrons ejected by *X*-rays. E. C. Watson (Proc. Nat. Acad. Sci., 1927, **13**, 584—588).—The theory of nuclear scattering, together with the assumption that the electrons all start from the parent atom in the same direction, explains in a satisfactory way all the details of the observed space distribution of the photo-electrons ejected by *X*-rays. R. A. Morton.

Surface layers on tungsten produced by active nitrogen. C. Kenty and L. A. Turner (Nature, 1927, **120**, 332).—A clean tungsten surface at a dull-red heat, if placed in an atmosphere of nitrogen activated either by a condensed discharge or by electron bombardment at more than 22 volts, appears to become covered with a layer of nitrogen of the

order of one atom deep, and the surface is cooled. At relatively high temperatures the layer is probably so unstable that only a small fraction of the surface can be covered at any moment. The flashing of a covered filament in the neighbourhood of a clean filament causes the production of a layer on the latter. It is suggested that active nitrogen may be produced by the bombardment of gaseous nitrogen with 22-volt electrons. A. A. ELDRIDGE.

Total energy of binding of a heavy atom. E. A. MILNE (Proc. Camb. Phil. Soc., 1927, **23**, 794—799; cf. Thomas, this vol., 290).—Theoretical. Thomas' differential equation for the average field inside a heavy atom is analogous to Emden's equation for the polytropic equilibrium of a star. Using this analogy, the total electrostatic energy, and hence the total energy of binding, of an atom built on Thomas' model is calculated. The total energy is found to be proportional to $N^{7/3}$, where N is the atomic number. W. E. DOWNEY.

Total ionisation due to the absorption in air of slow cathode rays. J. F. LEHMANN and T. H. OSGOOD (Proc. Roy. Soc., 1927, **A**, **115**, 609—624).—Experiments were made to measure the average ionisation produced by the absorption in air of an electron with definite initial energy. A stream of electrons obtained from a tungsten filament charged to a definite potential was passed through an ionisation chamber, the initial energy of the electrons ranging from 200 to 1000 electron-volts. The ratio of ionisation current to electron current gave the average number of ions produced by the absorption of an electron. The average energy used up in the formation of a pair of ions is determined by dividing the initial energy of the electrons by the number of positive ions per electron for complete absorption. The average ionisation per electron for complete absorption was found to be proportional to the initial energy of the electrons, and the average energy expended in the formation of a pair of ions is 45 electron-volts in air. L. L. BIRCUMSHAW.

Absorption of slow cathode rays in various gases. J. F. LEHMANN (Proc. Roy. Soc., 1927, **A**, **115**, 624—639; cf. preceding abstract).—The total ionisation due to the absorption of slow cathode rays has been measured in helium, argon, hydrogen, nitrogen, and carbon dioxide. The average ionisation per electron, for complete absorption, was found to be proportional to the initial energy of the cathode ray. The rate of absorption of electronic energy required to correlate the present measurements of the total ionisation and the measurements of the ionisation per unit path by Compton and Van Voorhis (A., 1926, 1074) and by Kossel (Ann. Physik, 1912, [iv], **37**, 393) has been computed. Concordant results were obtained by estimating the range of the cathode rays in air from the rate of absorption of electronic energy, and from the pressure necessary to absorb the rays within the length of the ionisation chamber. L. L. BIRCUMSHAW.

Ionisation efficiency of ultra-violet light in cæsium vapour. E. M. LITTLE (Physical Rev., 1927, [ii], **30**, 109—118).—The efficiency of ionisation (Einstein's probability of absorption coefficient) in cæsium vapour at 166° increases from $0{\cdot}17\times10^{-16}$ ion per atom per erg at 3345 Å. to $3{\cdot}4\times10^{-10}$ at 3135 Å. (±5% relative, 25% absolute). The theoretical threshold is at 3184 Å. For shorter wave-lengths the value is minimal ($1{\cdot}2\times10^{-10}$) at 2800 Å. A surface of cæsium–gold alloy is very active photo-electrically. A. A. ELDRIDGE.

Mobilities of ions in acetylene–hydrogen mixtures. L. B. LOEB and L. DU SAULT (Proc. Nat. Acad. Sci., 1927, **13**, 510—516; cf. A., 1926, 219, 449).—Erikson (A., 1926, 989) found that neither the positive nor the negative ion in acetylene showed a change in mobility with age within time intervals greater than 0·002 sec., whilst at the same time the mobility was slightly greater for the negative than for the positive ion. The initial ions, positive and negative, were regarded as unimolecular. Carefully purified acetylene shows mobilities of 0·787 and 0·844 cm./sec. per volt/cm., for positive and negative ions respectively (0·708 and 0·769 on the accepted scale and 0·846 and 0·906 on the true absolute scale). Wahlin (A., 1922, ii, 608) found the value 1·15 for the negative ion on the absolute scale. It is considered probable that the positive and negative ions in acetylene, once formed, have the same mobility of 0·846 on the absolute scale. The same is probably true for hydrogen. Cases in which the negative ion shows a higher mobility are explained by the existence of free electrons as carriers in the early part of the life of the ion. Within experimental error, the results for acetylene–hydrogen mixtures agree with the law of mixtures for non-reacting gases. There is no evidence for a very rapid ageing of ions in acetylene, nor for clustering effects. R. A. MORTON.

New mass-spectrograph and the whole number rule. F. W. ASTON (Proc. Roy. Soc., 1927, **A**, **115**, 487—515).—The construction of the latest form of mass spectrograph is described, and details are given relating to the discharge tube, the slit system, the electric field, the magnetic field, the camera, and the vacuum technique. The photographed spectrum is nearly 16 cm. long and includes more than one octave of mass, the dispersion scale varying, for a change of mass of 1%, from 1·5 mm. at the most deflected end to 3·0 mm. at the least deflected end. Three methods of measuring the mass ratios are described, including the method of coincidences, which consists in photographing in virtual coincidence the lines due to an unknown mass x and a known mass a by means of the application of suitable potentials the ratio of which differs by about 0·5% from the expected ratio $x:a$ (the magnetic field being kept constant). The intervals between the lines obtained in this way are measured with a Poynting's tilting plate micrometer, and converted into intervals of mass by multiplying by the dispersion constants calculated for the mid-point of each interval. The unit of mass chosen is the neutral oxygen atom O^{16}, and the masses measured in the mass-spectrograph are corrected for the mass of the electron. Details are given of recent work on hydrogen, helium, boron, carbon, nitrogen, fluorine, neon, phosphorus, sulphur, chlorine, argon, arsenic, bromine, krypton, tin, iodine, xenon, tungsten, and mercury, and measurements of

the masses (correct to 1 or 2 parts in 10,000) of 51 types of atom contained in the above elements have been made and are tabulated on the oxygen scale. The isotopic constitution of mercury has been settled, new isotopes have been discovered in tin and sulphur, and the two doubtful isotopes of xenon confirmed. The relations between tin and xenon previously announced have been found to be incorrect. Values for Li^6 and Li^7 are obtained by a re-calculation of Costa's results. A discussion is given of the "packing fraction," *i.e.*, the divergence of the atom from the whole number rule divided by its atomic mass, which is a measure of the gain or loss of mass per proton when the nuclear packing is changed from that of oxygen to that of the atom in question. Theoretically, this is regarded as being due to the fact that the protons and electrons may be so closely packed that their electromagnetic fields interfere, and a fraction of the combined mass is destroyed, whereas outside the nucleus, the distances between the charges are too great for this to occur. If the packing fractions of the atoms, expressed in parts per 10^4, are plotted against their mass numbers, it is found that, with the exception of light atoms of even atomic number, all lie roughly on a single curve which descends from hydrogen 77·8 to a minimum of −9 in the region of bromine. It then ascends again and recrosses the zero line in the region of mercury. The packing fractions of the light atoms of even atomic number lie well below this curve and approximate to a branch rising less steeply to helium 5·4.

L. L. Bircumshaw.

Revision of the at. wt. of yttrium. Analysis of yttrium chloride. II. O. Honigschmid and A. von Welsbach (Z. anorg. Chem., 1927, **165**, 284—288).—Yttrium chloride containing no spectroscopically detectable quantity of other rare-earth metals has been converted into silver chloride, giving as the most probable value of the at. wt. of yttrium the value 88·925 (±0·002). H. F. Gillbe.

Revision of the at. wt. of dysprosium. Analysis of dysprosium chloride. O. Honigschmid and A. von Welsbach (Z. anorg. Chem., 1927, **165**, 289—296).—Dysprosium sulphate, containing only about 0·1% of holmium, has been converted into the chloride, and analysed by conversion into silver chloride. Taking the at. wt. of silver as 107·88 and that of chlorine as 35·457, the most probable figure for the at. wt. of dysprosium is 162·46. H. F. Gillbe.

Tracks of α-particles through silver bromide in gelatin. L. Myssovski and P. Tschishov (Z. Physik, 1927, **44**, 408—420).—By developing specially prepared plates of film thickness greater than 50 μ after they have been exposed to α-particles, records have been obtained of the tracks of these particles in the gelatin film. The method can be adapted to a continuous registration of the emission of α-particles from a source by means of a moving film.

R. W. Lunt.

Electrical method of counting α- and H-particles. H. Greinacher (Z. Physik, 1927, **44**, 319—325).—The use of an oscillagraph is described to give continuous photograph records of the fluctuations in the plate current in the last valve in the amplifier which, in the author's technique (A., 1926, 553), is employed for the detection and counting of α- and of H-particles. R. W. Lunt.

High-speed β-rays from radioactive substances. D. K. Yovanovitch and J. d'Espine (J. Phys. Radium, 1927, [vi], **8**, 276—283; cf. A., 1925, ii, 732).—By using the magnetic spectrum method with a direct deviation apparatus, high-speed β-rays, or groups of rays, with the following values of HR (R the radius of the path of a ray in a magnetic field of strength H) have been detected: mesothorium-2 28,000, 21,000, 16,700, 10,000, and 6800; thorium-B+C 18,000, 11,000, 6800, and 5480; radium-B+C 27,000—15,000, 10,700, and 9960 gauss-cm. The energy of some of these rays is of the same order as that of α-particles. R. Cuthill.

Absorption of β-particles by matter. G. Fournier (Ann. Physique, 1927, [x], **8**, 207—277).—An extended account of earlier work (cf. A., 1925, ii, 622; 1926, 880). R. A. Morton.

Polarisation of atomic nuclei and its relation to the origin of γ-rays. W. Kuhn (Z. Physik, 1927, **44**, 32—35).—From a consideration of the order of magnitude of the electric moments of atoms, and of the frequency of γ-rays it is concluded that the latter are associated with H- or He-particles, and not with electrons, in the nucleus. R. W. Lunt.

Transmutation of mercury into gold. A. Piutti and E. Boggio-Lera (Rend. Accad. Sci. Fis. Mat. Napoli, 1925, [iii], **31**, 194—198).—See A., 1926, 699.

Interstellar calcium. O. Struve (Astrophys. J., 1927, **65**, 163—199).

Theory of the isotope effect in line spectra. G. Joos (Ann. Physik, 1927, [iv], **83**, 1054—1064).—The effect of nuclear mass on term values for higher atoms has been calculated on the basis of the scheme: nucleus, core, electrons. For deep orbits, the mass effect may be several times that valid for hydrogen-like systems, inasmuch as the dimensions of the core are little influenced, whereas for outer orbits the mass effect can be only a little greater or a little less than the hydrogen effect. R. A. Morton.

Free path and quantising of molecular translations. W. Heitler (Z. Physik, 1927, **44**, 161—169).—By applying Schrödinger's wave mechanics to the free electrons in a solid grating the characteristics of molecular spectra have been derived. The wave-length variation of the energy density of the radiation is shown to be equivalent to black-body radiation on which is superposed a weak fluctuation periodic with respect to wave-length. R. W. Lunt.

Quantum mechanics of linear oscillators. E. H. Kennard (Z. Physik, 1927, **44**, 326—352).—The dynamics of an electron moving in a uniform magnetic or electric field have been analysed by quantum mechanics by assuming that the wave packets of Schrödinger may be identified with the discontinuous probabilities of classical quantum theory. R. W. Lunt.

Quantum mechanics of degenerated gases. P. Jordan (Z. Physik, 1927, **44**, 473—480).—Mathematical. R. W. Lunt.

New derivation of quantum mechanics. II. P. JORDAN (Z. Physik, 1927, 44, 1—25).—Mathematical. R. W. LUNT.

Electron as a vector wave. C. G. DARWIN (Proc. Roy. Soc., 1927, A, 116, 227—253).—Mathematical.

Energy exchange according to the wave mechanics. E. SCHRODINGER (Ann. Physik, 1927, [iv], 83, 956—968).—Mathematical.

Characteristic values in the limiting value problem of wave mechanics. K. BECHERT (Ann. Physik, 1927, [iv], 83, 905—912).

Photographic method of spectro-photometry in the red and infra-red. A. L. SCHOEN (Brit. J. Phot., 1927, 74, 475—477).—See this vol., 394.

Hydrogen band spectrum : new band systems in the violet. O. W. RICHARDSON (Proc. Roy. Soc., 1927, A, 115, 528—548).—A system of bands is described which includes much of the strength of the secondary hydrogen spectrum when this is excited by a sharply limited electron stream on the H_2 molecule. A provisional arrangement of the bands is suggested. There are two band systems (*A* and *B*), the first very strongly developed. The nucleus of the first band is at 21573·81. Only the *Q* branches of the bands are given, although there are indications that *P* and *R* branches exist also. The *Q* branch of the $1\longrightarrow0$ band is the series $20Q(m)$ of Richardson and Tanaka (A., 1925, ii, 909). All the bands are degraded towards the violet, and each line is accompanied by a fainter component on the long-wave side of it. The final states of the present bands appear to be the same as the initial states of the Lyman bands in the far ultra-violet. The lines with their properties and the initial and final vibration term differences are tabulated for both the *A* and the *B* bands. L. L. BIRCUMSHAW.

Structure of certain bands in the visible spectrum of boron monoxide. F. A. JENKINS (Proc. Nat. Acad. Sci., 1927, 13, 496—503).—The bright light emitted by boron trichloride in active nitrogen is due to boron monoxide. The spectrum consists of three electronic systems : α-bands extending from the red to the near ultra-violet and showing quadruple heads shaded towards the red, β-bands in the ultra-violet with single heads also shaded towards the red, and a combination system. The α-bands have now been photographed under high dispersion and their structure has been analysed. In each complete band there are two origins with four series proceeding from each. The interpretation follows the theoretical lines laid down by Mulliken (A., 1926, 452, 1079) and Hund (A., 1926, 657). Band systems for two boron isotopes have been established, and the moment of inertia for the vibrationless molecule has been computed for $B^{11}O$ and $B^{10}O$. As expected, the latter is much the smaller value, but the nuclear separation is identical for the two isotopic molecules. The structure of the α-bands is very similar to that of the CO^+ comet-tail bands. The analogy also extends to the β- and combination bands which resemble the negative Deslandres group of carbon and the Baldet–Johnson combination bands. R. A. MORTON.

Spectrum of carbon dioxide. G. W. FOX, O. S. DUFFENDACK, and E. F. BARKER (Proc. Nat. Acad. Sci., 1927, 13, 302—307).—The wave-lengths and intensities of most of the band edges in the absorption spectrum of carbon dioxide (which extends from 2800 to 5000 Å.) are recorded. The continuous flow method (A., 1925, ii, 1017) was employed. Several strong band groups occur in which two or more band systems overlap. During the electrical discharge through carbon monoxide the reaction $2CO \longrightarrow CO_2+C$ occurs to some extent. S. K. TWEEDY.

Electronic states and band spectrum structure in diatomic molecules. V. Bands of the violet CN ($^2S\longrightarrow{}^2S$) type. R. S. MULLIKEN (Physical Rev., 1927, [ii], 30, 138—149).—Theoretical intensity formulæ applicable to bands of the violet CN($^2S\longrightarrow{}^2S$) type are obtained, and two *Q* branches are predicted. Predicted intensity relations appear to be confirmed in the CaH, N_2^+, and violet CN bands. The nature of the energy differences between the $2S$ terms corresponding with parallel and anti-parallel orientations of the electron spin vector is considered. It is suggested that the ^2S state in the *B* bands of CaH is of an unusual type. A. A. ELDRIDGE.

Electrical properties and nature of active nitrogen. P. A. CONSTANTINIDES (Physical Rev., 1927, [ii], 30, 95—108).—The electrical behaviour of glowing active nitrogen indicates that the conductivity between electrodes in the gas is not due to ions drawn from the discharge chamber, but to high-velocity electrons emitted from the electrode surfaces, either photo-electrically or by direct action of the active nitrogen on the metal. The glow is unaffected by helium, but is extinguished by nitrogen, hydrogen, and oxygen in order of increasing effect. Active nitrogen does not ionise hydrogen or mercury vapour, but appears to ionise iodine vapour. It is therefore considered that active nitrogen is molecular nitrogen in a metastable state with energy between 9·4 and 10·4 volts. A. A. ELDRIDGE.

β-Bands of nitric oxide. I. Measurements and quantum analysis. F. A. JENKINS, H. A. BARTON, and R. S. MULLIKEN (Physical Rev., 1927, [ii], 30, 150—174).—Each complete band in the β-system of nitric oxide (2300—5300 Å.) consists of two sub-bands with *P*, *R*, and weak *Q* branches. The frequencies of the band lines are tabulated, as also are the combination differences in the (0, 10), (0, 11), and (1, 11) bands, mean values of $\Delta_2F(j)$ for various vibrational states, empirical coefficients in the rotational energy function, and the frequencies of band origins. The moment of inertia, I_0, and the internuclear distance, r_0, for the vibrationless molecules are evaluated as : $I_0'=(24{\cdot}80\pm0{\cdot}02)\times10^{-40}$ g.cm.^{2}, $I_0''=(16{\cdot}30\pm0{\cdot}02)\times10^{-40}$ g.cm.^{2}, $r'_0=1{\cdot}418\times10^{-8}$ cm., $r_0''=1{\cdot}150\times10^{-8}$ cm., I_0'' and r_0'' applying to the normal state of nitric oxide. Equations are given representing the frequencies of all observed lines, and the vibration frequencies for infinitesimal amplitudes are determined. All constants derived for the final state of the β-bands apply equally well to that of the γ-bands. The ultra-violet O_2^+ bands and certain SiN bands, the structure of which re-

sembles that of the NO β-bands, are probably also $^2P \longrightarrow {}^2P$ transitions. A. A. ELDRIDGE.

β-Bands of nitric oxide. II. Intensity relations and their interpretation. H. A. BARTON, F. A. JENKINS, and R. S. MULLIKEN (Physical Rev., 1927, [ii], 30, 175—188).—If it is assumed that the effective temperature of the emitting molecules is about 47°, the observed relative line intensities are in essential agreement with those predicted by Honl and London's equations. The actual absence of lines expected to be missing if the electronic transitions are $^2P_1 \longrightarrow {}^2P_1$ and $^2P_2 \longrightarrow {}^2P_2$ is confirmed. The predicted relative intensities of the β-bands are, as regards their principal features, in agreement with the observed relative intensities. A. A. ELDRIDGE.

Ultra-violet absorption of natural and artificial crystals of sodium and potassium chlorides. R. HILSCH (Z. Physik, 1927, 44, 421—430).—The ultra-violet extinction coefficients of natural and artificial crystals of the chlorides of potassium and sodium have been determined from 4000 to 1800 Å. in order to determine the most satisfactory method for preparing crystals of high transmissibility. It is found that artificial sylvine is as good as the natural product, and that the most effective method of purification is to agitate a solution of potassium chloride with a few drops of ammonium sulphide; the solution is then separated from precipitated sulphides by a Zsigmondy ultrafilter. Specimens were obtained in which the band at 2740 Å. was negligible and in which the extinction coefficient did not reach 0·04 mm.$^{-1}$ until 1900 Å. The extinction coefficient of artificial sodium chloride crystals, similarly purified, did not exceed 0·01 mm.$^{-1}$ until 2400 Å., a result comparable with many specimens of rock salt. The extinction coefficient of artificial potassium bromide crystals is less than 0·1 mm.$^{-1}$ below 2400 Å., and that of rubidium chloride less than 0·02 mm.$^{-1}$ below 1900 Å. R. W. LUNT.

Banded structure in aluminium and copper. C. F. ELAM (Nature, 1927, 120, 259).—Preliminary observations with *X*-rays on aluminium and copper show that the banded structure in these metals does not always represent twinning on the octahedral planes of the crystal. A. A. ELDRIDGE.

Deflexion of streams of electrical dipole molecules in non-uniform electric fields. E. WREDE (Z. Physik, 1927, 44, 261—268).—The deflexion of direction suffered by streams of potassium iodide, thallium iodide, cæsium chloride, sodium iodide, and rubidium bromide vapours when subjected to the asymmetric electric field produced by a wire and plate electrode system (wire axis parallel to plane of plate) has been observed for potentials of the order of 10^4 volts and a wire-plate spacing of 0·8 mm. The deflexions observed correspond with electric moments of the order of 10^{-17} c.g.s.u. in agreement with the theoretical values computed by Born and Heisenberg (A., 1924, ii, 434). R. W. LUNT.

Rotation spectra of the hydrogen halides. M. CZERNY (Z. Physik, 1927, 44, 235—255).—The technique previously described (A., 1925, ii, 1024) has been extended to determine the absorption maxima of the hydrogen halides in the range 140—40 μ. The data now obtained show that the rotation spectra of these substances are the same in character; they conform with the general equation $\nu = \alpha m - \beta m^3$ within 0·1% for hydrogen chloride and hydrogen bromide, and within 0·3% for hydrogen fluoride and hydrogen iodide. Values of moments of inertia have been derived which are in good agreement with those calculated from data relating to the rotation-oscillation spectra. R. W. LUNT.

Structure of the calcium fluoride band 6087 Å. S. GOUDSMIT (Proc. K. Akad. Wetensch. Amsterdam, 1927, 30, 355—361).—Danjon's views are criticised and the suggestion is made that the line is formed from a group of bands the successive members of which are superimposed, and the lines of which coincide and thus present the appearance of a continuous band. H. F. GILLBE.

Spectroscopic studies on the complex cyanides of iron. II. The reaction between nitroprussides and alkalis. L. CAMBI and L. SZEGÖ (Atti R. Accad. Lincei, 1927, [vi], 5, 737—740).—The absorption band which develops at 4050 Å. when alkali is added to aqueous solutions of sodium nitroprusside is thought to be associated with the reaction $[Fe(CN)_5NO^-] + 2OH^- \rightleftharpoons [Fe(CN)_5NO_2]^{----} + H_2O$. The equilibrium constant of this reaction has been calculated from measurements of the extinction coefficients of 0·0008*M*-sodium nitro-prusside and from 0·012 to 0·8*M*-sodium hydroxide. R. W. LUNT.

Resonance power of some metallic salts in solutions irradiated by the filtered light of the mercury arc. A. ANDANT and E. ROUSSEAU (Compt. rend., 1927, 185, 202—204).—The resonance phenomena previously observed by the authors (this vol., 738) are not confined to manganese, but are exhibited also by salts of magnesium, sodium, potassium, and uranium. After an exposure of 4 hrs. the salts of magnesium, manganese, and uranium exhibited a reversible effect, whilst after 4—6 hrs. the photolytic effect ceased suddenly if a salt of a univalent metal was employed as resonator. J. GRANT.

Absorption spectra of mercury, cadmium, and zinc at high pressure. F. L. MOHLER and H. R. MOORE (J. Opt. Soc. Amer., 1927, 15, 74—81).—The absorption spectra of mercury, cadmium, and zinc vapours in the ultra-violet have been photographed at pressures up to several atm. The spectra show wide regions of continuous absorption with series of flutings and diffuse bands some of which have previously been observed in emission. The flutings are regarded as poorly resolved band systems of diatomic molecules in which the excited electronic state is much more stable than the normal state. The long duration of fluorescence is accounted for by assuming that the molecule is first raised to a high vibration state by absorption so that in consequence, by a collision of the second kind, it drops to a low vibration state with a very small emission probability. R. A. MORTON.

Spectrum of auric chloride. W. F. C. FERGUSON (Nature, 1927, 120, 298).—The spectrum of vapour from auric chloride, in a stream of active nitrogen,

consists of intermingled green bands, shaded towards the red. The strongest band heads comprise two systems given by: $\nu = 19113{\cdot}8 + 312{\cdot}0(n' + \frac{1}{2}) - 382{\cdot}8(n'' + \frac{1}{2}) - 0{\cdot}70(n' + \frac{1}{2})^2 + 1{\cdot}30(n'' + \frac{1}{2})^2$, and $\nu = 19238{\cdot}3 + 316{\cdot}3(n' + \frac{1}{2}) - 382{\cdot}8(n'' + \frac{1}{2}) - 1{\cdot}45(n' + \frac{1}{2})^2 + 1{\cdot}30(n'' + \frac{1}{2})^2$. The common final vibrational level is probably the normal state of the aurous chloride molecule. Weaker heads corresponding with $AuCl^{37}$ ($\rho = 0{\cdot}9768$) were observed, but the isotopes of gold ($\rho = 0{\cdot}9992$) were not evident. The following gold lines were observed: 4792·6, 3122·8, 3029·2, 2748·3, 2676·0, 2641·5, 2428·0, and 2352·7 Å.

A. A. Eldridge.

Bead spectra. H. L. Howes and (Miss) M. K. Slattery (J. Opt. Soc. Amer., 1927, **15**, 77—24; cf. this vol., 607).—The positions of the transformation bands of an element are approximately the same in all fluxes. Conditions in a bead favouring perfect solubility for a rare earth and complete transparency are not sufficient to yield bead spectra; there must also be a transformation. The use of double fluxes enables better control and retardation of the transformations.

W. E. Downey.

Infra-red absorption spectra of acetylene, ethylene, and ethane. C. F. Meyer and A. A. Levin (Proc. Nat. Acad. Sci., 1927, **13**, 298—302).—The infra-red absorption spectra of the above gases were investigated by means of a grating spectrometer. The bands reveal fine structure and intense central maxima (*Q* branches) occur on the ethylene curve at 10·5 μ and the acetylene curve at 13·7 μ; the latter curve also exhibits an alternation in intensity of lines which persists down to 7·5 μ, where the *Q* branch is entirely absent. Between 11·9 μ and 11·6 μ the absorption curve for ethane is irregular.

S. K. Tweedy.

Shift in a near infra-red absorption band of some benzene derivatives. J. Barnes and W. H. Fulweiler (J. Amer. Chem. Soc., 1927, **49**, 2034—2037).—The infra-red absorption band of benzene at 8741 Å. has its position shifted to the wave-lengths quoted in the following benzene derivatives: toluene, 8758; ethylbenzene, 8772; *o*-xylene, 8781; *m*-xylene, 8793; *p*-xylene, 8808; diethylbenzene (mixture of *m*- and *p*-), 8799; and mesitylene, 8844 Å. A progressive shift towards lower frequency thus occurs as methyl groups are added, the shift being affected also by the relative positions of the two methyl groups if present. With a cell 80 cm. in length benzene shows an absorption band at 7134 Å.

F. G. Willson.

Ultra-violet absorption spectra of *cyclo*hexene, ethyl ether, methyl *n*-amyl ether, and ethylene chlorohydrin. H. de Laszlo (J. Amer. Chem. Soc., 1927, **49**, 2106—2110).—A correction to the work of Smith and co-workers (this vol., 608). Ethylene chlorohydrin vapour has no appreciable absorption above 2250 Å. and the liquid exhibits continuous absorption below 2300 Å. Pure ethyl ether, also, shows no absorption above 2100 Å. Smith and his co-workers found these substances, in common with *cyclo*hexene and methyl *n*-amyl ether, to have the same absorption spectra as benzene and it is concluded, therefore, that their compounds were contaminated with benzene. The presence of 0·0001 mg. would suffice to give the results recorded; hence the necessity that the sample examined is absolutely pure. The theoretical conclusions of Smith and his co-workers are also adversely criticised.

S. K. Tweedy.

Absorption spectra of plant colouring matter of the flavone series. IV. Anthocyanin, catechin, and xanthone derivatives. T. Tasaki (Acta Phytochim., 1927, **3**, 1—19; cf. A., 1925, i, 1445).—The absorption spectra of the following derivatives of anthocyanin, catechin, and xanthone in 0·0001*M*-alcoholic solution have been determined for wave-numbers (λ^{-1} in cm.) from 1000 to 4500: pelargoninidin chloride, pelargonin chloride, cyanin chloride, cyanidin chloride; the reduction products of chrysin, apigenin, acacetin, luteolin, galangin, campherol, campheriol, campheritrin, morin, quercetin, quercitrin, rutin, myricetin, myricitrin; catechin, catechin pentamethyl ether, penta-acetylcatechin, flavanone, flavone, xanthone, xanthene, 1-hydroxyxanthone, 1 : 7-dihydroxyxanthone, gentisein, and *iso*gentisein.

R. W. Lunt.

Colour and molecular geometry. V. Search for a crucial test of colour theories. J. Moir (J.C.S., 1927, 1809—1823).—Absorption data for oxygen compounds of anthracene and naphthalene are examined in the light of the author's theory (A., 1924, ii, 641), and by utilising W. H. Bragg's figures for the size of the molecules, an explanation is found for the similarity of behaviour of 1-hydroxy- and 1 : 5-dihydroxy-compounds, the visible colour of the anthrols and symmetrical anthradiols, and the high colour of 9-hydroxy-, 2 : 9 : 10-trihydroxy-, 1 : 2 : 9 : 10-tetrahydroxy-, and 1 : 4 : 9 : 10-tetrahydroxy-compounds, and derivatives containing two adjacent hydroxyl groups. A critical survey of the theories of Stieglitz and Deslandres is given.

F. S. Hawkins.

Relation between fluorescence and phosphorescence in solid and in fluid media. S. I. Vavilov and V. L. Levschin (Z. Physik, 1927, 44, 539).—A reply to the criticisms and claims of Gaviola and Pringsheim (this vol., 810).

R. W. Lunt.

Luminescence of Grignard compounds in electric and magnetic fields, and related electrical phenomena. R. T. Dufford, (Miss) D. Nightingale, and L. W. Gaddum (J. Amer. Chem. Soc., 1927, **49**, 1858—1864).—The oxidation of certain Grignard compounds (in ethereal solution) in powerful magnetic fields emits non-polarised light (oxyluminescence) in the most intense parts of the field. The effect is probably mechanical and apparently due to the oxidation products being sufficiently paramagnetic to be attracted to the poles. In electric fields (1500 volts) a distinct type of non-polarised luminescence appears at one or at both electrodes, the brightness of which is independent of the brightness of the oxyluminescence. Those saturated Grignard compounds which Evans and Diepenhorst (A., 1926, 506) claim to be oxyluminescent are found to be non-luminous when oxidised in ethereal solution, and the effect of mass on the brightness of the luminescence suggested by these authors is considered to be not

conclusively demonstrated. The light emitted during electrolysis of ethereal Grignard solutions is not connected with oxyluminescence but is probably due to the formation of $MgBr_2,2Et_2O$, which becomes luminous on electrolysis, depositing highly active magnesium. The latter is useful for preparing in good yield Grignard reagents otherwise difficult to make. Cells prepared by the immersion of two dissimilar metal electrodes (*e.g.*, gold and silver) in an ethereal solution of a Grignard reagent have high temperature coefficients; the *E.M.F.* are very sensitive to radiation in the visible or near ultra-violet regions, and after illumination become periodic functions of time. The *E.M.F.* of the cell Mg|$MgBr_2,2Et_2O$ (satd. soln.)|MgEtBr (1·5*M*)|Mg is about 0·2 volt. S. K. TWEEDY.

Doppler effect in canal-rays in hydrogen and the Balmer series. W. STEUBING (Ann. Physik, 1927, [iv], **83**, 822—834).

Quantum theory of molecular hydrogen ions and Born-Lande repulsive forces. A. UNSOLD (Z. Physik, 1927, **43**, 563—574).—The energy of the molecular hydrogen ion has been calculated by considering the wave mechanics of the free ion. The method, although less exact than that of Schrodinger, leads to values of the sum of the first and second order perturbations which pass through a minimum at 2·8 volts in exact agreement with the value obtained by Burrau (Kgl. Danske Videnskab. Selsk. math.-fys. Medd., 1927, **7**, 14) using Schrodinger's analysis. The analysis is used to discuss the changes in the polarisation of ions. R. W. LUNT.

Work of evaporation of thermions. G. MICHEL (Z. Physik, 1927, **44**, 403—407).—An argument, based on Schottky's theory (*ibid.*, 1923, **14**, 63), is developed to show that the thermionic emission for any group of oxides in the periodic system can be expressed in the form $\Delta\phi b^2$—constant, where $\Delta\phi$ is the work of evaporation in volts, and b the shortest distance between two atoms in the grating of the emitting substance. The values of b have been obtained from *X*-ray measurements; for beryllium, magnesium, calcium, strontium, and barium oxides the value of $\Delta\phi b^2$ is approximately constant about a mean of 8·8; for silicon, titanium, zirconium, and thorium oxides about a mean of 14·1; and for boron, aluminium, scandium, and yttrium oxides about a mean of 15·9. R. W. LUNT.

Continuous interchange between ionic and electronic conduction. C. TUBANDT, E. RINDTORFF, and W. JOST (Z. anorg. Chem., 1927, **165**, 195—220).—The mechanism of the conduction process in the three forms of cuprous iodide has been studied. In the α- and β-forms the conduction is purely electrolytic, the cation alone being mobile; the γ-form exhibits a complete and continuous change from purely electronic to purely ionic conduction as the temperature rises from 240° to 390°, the ionic current being carried by the cuprous ion. The temperature-conductivity curve of pure cuprous iodide between 10° and 700° indicates clearly the m. p. and the transition temperature, but the α–β transition temperature is not evident. The increase of the conductivity of cuprous iodide produced by the presence of iodine is of a metallic nature. Cuprous bromide and chloride exhibit the same phenomena as γ-cuprous iodide.

Voltage–current curves cannot be applied to distinguish between ionic and electronic conductivity at high temperatures. H. F. GILLBE.

Absolute determination of the dielectric constant of water by the ellipsoid method. R. FURTH (Z. Physik, 1927, **44**, 256—260).—The dielectric constant of water has been determined in an alternating electric field of frequency 50 cycles per sec. by the absolute ellipsoid method; the value obtained is 77·6. R. W. LUNT.

Investigation of aqueous solutions of electrolytes by Furth's ellipsoid method. R. PECHHOLD (Ann. Physik, 1927, [iv], **83**, 427—456).—Fürth's ellipsoid method (A., 1925, ii, 631) for the determination of dielectric constants for well-conducting liquids has been refined so that the dielectric constants of electrolytes can be determined to within 2—3%. The frequency employed was 50 per sec. The dielectric constants of aqueous solutions of potassium, sodium, and lithium chlorides, sodium hydroxide, and hydrochloric acid have been plotted against concentration. The curves all exhibit an initial decrease in dielectric constant with increasing concentration, which reaches a minimum at a value depending on the electrolyte. As the concentration is further increased the curve begins to ascend until the dielectric constant for water is exceeded: beyond this point the curve becomes less steep and a saturation value is finally reached. The steepness of the descending branch of the curves for chlorides follows the order K^+, Na^+, Li^+, H^+, for the cations. The minimum dielectric constant is smaller in the same order. Sommer (Diss., Berlin, 1923) has determined the variation of dielectric constant with concentration for lithium and potassium chlorides by a method involving frequencies of 10^6 per sec. As his results are in good agreement it is concluded that over the concentration range 0—0·005*N* and the frequency range 50—10^6 per sec. the solutions tested show no marked dispersion. Hellmann and Zahn (A., 1926, 1193) on the other hand used frequencies of 3×10^8 per sec. and found the dielectric constant of water to be affected only to a minor degree by the presence of dissolved salts. The dispersion range of the dielectric constant must therefore lie between frequencies of 10^6 and 3×10^8 per sec. The observations are in agreement with the view that the ions exert a polarising action on the water dipole, but that the formation of complex ions is also a factor in determining the shape of the function $\varepsilon(c)$. The radius of the solute ion also appears to influence the shape of the curve. R. A. MORTON.

Temperature variation of the dielectric constants of glycerol and of aqueous solutions of sodium and potassium chlorides at λ44·4 cm. B. VOIGT (Z. Physik, 1927, **44**, 70—90).—A technique appropriate to the determination of dielectric constants of strongly absorbing liquids at the frequency corresponding with λ 44·4 cm. is described; it is based on the second method of Drude (Ann. Physik,

1897, [ii], **61**, 466); spark-generated damped wave trains were employed, and the logarithmic decrement of the circuit, without absorbing media, was 0·06. The dielectric constant of water at ordinary temperatures was found to be independent of its conductivity in the range $0·3\times10^{-12}$ to $0·96\times10^{-14}$ reciprocal ohm per c.c., and solutions containing up to 0·03% of sodium or potassium chloride exhibited no change in the constant. As the salt concentration is increased from 0·06 to 0·18% the ratio of the constant of the solution to that of pure water decreases from 0·977 to 0·852, corresponding with the conductivity change $0·119\times10^{-11}$ to $0·374\times10^{-11}$. The dielectric constant and the absorption coefficient of glycerol have been determined at the same frequency from −20° to 200°. The former is constant at 3·4 up to 0° and then increases to 22 at 90°, above which temperature it again remains constant. The absorption coefficient increases from 0·14 to a maximum of 0·51 at 48° and then diminishes approximately linearly, attaining the value 0·12 at 195°. The data of other workers on glycerol are reviewed; it is shown that as the frequency is increased from 120 cycles per sec. the temperature maximum of the dielectric constant shifts from −60° to 90° at $6·76\times10^8$ cycles per sec.

R. W. Lunt.

Temperature dependence of the dielectric constants of vapours. I. Benzophenone. F. Maske (Physikal. Z., 1927, **28**, 533—545).—Methods are described for the accurate investigation of dielectric constants of vapours. Benzophenone has been studied over the temperature range 218—336°, the extreme values at atmospheric pressure of $(\varepsilon-1)$ being $0·0327\pm0·0013$, $0·0103\pm0·0003$ at 218° and 336°, respectively. To connect the values at different temperatures it is necessary to multiply the values of $(\varepsilon-1)_{dt}$ by $1+\alpha t$ (in which α is the expansion coefficient of the gas) so as to obtain the values of $(\varepsilon-1)_{dn}$. For these, the relation $(\varepsilon-1)/(\varepsilon+2)\times1/d_n\times(T-T')=k$; k is a constant 183·3.

R. A. Morton.

Dielectric constant and the wave mechanics. C. Manneback (Physikal. Z., 1927, **28**, 514).—A reply to Gans (this vol., 610). R. A. Morton.

Molecular volumes of simple and complex platinum halides. R. Klement (Z. anorg. Chem., 1927, **164**, 195—201).—The values of d_4^{25} for a number of the above compounds have been determined. In the chloride, bromide, and iodide of quadrivalent platinum, the molecular volume of the halogen is somewhat greater than the zero volume, but in the complex halides with potassium this excess has disappeared. The bivalent halides also have high molecular volumes, but these do not change in the complex salts. In the tervalent halides, the molecular volumes of the halogens are less than the zero volumes. All the salts examined satisfy Biltz's linear relationship (A., 1921, ii, 437). *Potassium tetrachlorodibromoplatinate*, $K_2PtCl_4Br_2$, has been obtained by the action of bromine on aqueous potassium chloroplatinite. R. Cuthill.

Molecular volumes at absolute zero. I. Density as a function of temperature. II. Zero volumes and chemical composition. S. Sugden (J.C.S., 1927, 1780—1785, 1786—1798).—I. The density of a number of liquids from the f. p. to the critical temperature is shown to follow the equation $D-d=D_0(1-T/T_c)^{3/10}$, where D and d are the densities of the liquid and its saturated vapour at $T°$ Abs., T_c is the critical temperature, and D_0 a constant which represents the density of the supercooled liquid at 0° Abs. For the normal liquids the densities of which have been determined by Young this equation holds over the whole range of temperature with an accuracy of about 1 in 500. Associated liquids give good agreement at lower temperatures, but at higher temperatures they often exhibit large deviations. The molecular volume V_0 at 0° Abs. obtained by dividing the mol. wt. by D_0 is found to be proportional to the critical volume for a number of substances; hydrogen gives, however, an exceptionally high value for the ratio V_0/V_c. A fortuitous proportionality exists between V_0 and the parachor for some organic liquids.

II. By means of the above relation the values of D_0 have been calculated from density data for a large number of substances. The corresponding molecular volumes at 0° Abs. ("zero volumes") are shown to be capable of representation as a simple additive function of a number of atomic and structural constants. Associated liquids can be included if density data below the b. p. are used and a small change is made for the constants for oxygen and nitrogen in alcohols and amines. Of 284 substances studied 235 have zero volumes within 2% of the value predicted by the additive relation. Zero volumes show a clear distinction between non-polar and semi-polar linkings, which are found to have constants of about 8·0 and zero respectively.

F. S. Hawkins.

Molecular and atomic volumes. XVI. Volumes of nitrato- and nitrito-cobaltammines. E. Birk (Z. anorg. Chem., 1927, **164**, 241—244; see this vol., 812).—The passage of anions in luteo-cobaltic compounds into the nucleus, with consequent expulsion of ammonia molecules, causes a decrease in molecular volume by an amount which is only about 0·75 of the volume of the ammonia in additively constituted compounds, and is independent of the nature of the anion. It is therefore probable that the close packing of the luteo-complex is due to a dense configuration of the ammonia groups.

Tetramminodinitratocobaltic nitrate, $[Co(NH_3)_4(NO_3)_2]NO_3,H_2O$ (red), has been obtained by the action of nitric acid on tetramminocarbonatocobaltic nitrate. R. Cuthill.

Nature of the luteo-complex. W. Biltz (Z. anorg. Chem., 1927, **164**, 245—255).—It is suggested that in the luteo-complex the middle shell of the cobalt assumes, by transfer and sharing of electrons in the outer levels of the nitrogen and cobalt atoms, the symmetrical configuration of the inert gases, the complex becoming at the same time diamagnetic. As a result of this process, there arises the possibility of a nearer approach of the cobalt and nitrogen atoms, which can in some cases be detected by X-ray measurements, and is also indicated by volume measurements (cf. preceding abstract). With reduction in the

number of ammonia groups, the diamagnetism diminishes and the volume of the ammonia molecules increases, whilst the characteristic stability of luteo-compounds gradually disappears. With hexammino-cobaltous or -nickelous complexes, the possibility of the formation of a symmetrical electron configuration is not present, and the compounds are therefore paramagnetic, have a larger lattice parameter than the luteo-compounds, and are less stable.

R. CUTHILL.

Molecular diffusion of light in liquids. Experimental test of theoretical formulæ. J. CABANNES (J. Phys. Radium, 1927, [vi], 8, 321—335).—The fraction of the incident light scattered per cm.^{3} is for benzene $(10{\cdot}7\pm0{\cdot}55)\times10^{-6}$ cm.$^{-1}$ at 25° and 5440 Å., and for ether $9{\cdot}2\times10^{-6}$ cm.$^{-1}$ at 20° and 4358 Å. Investigation of the relative values obtained for organic liquids shows that Einstein's formula, corrected for anisotropy, as proposed by Ramanathan is more accurate than the form proposed by King; the values of the Avogadro constant obtained by this formula, however, are more than 20% too large. Measurements made on liquids and their vapours suggest that the benzene nucleus is rigid, and that open-chain molecules are deformed in the liquid state. F. S. HAWKINS.

Molecular scattering of light in aqueous solutions. II. S. VENKATESWARAN (Indian J. Physics, 1927, 1, 393—400).—By a method previously described (this vol., 713), the molecular scattering of light in aqueous solutions of acetic, propionic, and butyric acids has been investigated. Unlike the solutions of inorganic acids previously studied, the fatty acids show an appreciable concentration scattering characteristic of mixtures, and the magnitude increases rapidly from acetic to butyric acid. The light scattered by acetic acid is less completely polarised than that scattered by propionic and butyric acids. With butyric acid, which has a critical solution temperature at −3·8°, the scattered light becomes almost completely polarised as the critical point is approached. This is in accordance with Raman and Ramanathan's theory of light-scattering in binary liquid mixtures (Phil. Mag., 1923, [vi], 45, 213). M. S. BURR.

Changes in the optical properties of quartz under the influence of the electric field. NY TSI ZE (Compt. rend., 1927, 185, 195—197).—If the extremity of the electric axis of a rectangular parallelepiped of quartz is charged positively, the refractive indices of the crystal in the three directions defined by the edges of the solid, diminish in such a manner as to correspond with an increase in birefringence in the direction of the electric axis, and a diminution in the direction normal to the optical and electric axes. The effects change sign on reversal of the electric field and their magnitude is proportional to its strength. They are not secondary effects due to the electric dilatation of quartz, and cannot be explained by the Kerr effect. J. GRANT.

Total reflexion of *X*-rays and the index of refraction of certain metals. H. W. EDWARDS (Physical Rev., 1927, [ii], 30, 91—94).—Values of $\delta\times10^5$ ($\delta=1-\mu=\theta^2/2$, where μ is the index of refraction and θ is the critical angle) for *X*-rays of 0·7078 Å. are: crown glass 1·711, tin 3·97, silver 5·78, selenium 2·67, zinc 4·59, the experimental values agreeing with those calculated by means of the Drude–Lorentz dispersion formula to within about 0·5%. Each metallic atom evidently contains two electrons which have the critical *K* absorption frequency, and these frequencies function in the phenomenon of reflexion. A. A. ELDRIDGE.

Molecular transformations and electronic theories of valency. A. GILLET (Bull. Soc. chim., 1927, [iv], 41, 927—932).—Addition to conjugated double linkings first occurs at the 1 : 2-positions, and this is followed by an isomeric change which leaves the added substituents in the 1 : 4-position. This is not adequately explained by Thiele's hypothesis. According to spectroscopic measurements by Fowler, the energy of one pair of the valency electrons of carbon differs from that of the other pair, and so they form two identical symmetrical couples, each of which possesses a certain solidarity, even within a molecule, thus enabling carbon to act as a bivalent element. F. S. HAWKINS.

Co-ordinated linkings and atomic structure. H. LESSHEIM, J. MEYER, and R. SAMUEL (Z. anorg. Chem., 1927, 165, 253—283).—Difficulties in the existing theories of valency are discussed in the light of modern theories of atomic structure. It is suggested that co-ordination compounds owe their existence to a special type of non-polar linking, differentiated from the homopolar linking only in that it is concerned with the complete shell of electrons lying immediately inside the outer incomplete shell which is the seat of the normal valency of the atom. This complete shell is thus that which is exposed when the outer electrons are detached in the process of ionisation. H. F. GILLBE.

Models for monatomic and diatomic molecules based on those of helium and hydrogen. F. J. VON WISNIEWSKI (Z. Physik, 1927, 44, 385—391).—The models suggested for monatomic and diatomic molecules (A., 1926, 779) have been further investigated by calculating the diamagnetic susceptibilities, the ionisation and resonance potentials of hydrogen, helium, and carbon dioxide from the following equation for the dielectric constant k, $1+4\pi N_0 p/3E$, where N_0 is Loschschmidt's number, E the external electric field, and p the mean component of the electric moment of a molecule in the direction of the field. For monatomic molecules $p=Er^3$, where r is the radius of the outermost orbit, and $r=0{\cdot}52n^2\times10^{-8}$, where n is the quantum number; for diatomic molecules $p=13{\cdot}5\sqrt{3}d^3E$, and $d=0{\cdot}579n^2\times10^{-8}$. It is shown that $\sqrt{k_{\mathrm{H}}}=1+12{\cdot}82n_{\mathrm{H}}{}^6\times10^{-5}$ and $k_{\mathrm{H_2}}=1+5{\cdot}01\ {}_{\mathrm{Ic}}{}^6\times10^{-5}$; by substituting the known values of the dielectric constants in these equations n_{H} and $n_{\mathrm{H_2}}$ are evaluated. The values so obtained are used to compute the diamagnetic susceptibility of the models advanced by the author for hydrogen and helium; the values obtained are $-1{\cdot}47\times10^{-10}$ and $-0{\cdot}81\times10^{-10}$, in good agreement with experiment. The corresponding ionisation potentials are 28·82 volts (Horton and Davies 29·4 volts) and 11·75 volts (Davies 12·75 volts).

Similarly if the carbon dioxide molecule is considered to consist of two positive ions, CO^+ and O^+, and two electrons in analogy with hydrogen the diamagnetic susceptibility is calculated to be $-0{\cdot}504\times10^{-6}$, in good agreement with Lehrer's value $-0{\cdot}52\times10^{-6}$. R. W. LUNT.

Chemical constants of diatomic molecules. F. J. VON WISNIEWSKI (Z. Physik, 1927, 44, 392—395).—The expression of Ehrenfest and Trkal for the chemical constant i of diatomic molecules can be expressed in the form (pressures in atm.) $i=36{\cdot}82+1{\cdot}5\log(m_1+m_2)+\log$ $\log\sigma$, where the mass m of the molecule is given by J is its moment of inertia, and σ the coefficient of symmetry. The distance d separating the two atoms in the molecule is calculated from the value of the dielectric constant k, according to an analysis previously described (cf. preceding abstract), $\sqrt{k}=1+66{\cdot}06d^3\times10^{19}$; from these values the corresponding values of J are calculated. By putting $\sigma=1$ the values of i for the following substances have been obtained in satisfactory agreement with the accepted values: chlorine 1·40, bromine 2·41, iodine 3·06, hydrogen −3·26, carbon dioxide 0·73, ammonia −1·33, and hydrogen chloride −0·44. R. W. LUNT.

Adsorption and shape of the carbon dioxide molecule. N. STARK and O. BLÜH (Physikal. Z., 1927, 28, 502—504).—The data for the heat of adsorption of carbon dioxide by wood charcoal determined by Magnus and Brauer (A., 1926, 346) require that even if the dipole theory of adsorption is true the dipoles cannot be rigid. In the simple carbon dioxide molecule the three atoms cannot be in the same straight line if the molecule is to exhibit an electric moment. Eucken, however (A., 1926, 882), argued against the alternative triangular shape. The assumption of a four-pole, bar-shape structure is shown to be consistent with the adsorption data. The moment of inertia calculated on this basis from the data of Magnus is $\tau=3{\cdot}74\times10^{-26}$, whilst on the Debye theory of the van der Waals' forces $\tau=3{\cdot}9\times10^{-26}$. R. A. MORTON.

Influence of water of crystallisation on the photo-electric effect in crystal hydrates. II. A. PREDVODITELEV and W. BLINOV (Z. Physik, 1927, 44, 207—215; cf. this vol., 497).—The change in photo-electric emission during the initial stages of the hydration by water vapour of anhydrous copper sulphate, potassium alum, and manganous sulphate has been investigated. It is shown that the photo-electric current i can be expressed as a function of the number of molecules of water per molecule of anhydrous salt n in the following form: $i-\alpha-\beta(1-e^{-kn})$, where α is the current given by the anhydrous salt, β the maximum value observed during hydration, and k a constant. Curves are given showing i/β as a function of n. With copper sulphate $i/\beta=0{\cdot}94$ at $n=0{\cdot}926$ and is approximately 1 at $n=1{\cdot}5$, when $\beta/\alpha=5{\cdot}75$: it is therefore concluded, since the first molecule of water absorbed produces the maximum value of i, that this molecule must be attached to the $CuSO_4$ molecule in a different way from the remaining four, and not symmetrically according to Werner's formula $[Cu(OH_2)_4](SO_4,H_2O)$. When the incompletely dehydrated salt $2Al_2K_2(SO_4)_4,H_2O$ is used as the initial material i/β becomes 1 at $n=0{\cdot}209$, when $\beta/\alpha=8{\cdot}0$ corresponding with the formation of $Al_2K_2(SO_4)_4,H_2O$. As manganese sulphate is gradually hydrated i/β reaches 1 at $n=0{\cdot}25$, falls to a minimum at $n=0{\cdot}50$, and finally increases to a second, but lower, maximum at $n=1{\cdot}00$; in some experiments, however, i/β increases continuously to a limiting value at $n=0{\cdot}50$ at which there is a point of inflexion in the curve, which then increases asymptotically to the limit corresponding with $n=1{\cdot}00$; in others i/β increases continuously to the limiting value of unity at $n=1{\cdot}00$. These data therefore indicate the existence of the following hydrates: $4MnSO_4,H_2O$, $2MnSO_4,H_2O$, and $MnSO_4,H_2O$; the corresponding values of β/α are 4·25, 1·8, and 2·6.

The authors conclude from these experiments that Werner's co-ordination hypothesis represents only approximately the spatial orientation of the water molecules in the substances examined. R. W. LUNT.

Hydration of ions. E. N. GAPON and I. S. HASKES (J. Russ. Phys. Chem. Soc., 1926, 58, 1384—1397).—It is considered that when a substance crystallises with some of the solvent, the latter can be united with it, either mechanically, or co-ordinated inside the molecule. Five cations have been examined in which water of crystallisation is co-ordinated inside the molecule to give compounds of the type: $[R(OH_2)_x]^{++\cdots}$. The following cations are said to give these complexes: $Ca,8H_2O^{++}$, $Ca,6H_2O^{++}$, $Ca,4H_2O^{++}$, $Ca,2H_2O^{++}$, $Mn,8H_2O^{++}$, $Mn,6H_2O^{++}$, $Mn,4H_2O^{++}$, $Cu,8H_2O^{++}$, $Cu,6H_2O^{++}$, $Cu,4H_2O^{++}$, $Hg,2H_2O^{++}$, $K,5H_2O^{+}$, $K,2H_2O$. E. ROTHSTEIN.

Stereochemistry of the platinous salts. A. GRUNBERG (Z. anorg. Chem., 1927, 164, 207—213).—Polemical against Reihlen and Nestle (this vol., 189). It appears probable that in the complex platinous salts the arrangement of the co-ordinated groups about the metal atom is influenced by their electrochemical nature, the experimental data yielding some measure of support for a plane, pyramidal, or a tetrahedral configuration. R. CUTHILL.

Homologous series and *cis*- and *trans*-forms. B. NEKRASSOV (Z. physikal. Chem., 1927, 128, 203—229).—In view of the fact that X-ray measurements with thin layers of substances with a normal carbon chain show that the increment in length produced by a CH_2-group varies from series to series, it seems probable that the molecules are not normal to, but inclined at various angles to the reflecting surface, the observed value depending on the angle of inclination. The experimental data also indicate that the angle between the two lines joining the centres of two adjacent carbon atoms of a zigzag chain is not necessarily equal to that between the normals to the two tetrahedra, but depends on the chemical nature of the two end groups. With such a zigzag configuration, there should be the possibility of the existence among saturated compounds of a phenomenon resembling geometrical isomerism among unsaturated compounds, the end groups being in the *cis*- or *trans*-

positions according as the number of intermediate CH_2-groups is odd or even. This view is in accordance with certain features of the chemical reactivity of these compounds, and now receives further support from an examination of the physical constants. In homologous series of saturated compounds, the peaks on the curve representing the oscillation of the m. p. with increase in the number of carbon atoms usually correspond with *trans*-forms. The effect of the end groups on the amplitude and direction of the oscillation is qualitatively the same as for geometrical isomerides with a single ethenoid linking. A similar differentiation between members with even and odd numbers of CH_2-groups is also reflected in the solubility, dielectric constant, surface tension, ionic mobilities, magnetic rotation, and molecular volumes, the effects observed being analogous to those observed with ordinary geometrical isomerides. The existence of dimorphism among monobasic acids which the present theory would indicate to be of the *cis*-type (Garner and Randall, A., 1924, ii, 385) is probably because the repulsion of the end groups causes a rotation of the carbon atoms with production of a *pseudo-trans*-form. That the potential energy of the *cis*- is greater than that of the *trans*-form is shown by examination of the data for heats of combustion and latent heat of fusion. With primary alcohols, the reverse is the case, the terminal groups being assumed to attract each other. In the molten state or in solution, the difference between the *cis*- and *trans*-members of a homologous series is much less marked than it is in the solid state; this is ascribed to the co-existence of the two forms in equilibrium. With increase in temperature, the resistance of the chain to rotation may be expected to decrease, so that both types of isomeride gradually approximate to the same configuration, and with properties such as the m. p. the oscillation which occurs among the earlier members of the series becomes less and less as the series is ascended. The tendency for rotation to occur depends to some extent on the nature of the terminal groups, which explains why a particular property may oscillate in one series but not in another. The oscillation in the m. p. of the *cyclo*paraffins may be explained by the rotation which must occur when a chain of an odd number of carbon atoms closes but need not occur with a chain of an even number.

R. CUTHILL.

Wave mechanics of neutral atoms and homopolar linkings. W. HEITLER and F. LONDON (Z. Physik, 1927, **44**, 455—472).—Mathematical.

R. W. LUNT.

Calculation of atomic diameters from photo-electric data. E. N. GAPON (Z. Physik, 1927, **44**, 535—536).—On the assumption that the radius r of the electron emitted in the photo-electric effect is equal to half the distance separating the centres of two adjacent atoms the energy of this electron is $e/2r$. If the work associated with the electron leaving the emitting surface be neglected, the energy of the electron in its orbital motion $e^2/2r$ may then be equated to the quantum $h\nu_0$ characteristic of the ow wave-length limit of the photo-electric effect; the atomic radius is then given by $r=5{\cdot}808\lambda_m\times10^{-12}$ Å. e following values have been computed from existing data for magnesium, calcium, zinc, cadmium, lead, arsenic, antimony, bismuth, and selenium: 1·92, 2·15, 1·75, 1·82, 1·81, 1·37, 1·79, 1·88, 1·28 Å, respectively. The values agree approximately with those of Bragg. Carbon gives a value approximately twice that of Bragg, which is thought to indicate that the molecule contains two atoms. For oxygen $r=3{\cdot}14$ Å. in approximate agreement with the value given by the kinetic theory, 2·70 Å.

R. W. LUNT.

X-Ray studies on the decomposition of austenite. O. E. HARDER and R. L. DODWELL.—See B., 1927, 724.

X-Ray investigation of the internal stress in metals [copper]. S. SEKITO.—See B., 1927, 725.

Crystallisation and structure of metals and alloys. A. PORTEVIN (Bull. Soc. chim., 1927, [iv], **41**, 961—987).—A lecture delivered before the Société Chimique de France on 25 February, 1927.

Active iron compounds. A. BICKEL and C. VAN EWEYK (Biochem. Z., 1927, **186**, 178—180).—Whereas a sample of magnetic iron oxide (Baudisch) retained its power to give the benzidine reaction after keeping in conductivity water for 5 months, another sample (ferrosoferric carbonate) which was originally non-magnetic but gave a powerful benzidine reaction, with similar treatment became unable to give the reaction.

P. W. CLUTTERBUCK.

Diffraction of X-rays in fused sodium and potassium. W. H. KEESOM (Proc. K. Akad. Wetensch. Amsterdam, 1927, **30**, 341—343).—The Debye–Scherrer diagrams of fused sodium and potassium at about 25° above the m. p. give as the distance between neighbouring atoms of potassium 5·13, and of sodium 4·04 Å.; the values calculated on the assumption that the atoms in the liquid are packed as closely as possible are 4·80 and 3·88 Å., respectively.

H. F. GILLBE.

Lattice constants of calcium oxide, sulphide, selenide, and telluride. I. OFTEDAL (Z. physikal. Chem., 1927, **128**, 154—158).—The following values of a (in Å.) have been determined by the powder method: calcium oxide, 4·802; calcium sulphide, 5·686; calcium selenide, 5·912; calcium telluride, 6·345. The greatest error of the measurements is 0·008.

H. F. GILLBE.

Crystalline and atomic structure of ferrous hydroxide. G. NATTA and E. CASAZZA (Atti R. Accad. Lincei, 1927, [vi], 5, 803—807).—Pure ferrous hydroxide has been prepared by precipitation with concentrated sodium hydroxide in an atmosphere of hydrogen. The molecular structure of a sample preserved under paraffin has been determined by the Debye–Scherrer method. The elementary cell has the following dimensions: $a=3{\cdot}24$, $c=4{\cdot}47$ Å.; $c/a=1{\cdot}38$; the crystals appear to belong to the holohedric class of the rhombohedric system.

R. W. LUNT.

Crystal structure of hexamminocobaltic iodide. H. MEISEL and W. TIEDJE (Z. anorg. Chem., 1927, **164**, 223—240).—Determination of the crystal structure of hexamminocobaltic iodide has given results essentially the same as those obtained by Wyckoff and McCutcheon (this vol., 400).

R. CUTHILL.

Crystal structures of the nickel arsenide type. I. Oftedal (Z. physikal. Chem., 1927, **128**, 135—153).—The lattice constants (in Å.) have been determined by the powder method of a number of compounds of the nickel arsenide type. For cobalt selenide $c=5{\cdot}278$, $a=3{\cdot}614$; chromium telluride, $c=6{\cdot}211$, $a=3{\cdot}981$; manganese telluride, $c=6{\cdot}698$, $a=4{\cdot}124$; cobalt telluride, $c=5{\cdot}360$, $a=3{\cdot}886$; nickel telluride, $c=5{\cdot}354$, $a=3{\cdot}957$; chromium antimonide, $c=5{\cdot}468$, $a=4{\cdot}107$; manganese antimonide, MnSb, $c=5{\cdot}784$, $a=4{\cdot}120$; Mn_3Sb_2, $c=5{\cdot}744$, $a=4{\cdot}131$; FeSb, $c=5{\cdot}130$, $a=4{\cdot}064$; Fe_3Sb_2, $c=5{\cdot}168$, $a=4{\cdot}123$; cobalt antimonide, $c=5{\cdot}188$, $a=3{\cdot}866$; nickel antimonide, $c=5{\cdot}133$, $a=3{\cdot}907$. The minimum distances between the lattice units exhibit similar variations in the selenide, telluride, and antimonide series, being smallest for the cobalt compounds and greatest for the manganese compounds. The magnitude of the variations of the minimum distance is greater for the tellurides than for the antimonides. The theoretical significance of these variations is discussed.

H. F. Gillbe.

Crystal structure of molybdenum silicide and tungsten silicide. W. Zachariasen (Z. physikal. Chem., 1927, **128**, 39—48).—The lattice constants (in Å.) of the tetragonal crystals of $MoSi_2$ and WSi_2 have been determined by the powder method. For $MoSi_2$ $a=3{\cdot}200\pm0{\cdot}005$, $c=7{\cdot}861\pm0{\cdot}005$; for WSi_2 $a=3{\cdot}212\pm0{\cdot}005$, $c=7{\cdot}880\pm0{\cdot}005$. The elementary cell contains two molecules, and the atomic arrangement is derived from the holohedral space grouping D_{4h}^{17}. The atomic positions are Mo (or W) (0, 0, 0) $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$; Si (0, 0, u), (0, 0, $\bar{u}$), $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}+u)$, $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}-u)$, where $u=0{\cdot}333\pm0{\cdot}015$. The structure thus belongs to a new type: each molybdenum atom is surrounded by 10 silicon atoms at a distance of 2·617 Å. (2·625 Å. for tungsten), and each silicon atom by 5 molybdenum and 5 silicon atoms at the same distance.

H. F. Gillbe.

Atomic structure of the antimony oxides. U. Dehlinger and R. Glocker (Z. anorg. Chem., 1927, **165**, 41—45).—Antimony pentoxide, tetroxide, and trioxide, and the oxide Sb_6O_{13} all possess a cubic or pseudocubic lattice. All the lines in the X-ray spectra of the tetroxide may be developed from those of the trioxide, and are of the same relative intensities, whilst Sb_6O_{13} exhibits all the lines given by the tetroxide, both as to the intensity and position; there are in addition a few faint lines. No discernible difference exists between the spectra of the pentoxide and tetroxide. The lattice constants of antimony pentoxide and tetroxide and of Sb_6O_{13} are identical to within 0·1%. The theoretical significance of these results is discussed.

H. F. Gillbe.

Space lattice of yellow lead monoxide. F. Halla and F. Pawlek (Z. physikal. Chem., 1927, **128**, 49—70).—Yellow lead monoxide has been prepared by dissolving lead hydroxide in hot potassium hydroxide solution and cooling the solution rapidly. Attempts to obtain the yellow form in large crystals resulted always in partial transformation into the red modification. Investigations by the powder method show that yellow lead monoxide crystallises in the rhombic system; the elementary cell has $a=5{\cdot}50$, $b=4{\cdot}72$, and $c=5{\cdot}880$ Å., and contains four lead oxide molecules. The lattice is composed of double molecules.

H. F. Gillbe.

***X*-Ray diffraction patterns from liquids and colloidal gels.** G. L. Clark, R. H. Aborn, E. W. Brugmann, and R. L. Davidson (Proc. Nat. Acad. Sci., 1927, **13**, 549—552).—Using the monochromatic, pinhole method, the X-ray pattern for unstretched rubber latex films exhibits two principal rings corresponding with spacings of 6·03 and 14·76 Å. in agreement with the values 6·05 and 14·88 Å. obtained by Hauser and Rosbaud (cf. B., 1927, 789). If, however, the rubber is purified rigorously the spacings 5·97 and 11·15 Å. are obtained. Cellulose nitrate in the fresh, dry, untreated condition shows the spacings 7·18 and 4·02 Å., and after ageing (heat) the values 6·98 and 3·92 Å. are obtained. In the presence of residual solvent the spacings are 9·30 and 4·47 Å. Swelling or combination with solvent or oil has a much greater effect on the X-ray pattern than ageing. Small but definite differences in spacings are observed with tung oil and linseed oil during polymerisation and drying.

R. A. Morton.

***X*-Ray diffraction in liquids.** C. M. Sogani (Indian J. Physics, 1927, **1**, 357—392).—Improvements in the apparatus for examining X-ray diffraction in liquids, by the Debye–Scherrer powder-photograph method, are described. These include the replacement of the usual glass or celluloid containers, which give liquid-like patterns themselves, by a cell with mica windows, and also a reduction in the width of the incident pencil of rays. Twenty-two liquids belonging to the aliphatic and aromatic groups were studied. The results show that the assumption of hexagonal closest packing in all liquids, made by Keesom and Smedt (Proc. K. Akad. Wetensch. Amsterdam, 1923, **25**, 118; **26**, 112), is not justified, especially for long-chain or asymmetric molecules. The influence of compressibility on the sharpness of the halo, predicted by Raman and Ramanathan (A., 1924, ii, 816), is confirmed. The scattering at small angles is not negligibly small, and is relatively greater for liquids of high compressibility or with comparatively unsymmetrical molecules. A comparison of the diffraction haloes of a number of benzene derivatives reveals the extent to which the principal halo may be modified in passing to more and more complex derivatives. Distinct differences are found, even between the patterns of isomeric molecules.

M. S. Burr.

Mechanism of electrolytic conductivity in crystals. A. Reis (Z. Physik, 1927, **44**, 353—358).—The experimental data on the conductivity of crystals exhibiting electrolytic conductivity are discussed with reference to the deformation of the gratings of the ions forming the crystals.

R. W. Lunt.

Iron crystals. III. Magnetic properties in different directions. E. Dussler and W. Gerlach (Z. Physik, 1927, **44**, 279—291; cf. A., 1926, 1085).—The B–H curves have been determined for 15 cm. iron rods containing well-developed crystals from 0·5 to 3 cm. long. They are initially approximately linear and inflect abruptly, slowly attaining satur-

ation. The initial permeability in the tetragonal direction is greater than in the diagonal direction; in the former saturation is more rapidly attained although the actual values for the two directions are the same, and the points of inflexion in each direction occur at approximately the same value of the magnetising flux. R. W. LUNT.

Magnetic transitions of ferromagnetic metals. R. RUER (Z. anorg. Chem., 1927, **165**, 142—148).—On both the heating and cooling curves of pure electrolytic iron there is an arrest at 769°, indicating that the change in magnetic properties is due to a true polymorphic transition. H. F. GILLBE.

Magnetic anisotropy of crystalline nitrates and carbonates. K. S. KRISHNAN and C. V. RAMAN (Proc. Roy. Soc., 1927, **A**, **115**, 549—554).—The relation between the magnetic anisotropy and structure of the nitrates and carbonates is briefly considered. The magnetic anisotropy of the nitric acid molecule is calculated from the Cotton–Mouton constant and the optical constants. Crystals of sodium and potassium nitrates exhibit a marked diamagnetic anisotropy, the susceptibility perpendicular to the plane of the nitrate ion being greater than that for directions in this plane; the difference of susceptibility in the two directions is the same for the two crystals. If this anisotropy is attributed to that of the nitrate ion, its magnitude is exactly that to be expected from the known value of the magnetic birefringence of liquid nitric acid. This is explained on the basis of the electronic structure of the ions, involving the sharing of certain electron orbits. The carbonate ion, which has an essentially similar structure, exhibits a magnetic anisotropy almost the same as that of the nitrate ion. L. L. BIRCUMSHAW.

Temperature variation of the elasticity of sodium potassium tartrate. R. M. DAVIES (Nature, 1927, **120**, 332—333).—As with the piezo-electric modulus (Valasek, Physical Rev., 1922, [ii], 19, 478; A., 1923, i, 649), discontinuities occur at −15° and 23°. A. A. ELDRIDGE.

Reflexion of electrons from crystal lattices. F. ZWICKY (Proc. Nat. Acad. Sci., 1927, **13**, 518—525).—Davisson and Germer (this vol., 492) have interpreted their results on the reflexion of electrons from a single crystal of nickel by the analogy of reflexion of *X*-rays from crystals. The incompleteness of the analogy is pointed out and differences are made clear in terms of wave mechanics.
R. A. MORTON.

New kinds of mixed crystals. D. BALAREV [with N. GANTSCHEV and B. SREBROV] (Z. anorg. Chem., 1927, **165**, 192—194).—The simultaneous precipitation of zinc sulphide with copper sulphide from a fairly strongly acid solution by hydrogen sulphide is not due, as has been previously suggested, to the formation of complex zinc copper sulphide, but is a purely capillary effect. H. F. GILLBE.

Modified micro-method for the determination of mol. wt. J. REILLY and G. T. PYNE (Sci. Proc. Roy. Dubl. Soc., 1927, **18**, 489—493).—The method depends on the alteration in the cooling curve of pure camphor produced by minute amounts of dissolved substances. Examples are given of the use of the method for acetanilide, strychnine, palmitic acid, and other compounds. G. W. ROBINSON.

Method of determination of the mol. wt. of organic substances in small quantities by means of f.-p. depressions. B. KUBOTA and T. YAMANE (Bull. Chem. Soc. Japan, 1927, 2, 209—212).—Two metres of silver wire are wound around a thin glass tube. A test-tube with stirrer just fits in this tube, and the whole is hung in a vacuum flask. The test-tube holds a suitable solvent, and the depression of its f. p. is measured by the change of resistance of the silver wire. Determinations can be carried out with 4—8 mg. of material. With benzene, nitrobenzene, and ethylene bromide as solvents determinations have been made accurate to 1—3%. F. S. HAWKINS.

Electric moment of the sulphur complex. A. M. TAYLOR and E. K. RIDEAL (Proc. Roy. Soc., 1927, **A**, **115**, 589—609).—The electric moment of the sulphur molecule is considered with regard to the possibility of a homopolar linking being accompanied by such deformation of the atoms as to give rise to a pseudo-heteropolar linking, with consequent electromagnetic vibration frequencies. True homopolar linking should give no active frequencies of vibration, or, if any exist, they should be of weak resonant amplitude and give rise to radiation of wave-length comparable with the atomic spacing. Experiments are made to determine the wave-length at which maximum absorption of infra-red radiation occurs, and the value of the extinction coefficient for this maximum for the different allotropic forms of sulphur and also the liquid phase. Characteristic vibration frequencies are found to be the same in all phases: rhombic solid, prismatic solid, plastic or supercooled liquid, and molten liquid. From the data obtained it is concluded that electric doublets are present in the sulphur complex, and these are considered to be due to the linking in pairs of the sulphur atoms forming units S_2. These units are built into groups $[S_2]_8$ corresponding with groups of mass 512, the centre of gravity of which has been shown by Mark and Wigner (A., 1924, ii, 650) to occupy the points of the diamond-type space lattice of rhombic sulphur. The frequencies due to the S_2 unit persist through all the phases investigated. The electric moment of the complex S_2 is found to be $7{\cdot}5\times10^{-18}$ e.s.u., which agrees with the value calculated from the heat of vaporisation and the heat of dissociation of sulphur. The effective charge on the atoms is found to be 0·77 e.s.u.
L. L. BIRCUMSHAW.

Electrical conductivity at low temperatures. J. C. MCLENNAN and C. D. NIVEN (Phil. Mag., 1927, [vii], 4, 386—404).—Investigation of the temperature-resistance curves of lead and indium has shown that these metals become superconducting at 7·5° and 3·38° Abs., respectively, in agreement with the results obtained by Onnes. Cadmium showed no signs of superconductivity at temperatures down to 3·6° Abs. The residual resistance was found to be $7{\cdot}80\times10^{-4}$, which is in close agreement with the value obtained by Meissner (A., 1926, 1086). None of the metals beryllium, chromium, rubidium, or thorium showed any indication of superconductivity. The

results showed that the temperature gradient was small for all pure metals except for those which became superconducting. Even with these the temperature gradient rapidly diminished just before the sudden disappearance of the resistance. The resistance–temperature curve of a sodium–potassium alloy was examined down to the temperature of liquid hydrogen. The curve was similar to that of either sodium or potassium but indicated that the residual resistance at 0° Abs. was much higher than that of either of the constituent metals. A. E. MITCHELL.

Hall effect in single crystals of iron. W. L. WEBSTER (Proc. Camb. Phil. Soc., 1927, **23**, 800—803).

Relation between temperature and Hall effect in some alloys. J. OBATA.—See B., 1927, 726.

Thermodynamic treatment of certain magnetic effects. Proposed method of producing temperatures considerably below 1° Abs. W. F. GIAUQUE (J. Amer. Chem. Soc., 1927, **49**, 1864—1870).—For a substance in a magnetic field the second law of thermodynamics gives the equation (i): $\mathbf{H}dI+TdS=dU+pdv$, where $\mathbf{H}$ is the strength of the field, I the intensity of magnetisation in excess of that which would be in the same space if unoccupied by matter ($\mathbf{H}/I=\chi$, the molal magnetic susceptibility), U the intrinsic energy, and S the entropy. Further, the enthalpy H is (ii) $U+pv-\mathbf{H}I$ and hence the work done when one mole of substance is reversibly drawn into a magnetic field is (iii) $-\Delta F=\int_{\mathbf{H}}I d\mathbf{H}$; also, (iv), $(\partial S/\partial\mathbf{H})_{p,T}=(\partial I/\partial T)_{p,\mathbf{H}}=\mathbf{H}(\partial\chi/\partial I)_{p,\mathbf{H}}$. The value of ΔS for the reversible transference of an ideal paramagnetic substance obeying Curie's law from a field $\mathbf{H}=0$ to the field $\mathbf{H}=\mathbf{H}$ is, from (iv), (v) $\Delta S=-\mathbf{H}^2C/2T^2$. For gadolinium sulphate octahydrate equations (iii) and (v) show that at 1·3°Abs. in a field of 20,000 gauss ΔS is −3·3 g.-cal./1° per g.-atom of gadolinium. It is proposed to conduct this heat away by gaseous conduction to liquid helium, and, after evacuation of the space between the working substance and the liquid, to demagnetise the former, and so on. Suggested applications of the temperatures it is thus hoped to attain are appended.

S. K. TWEEDY.

Paramagnetism and the third law of thermodynamics. Interpretation of the low-temperature magnetic susceptibility of gadolinium sulphate. W. F. GIAUQUE (J. Amer. Chem. Soc., 1927, **49**, 1870—1877).—Equations are developed for ΔS and I for gadolinium sulphate octahydrate (cf. preceding abstract), the latter equation representing the low-temperature susceptibility data of the salt with great accuracy. It is suggested that the equations be used in paramagnetic thermometry and in the magnetic mixture method of low-temperature calorimetry. With substances with positive susceptibility it is not always feasible to obtain an absolute value of entropy from heat capacity data alone, as the entropy due to the distribution of magnetic moment in the various possible states will usually be neglected. The method of correction is indicated.

S. K. TWEEDY.

Theory of paramagnetism. B. CABRERA (J. Phys. Radium, 1927, [vi], **8**, 257—275).—Assuming that when atoms approach within a certain distance the configuration of the electrons in the outer levels is altered, the rearrangement occurring in such a way that the magnetic moment is not changed, a relation which is practically equivalent to the Curie–Weiss formula connecting the susceptibility and temperature of paramagnetic substances is arrived at. Langevin's reasoning must be regarded as inadequate, since it leads only to the Curie law, which is of restricted applicability. It is shown, further, that the magnetisations in the three principal directions of a crystal obey the same Curie–Weiss law, with the same constant. The various values of the constant C in this expression are found empirically to obey the relation $\sqrt{C}-nK$, where K is a universal constant and n is integral. It appears probable that the variations of the constant Δ with the concentration for the cations of certain electrolytes is frequently to be attributed to the formation of complexes, such as hydrates.

R. CUTHILL.

Paramagnetism of palladium and platinum groups. B. CABRERA and A. DUPERIER (Compt. rend., 1927, **185**, 414—416).—The specific magnetic susceptibilities of the chlorides of the metals of the palladium and platinum groups have been measured. The atomic susceptibilities (c.g.s.u. $\times10^{-6}$) are calculated to be Ru^{+++}+1912, Rh^{+++}+45·5, Pd^{++}+3·38, Os^{++}+82·75, Ir^{+++}+47·2, Pt^{++}−17·4. The variation with temperature is discussed.

C. W. GIBBY.

Refraction and dispersion of gaseous carbon tetrachloride. H. LOWERY (Proc. Physical Soc., 1927, **38**, 421—423).—Using a Jamin interferometer, the refractive index of gaseous carbon tetrachloride has been shown to be 1·0001799 for the green mercury line at 5461 Å. This value applies to the same number of molecules as are contained in 1 c.c. of hydrogen at 0° and 760 mm. The refractivity has been measured for seven lines over the range 6708—4800 Å. and the results are shown to be reproduced by Sellmeier's dispersion formula $\mu-1=13{\cdot}543\times10^{27}/(7831{\cdot}7\times10^{27}-\nu^2)$, in which ν is the frequency of the light used.

R. A. MORTON.

Heats of condensation of positive ions and the mechanism of the mercury arc. K. T. COMPTON and C. C. VAN VOORHIS (Proc. Nat. Acad. Sci., 1927, **13**, 336—341).—The heat of condensation ϕ of argon ions neutralised at a molybdenum surface is measured experimentally and the relation between the heat of evaporation of electrons ϕ', the ionising potential V_i, and the latent heat of condensation L of the neutral gas is corrected to (cf. Compton, Physical Rev., 1923, [ii], **21**, 266): $\phi=rV_i+L-\phi'$, in which r is less than 0·5 by an amount depending on the (electron) reflecting power of the electrode. Values of ϕ obtained from this equation are used in the calculation of the energy balance at the cathode of a mercury arc; from this it appears that electrons are withdrawn by the intense space charge field (Langmuir, Gen. Elec. Review, 1923, **26**, 731) and mercury is lost by the cathode in drops containing numbers of atoms.

S. K. TWEEDY.

Wire method for the m. p. of palladium. C. E. MENDENHALL and C. L. UTTERBACK (J. Opt. Soc. Amer., 1927, **15**, 62—63).—An experimental method

for obtaining concordant results in the determination of the m. p. of palladium, called a wire method, is described. W. E. Downey.

Rates of evaporation and vapour pressures of tungsten, molybdenum, platinum, nickel, iron, copper, and silver. H. A. Jones, I. Langmuir, and G. M. J. Mackay (Physical Rev., 1927, [ii], **30**, 201—214).—Values of the rate of evaporation, vapour pressure, and latent heat of evaporation for the above metals are tabulated, together with those of the energy losses by radiation and evaporation from nickel, copper, and silver surfaces. The latent heats of evaporation (g.-cal./g.-at.) and b. p. (Abs.) are, respectively: tungsten, 191,880, 6970; molybdenum, 146,000, 5960; platinum, 127,500, 4800; nickel, 89,440, 3650; iron, 89,025, 3475; copper, 82,060, 3110; silver, 71,320, 2740.

The validity of the third law of thermodynamics was assumed in all the calculations. The latent heat of fusion of tungsten and molybdenum is estimated (±10%) to be 11,200 and 8380 g.-cal./g.-atom, respectively. A. A. Eldridge.

Vapour pressures of solid and liquid neon. C. A. Crommelin and R. O. Gibson (Proc. K. Akad. Wetensch. Amsterdam, 1927, **30**, 362—364).—The vapour pressure of neon at −257·62° (solid) is 0·00072 atm., rising at −228·66° (liquid) to 26·049 atm. The triple point is given as T_c=−248·52°, p_c=32·35 cm. H. F. Gillbe.

Dissociation pressures of ammonium orthophosphates. T. E. Warren (J. Amer. Chem. Soc., 1927, **49**, 1904—1908).—The ammonia dissociation pressures of di- and tri-ammonium orthophosphates are recorded between 80° and 125°. The pressure over the mono-salt is 0·05 mm. at 125°. The results are confirmed by the individual formation of the pure salts on passing ammonia diluted to the appropriate pressure through concentrated phosphoric acid at the corresponding temperature. The following heats of reaction are calculated: $(NH_4)_2HPO_4$(solid)=NH_3(gas)+$NH_4H_2PO_4$(solid)−19,050 g.-cal.; $(NH_4)_3PO_4$(solid)=$(NH_4)_2HPO_4$(solid)+NH_3(gas)−9400 g.-cal. S. K. Tweedy.

Density and temperature. VI. W. Herz (Z. Elektrochem., 1927, **33**, 348—349; cf. A., 1925, ii, 1141).—The relation $(d-d_c)/a(T-T_c)^b=1$, where d is the density of a liquid at any temperature T, d_c and T_c are its critical density and temperature, and a and b are constants for a given liquid, is shown to apply satisfactorily to a number of liquids, normal or associated, including liquefied gases (cf. this vol., 193). With nitrogen the agreement is much less satisfactory than with argon. H. J. T. Ellingham.

Gas theories and the equation of state. J. Duclaux (J. Phys. Radium, 1927, [vi], **8**, 336—343).—It is assumed that gas molecules have no attraction for each other, and imperfect gases consist of an equilibrium of single and double molecules. By applying the mass action equilibrium equation and van 't Hoff's isotherm, an equation of state and Sutherland's viscosity formula are deduced, and the variation of the constant of the latter is predicted. Values of C_v for carbon and C_p for air are calculated and found to agree with experimental results. F. S. Hawkins.

Rotation-vibration entropy of a diatomic gas. K. Szell (Physikal. Z., 1927, **28**, 546—549).—Theoretical. R. A. Morton.

Compressibility isotherms of hydrogen, nitrogen, and mixtures of these gases at 0° and pressures to 1000 atm. E. P. Bartlett (J. Amer. Chem. Soc., 1927, **49**, 1955—1957).—A correction. An accurate recalibration of the pressure gauge used in the previous investigation (this vol., 404) reveals that the results then recorded have a maximum error of 0·62%, at 200 atm. The corrected results are tabulated; the agreement with Amagat's figures is almost exact at 200 atm. and differs by a maximum of 0·34% above this pressure. S. K. Tweedy.

Compressibility of tellurium. R. F. Mehl and B. J. Mair (J. Amer. Chem. Soc., 1927, **49**, 1892—1900).—The compressibility coefficients at 25° of tellurium (d 6·261) and water between 100 and 500 megabars are $5{\cdot}00\times10^{-6}$ and $41{\cdot}54\times10^{-6}$ megabar^{-1}, respectively. The former value falls on the smooth atomic volume–compressibility curve for the elements, indicating that the mass of the nucleus has a negligible effect on compressibility. The negative linear compressibility coefficient of tellurium (Bridgman, A., 1924, ii, 818) is not in contradiction to the principle of Le Chatelier; it is due to the crystal not having a closely-packed structure so that an increase in length along the screw (trigonal) axis causes a decrease in length of the side of the unit basal triangle and of the radius of the helix and thus increases the density. Under suitable conditions other substances might show the same phenomenon. It is predicted that selenium will have a very small positive linear compressibility coefficient along the screw axis. S. K. Tweedy.

Determination of surface tension by capillary rise. Surface tension of water, ethyl alcohol, boron trichloride, and silicon tetrachloride. H. Mills and P. L. Robinson (J.C.S., 1927, 1823—1832).—The surface tensions were determined in a vacuum by measuring the difference of capillary rise between three tubes of different bore. The values at 20° are: water 72·90, alcohol 22·05, boron trichloride 16·70, and silicon tetrachloride (provisional value) 19·71 dynes/cm. The height of liquid in each tube varied irregularly with time until a period of about 10 hrs. had elapsed, after which a steady equilibrium was maintained. F. S. Hawkins.

Viscosity of liquids above their b. p. III. T. Titani (Bull. Chem. Soc. Japan, 1927, **2**, 196—201).—The relations between molecular fluidity and molecular volume, and molecular fluidity and temperature previously deduced (this vol., 616, 819) give satisfactory agreement for a number of organic substances. From these two equations, the relation $V_c^{2/3}-V^{2/3}=A(T_c-T)^{1/5}$ was deduced, and found to hold with good accuracy. F. S. Hawkins.

Relation between refractive index and composition of binary mixtures. I and II. G. S. Pavlov (J. Russ. Phys. Chem. Soc., 1926, **58**, 1302—1308, 1309—1320).—I. Data for binary mixtures of

benzene and *cyclo*hexane satisfy the formula $V_0 - V = Km_1m_2$, where and m_2 are the molecular percentages of the components, V is the observed volume of 100 mols. of the mixture, and V_0 is the volume calculated; K has the value 0·0255.

II. The refractive indices for various mixtures of benzene and *cyclo*hexane have been measured at 20° for the sodium D line, and the hydrogen C, F, and G' lines. Curves obtained by plotting refractive index against molecular percentage of benzene are slightly concave to the composition axis, as is the case when dispersive power is plotted against benzene concentration. Equations are derived from the ordinary formulæ connecting refractive index and composition which enable the concentration of benzene in a given mixture of benzene and *cyclo*hexanone to be determined by measurement of the refractive index.

E. Rothstein.

Effect of solutes on density of solvents. H. Grunert (Z. anorg. Chem., 1927, **164**, 256—262).—The densities of solutions of naphthalene, phenanthrene, and iodine in carbon disulphide, acetone, benzene, chloroform, and carbon tetrachloride have been determined at 20°, 40°, and 60°. When the solute is denser than the solvent, the densities of the solutions are greater than that of the pure solvent, and *vice versa*, the differences being approximately proportional to the concentration of the solution, for a given temperature. For a particular solvent, the difference in density between two solutions of the same concentration does not vary much with the temperature. No general relationship exists between the solution volume of the solute and the temperature.

R. Cuthill.

Distillation and rectification of complex mixtures. L. Gay (Chim. et Ind., 1927, **18**, 187—203; cf. B., 1926, 223).—A quaternary mixture of ethyl, propyl, butyl, and *iso*amyl alcohol closely approximates to an "ideal solution." Binary mixtures are first considered and the compositions of the liquid and vapour phases, and the heat transfers at varying temperatures calculated. The variations of specific heat and latent heat with temperature may be neglected. The relations between composition and heat transfer are also depicted graphically. For the separation of a quaternary mixture three columns are necessary and five methods of operation possible. Each method is discussed in detail. The quaternary mixture is represented graphically as a tetrahedron, the faces of which correspond with ternary mixtures etc. In this way the relations between heat transfer and composition are fully worked out, the basis of the whole calculation being the vapour pressures of the components.

C. Irwin.

Miscibility-gap in molten iron–copper alloys. R. Ruer (Z. anorg. Chem., 1927, **164**, 366—376).—The existence of the lower critical point for the miscibility of molten iron and copper observed by Muller at 1500—1520° (this vol., 627) is denied.

R. Cuthill.

Effect of radon on the solubility of lead uranate. K. C. Bailey (Phil. Mag., 1927, [vii], 4, 404—407).—The effects of α-particles from radon on the solubility of lead uranate have been examined. In the presence of sodium chloride both lead and uranium are dissolved. In the absence of sodium chloride some lead goes into solution unaccompanied by uranium. The results indicate that the lead–uranium ratio of a uranium mineral may be considerably affected by the dissolution of either or both lead and uranium under the influence of the radioactive field due to the mineral itself. It then follows that estimates of geological time based on the lead–uranium ratio must err on the side of insufficiency. It must be assumed therefore, in contradistinction to the views of Holmes (A., 1926, 654), that the removal of lead from rocks has taken place at least as rapidly as its genesis and it is therefore doubtful if any differential removal of thorium-lead as compared with uranium-lead can be safely assumed (cf. Holmes, *loc. cit.*).

A. E. Mitchell.

Adsorption of mercury vapour by charcoal. A. S. Coolidge (J. Amer. Chem. Soc., 1927, **49**, 1949—1952).—Charcoal adsorbs negligible amounts of mercury vapour at the ordinary temperature; at high temperatures (300—500°) small amounts are adsorbed, the quantity decreasing with rising temperature when the vapour is kept at constant pressure, but increasing when the vapour is kept saturated. The heat of adsorption is 8900 g.-cal./mol., which is smaller than the heat of evaporation (cf. this vol., 406), but larger than the heat of adsorption of many true gases. It follows that mercury vapour may displace such gases from charcoal. An observation in support of this is cited.

S. K. Tweedy.

Adsorption. XII, XIII. Heat effect of adsorption of carbon dioxide. A. Magnus and W. Kalberer (Z. anorg. Chem., 1927, **164**, 345—356, 357—365; cf. this vol., 105).—XII. The heat of adsorption of carbon dioxide by wood charcoal at 0° begins to rise rapidly when the equilibrium pressure falls below about 40 mm. This confirms the theory previously advanced (A., 1926, 1001) that the roughening of the surface due to loss of gases and formation of cavities with higher adsorption potential must lead to an increase in the heat of adsorption at very low pressures. As would be expected on this view, the pressure at which the rapid rise commences is the higher, the more thoroughly the adsorbent has been freed from gas at the outset. Extrapolation of the rectilinear portion of the curve connecting heat of adsorption and equilibrium pressure to zero pressure gives a value of 7450 g.-cal. for the molecular heat of adsorption. Henry's law requires a constant heat of adsorption over the whole range of validity, and therefore breaks down completely in the present instance (cf. *loc. cit.*).

XIII. The molecular heat of adsorption of carbon dioxide by silica gel decreases linearly with increasing pressure at low pressures. This behaviour can be accounted for in an approximately quantitative manner on the assumption of a Joule–Thomson effect. Determination of the adsorption isotherms at 0°, 25°, and 50° gives a value of 3950° for the constant C in Lorenz and Landé's adsorption law. At 0° and 25°, the values of α' in Magnus' equation of state are fairly constant, but the values for the two temperatures are not the same.

R. Cuthill.

Adsorption of substances from dilute aqueous solutions. M. DUBININ (J. Russ. Phys. Chem. Soc., 1926, 58, 1187—1202).—See A., 1926, 1090.

Adhesive forces in solutions. IX. Adsorption of substances from dilute aqueous solutions in presence of non-electrolytes. M. DUBININ (Z. physikal. Chem., 1927, **128**, 266—284; cf. A., 1926, 1200).—The adsorption of hydrochloric or acetic acid by activated charcoal from aqueous solution is reduced by addition to the solution of solvents with capillary activity, such as methyl alcohol, ethyl ether, and acetone. With hydrochloric acid, the form of the adsorption isotherms gradually approximates to that characteristic of the adsorption of non-electrolytes, presumably because the active solvent accumulates in the interface and represses the ionisation. The relative decrease in adsorption is the greater with acetic acid, and here the isotherms tend to become straight lines. For hydrochloric acid, the value of n in the equation $C_n=KC^{1/n}$, where C_n is the amount of substance adsorbed and C is the amount remaining in the liquid phase, is approximately a linear function of the concentration of active solute. The amount of hydrogen chloride adsorbed from pure aqueous solutions is reduced by addition of small quantities of sucrose, which has no capillary activity, but with increasing amounts passes through a minimum and rises again, ultimately exceeding the original amount. At the same time, the concentration of sugar in the solution passes through a minimum. Sucrose has a similar effect on the adsorption of acetic acid. As is required by Gibbs' theory, the amounts of ethyl ether, acetone, and methyl alcohol adsorbed by charcoal decrease in this order, which is the order in which the surface tension and the effect on the adsorption of hydrochloric and acetic acids decrease.

R. CUTHILL.

Adsorption from solution by ash-free adsorbent charcoal. III. Comparison of results obtained with ash-free and impure charcoal. E. J. MILLER (J. Physical Chem., 1927, **31**, 1197—1211).—A recapitulation of the results of previous work (cf. A., 1923, ii, 464; 1924, ii, 664; 1925, ii, 656; 1926, 898, 1090) in which attention is directed to the hydrolytic adsorption by active charcoal, the non-adsorption of inorganic bases, the positive and negative adsorption from salt solutions, and the fact that all adsorbent charcoals when freed from organic and inorganic impurities have the same adsorbent properties. The contradictory results obtained by previous workers are due to the presence of acidic or basic impurities in the charcoal used, and additional data are now given supporting the conclusion that the adsorption of bases by unpurified charcoals is due to reaction with acid impurities contained therein. The significance of these results in the determination of the order of adsorbability of salts and ions is discussed.

L. S. THEOBALD.

Solubility and adsorption of electrolytes. N. A. SCHILOV and M. L. TSCHEPELEVETSKI (J. Russ. Phys. Chem. Soc., 1926, 58, 1203—1221; cf. A., 1926, 1200).—The adsorption of the halogen salts of rubidand cæsium by charcoal has been measured. When compared with that of the corresponding sodium and potassium salts, it is found that the adsorption increases linearly with the mass of the cation.

E. ROTHSTEIN.

Effect of p_H on adsorption by carbon. S. M. HAUGE and J. J. WILLAMAN (Ind. Eng. Chem., 1927, **19**, 943—953).—The adsorption of caramel by different types of decolorising carbons increases as the p_H value diminishes. This is also true of benzoazurin, both compounds being electronegative colloids. With electropositive substances, such as methylene-blue, the relations are reversed. Removal of the ash from bone-black was found to modify its adsorbent properties in this case. With proteins maximum adsorption occurs at a particular p_H value; this varies with the carbon used. In the case of dextrose no such variation is observed. Comparisons between different types of carbons are useless unless the p_H of the solution is specified.

C. IRWIN.

Influence of electric fields on adsorption. O. BLUH and N. STARK (Z. Physik, 1927, **43**, 575—590).—The energy of a dipole molecule in proximity to a plane has been computed by identifying this energy with that of the system comprising the dipole and its image relative to the plane. The potential energy U_0 of a dipole of moment μ—el is given by $U_0=-\mu^2h^{-3}(1+\cos^2\theta)$, where $2h$ is the distance between the mid-points of the dipole and its image and θ is the angle between the dipole and the normal to the adsorbing plane. Using the Maxwell–Boltzmann distribution the mean energy of a number of layers of molecules is therefore $u_0=\int_1^{\pm}u_0e^{-U_0k^{-1}T^{-1}}d\cos\theta(\int_1^{\pm}e^{-U_0k^{-1}T^{-1}})^{-1}$, where T is the absolute temperature, and k the Boltzmann constant; the potential energy due to a field E normal to the plane is given by $u=-\mu E\cos\theta$, and the total energy in the neighbourhood of the plane, u'_0, is obtained similarly by replacing u_0 in the above integrals by $U'_0=U_0+u$. The difference U'_0-U_0 then gives the increase in the adsorption energy due to the field E. For dipoles of $\mu=10^{-18}$ and $T=300°$ Abs. $U_0=-0{\cdot}23\times10^{-12}$, $u'_0=-0{\cdot}4\times10^{-12}$ erg for $E=9\times10^8$ volt cm.$^{-1}$; $\Delta U=0{\cdot}17\times10^{-12}$ erg. The ratio of the amount of material adsorbed in the field, N_E, to the amount N_0 adsorbed when $E=0$, is given by $N_E/N_0=e^{\Delta Uk^{-1}T^{-1}}$—9111%; assuming a linear relationship this corresponds with 1% increase in adsorption due to practically realisable fields of 10^5 volt cm.$^{-1}$ An alternative but approximate analysis based on the procedure of Magnus (this vol., 105) leads to values of the same order of magnitude.

R. W. LUNT.

Surface tension of molten metals. I. Copper. E. E. LIBMAN (Proc. Nat. Acad. Sci., 1927, **13**, 588—592).—The surface of a liquid in contact with a vertical plane which it does not wet is depressed by an amount h given by the equation $h^2=a^2(1-\sin\theta)$, a^2 being the capillary constant defined by $a^2=\sigma/dg$. On the other hand, the surface of a liquid within a circular tube, of radius r, connected to a large reservoir is similarly depressed by an amount H, given by $a^2=rH/(-\cos\theta)+C$. The unknowns a^2 and θ may be determined if h and H can be measured since C may be expressed in terms of the other magnitudes.

An arrangement has been devised in which the metal is melted in a crucible in which the vertical

plane and the tube are combined. The heating is carried out by means of a high-vacuum molybdenum-wound furnace and the temperature is measured by means of the resistance of the winding. An *X*-ray photograph is taken through the entire furnace and h and H are measured thereon. Pure copper (0·019% of impurities) gave $a^2=0{\cdot}308\pm0{\cdot}0017$ at 1083° and 0·297 at 1318°, whereas impure copper (Fe_2O_3,Al_2O_3, 0·07%; SiO_2, 0·04%) gave $a^2=0{\cdot}301$ at 1083° and 0·275 at 1335°. The effect of impurities increases as the temperature rises. R. A. MORTON.

Plastic films and the drop-weight method of interfacial tension measurement. S. S. KURTZ, jun. (J. Amer. Chem. Soc., 1927, 49, 1991—1994).—If a plastic film surrounding a drop touches the dropping tip there is no liquid–liquid interface and a correct measure of interfacial tension is not obtained. When the plastic film approaches, without touching, the tip, it influences the interfacial tension only by affecting the shape of the drop during its development. S. K. TWEEDY.

Surface energy and specific adsorptive power of various boundary surfaces. P. REHBINDER (Biochem. Z., 1927, 187, 19—31).—The degree of surface adsorption of an active substance, as expressed by surface energy, increases with the difference in polarity of the phases separated by the surface in question; thus in the case of dyes, adrenaline, or fatty acids it is greater at a water–hydrocarbon than at a water–air surface. The surface energy of a given substance at the surface separating given solvents can be determined from the partition coefficient of the substance with respect to these solvents and from the surface energy of the surface separating the solvents in the pure condition. Surface energy measurements can be used as a criterion of purity in the case of adrenaline; natural adrenaline exhibits greater activity at a water–benzene surface than does synthetic adrenaline. C. R. HARINGTON.

Effect of temperature on surface energy of solutions and biological liquids. P. REHBINDER (Biochem. Z., 1927, 187, 32—36).—The effect of temperature on the surface energy of aqueous solutions is different according as the solute exhibits surface activity or not; a means is therefore afforded of demonstrating the presence of such active substances in solution. C. R. HARINGTON.

Structure in surfaces of liquids. J. W. MCBAIN (Nature, 1927, 120, 362).—Hatschek's observation, that colloidal solutions and suspensions of solids in liquids possess a coefficient of viscosity that depends on the rate of shear, appears to be one manifestation of a general property of all surfaces involving liquids. The fact that the surface of a liquid possesses a depth which is considerable in comparison with the diameter of a molecule, and the inference that the surface, even of pure liquids, is a single complete layer of oriented molecules with numerous unstable chains of oriented molecules extended therefrom into the liquid, suggest a quasi-rigidity in the neighbourhood of all surfaces bounding a liquid, and explain Hatschek's results (cf. Nature, 1927, 119, 857). The author upholds his explanation of the high apparent viscosity of many colloidal solutions. A. A. ELDRIDGE.

Tangential force in the surface layers of liquids. H. HULSOF (Z. physikal. Chem., 1927, 128, 110—134).—Mathematical. The van der Waals equation has been applied to derive the tangential forces at liquid–solid interfaces. Both osmotic pressure and osmotic flow are ascribed to forces of this nature. The influence of tangential forces on the rise of sap in plants is discussed. H. F. GILLBE.

New capillary phenomenon. A. JANEK (Koll.-Chem. Beih., 1927, 24, 418—448; cf. A., 1923, ii, 395, 620).—A detailed investigation has been carried out on the formation of a banded membrane which forms on the surface of a drop of water covering a crystal of silver nitrate, which rests on a thin layer of gelatin gel impregnated with potassium dichromate. The formation of bands is independent of the concentration of the potassium dichromate, but depends on the thickness of the gelatin layer. Experiments on the age of the gelatin layer and on the effect of inclining the glass plate supporting the gelatin, showed that the velocity of spreading of the drop is the most important factor. A critical velocity of 0·13 mm. per sec. must be exceeded for band formation to occur. The width of the bands is, in general, between 0·05 and 0·3 mm. The cause of the phenomenon is the periodic spreading out of the drop of water, containing silver nitrate dissolved from the crystal, between the gelatin layer and the glass plate. At the edge of the drop, a precipitate of silver dichromate forms, which causes the gelatin to adhere less firmly to the glass plate. The bands are not Liesegang rings, although the latter may also form after a time. These are considerably smaller, having a width of 0·03—0·04 mm. Banded membranes were also obtained when potassium dichromate was contained in the gelatin, and when the gelatin was replaced by agar. When the gelatin layer contained silver nitrate, and a crystal of potassium dichromate was placed on it and covered with a drop of water, a banded membrane was obtained, but not when a crystal of sodium chloride or sodium hydroxide was used. Using sodium hydroxide on a gelatin layer containing calcium chloride, Liesegang rings of calcium hydroxide formed, but no banded membrane. E. S. HEDGES.

Cause of the colours shown during the oxidation of metallic copper. F. H. CONSTABLE (Proc. Roy. Soc., 1927, A, 115, 570—588).—The colours shown by a copper oxide film may be made truly homogeneous if special precautions are taken in the preparation and activation of the film, so that the oxidation of all parts of the surface occurs at an equal rate. A method is described which produces such uniformity, and considerable evidence is adduced that the production of the colours is due to interference in a thin layer of oxide. The order of production of the colours corresponds with the order tabulated by Rollet for the interference colours of air films of increasing thickness seen by transmitted light. It is found that the fall in electrical conductivity of the oxidised film supported on china clay is proportional to the equivalent air thickness of the oxide film, *i.e.*, to the thickness of an air film which would produce the same colour as the copper oxide film. The equivalent air thickness is approximately

proportional to the quantity of metal oxidised. The wave-lengths of the maxima in the absorption or reflexion bands in the spectrum of the light reflected from the film move towards the red as the thickness increases. The absolute thickness of the oxide film, calculated from the density and the mass of oxygen taken up per cm.^{2} of the surface, agrees moderately well with the thickness calculated from the position of the absorption band and the corresponding refractive index. It is shown that the interference theory is supported by Hinshelwood's observations (A., 1923, ii, 29), which are confirmed by the present work.

L. L. Bircumshaw.

Optical anisotropy of selectively absorbing dyes. H. Zocher and F. C. Jacoby (Koll.-Chem. Beih., 1927, 24, 365—417).—The relation between dichroism and double refraction and the optical properties of selectively absorbing dyes is discussed, and the spectral relations of double refraction for the various possibilities of dichroism are derived by application of the rule of anomalous dispersion. For the case of simple dichroism, the most strongly absorbed rays suffer the greatest refraction, except in the short-wave region of the spectrum, where they are more weakly refracted. Experimental data were obtained from a study of various dyes, which were made anisotropic by four methods: (1) through unidirectional rubbing on a glass plate, (2) through the streaming of sols with non-spherical particles, (3) by illumination of coloured collodion layers with linearly polarised light, (4) by orientation of non-spherical particles by pressure between two glass surfaces. About 160 different dyes were made anisotropic by method (1), of which three fourths showed simple dichroism agreeing with the above rule. The dry substances showed positive dichroism, becoming negative in many cases when the substance was rubbed in the wet state. In a series of dyes, good agreement was found between the maximal absorption and the reversal point of double refraction. A new optical bench, specially constructed for the purpose, enabled the construction of curves showing the dependence of dichroism and double refraction on the wave-length of the light. The results support the former conclusions. E. S. Hedges.

Chemical action at an interface. Production of acidity in neutral salt solutions. N. V. Achar and F. L. Usher (J.C.S., 1927, 1875—1882).—Measurements of the acidity produced in solutions of potassium chloride and sulphate by a colloidal suspension of stearic acid support the theory that the molecules in the surface of an insoluble acid undergo dissociation in contact with water, but have a range of movement limited by the electrostatic field due to the acid anions. In the presence of a neutral salt, exchange occurs between the hydrogen ions and the cations of the salt. The action can be regarded as a reversible chemical action at an interface, and the assumption of the adsorption of any ion is unnecessary.

F. S. Hawkins.

Creeping of solutions. E. R. Washburn (J. Physical Chem., 1927, 31, 1246—1248).—Creeping occurs only when the solution wets the surface with which it is in contact. Capillary layers between the crystals themselves or more generally between the crust of crystals first formed and the walls of the vessel are responsible for the climbing of solutions, which is prevented by the presence of grease, oil, or paraffin over the surface. L. S. Theobald.

Cataphoretic transference velocities of large particles in sols and gels. H. Freundlich and H. A. Abramson (Z. physikal. Chem., 1927, 128, 25—38).—The cataphoretic velocity of zinc dust particles in a 1% gelatin sol shows no change when the sol passes over into the gel form. The resulting gel is so rigid that the zinc particles do not fall appreciably under the influence of gravity even after several hours. The transference velocity is directly proportional to the applied *P.D.* Since the zinc particles do not move independently, but are always associated with gelatin, the study of their movements serves to indicate the nature of the motion of the invisible sol and gel particles. Independently of whether the colloid is in the sol or gel form, the gelatin particles move with the same velocity relatively to the other particles in the solution and to the dispersion medium. It is suggested that some of the colloidal particles are attached to more solid matter, which determines the apparent solidity. Thus although the gel as a whole behaves as a solid, the fraction which is observed under the microscope may approximate to the liquid state. The motions of the particles in this portion of the gel will therefore be similar to the movements in the corresponding sol.

The erythrocytes of horse blood are always negatively charged, and move in the serum at the ordinary temperature with a velocity of 1·01 μ/sec. for a potential gradient of 1 volt/cm. When piled together their velocity does not differ appreciably from that of single red corpuscles. The leucocytes and lymphophytes are also negatively charged, the rate of transference of the former being about 50%, and that of the latter about 30%, that of the erythrocytes. In these cases also the form of the particles has no influence on the transference velocity, which is again proportional to the applied *P.D.*

These results do not accord with the Debye–Hückel theory, according to which the transference velocity should be related to the form of the particle. The anomaly is explained by referring the cataphoresis, not to the initial condition of the particles, but to the altered condition which is brought about by distortion of the electrical double layer.

H. F. Gillbe.

Selective permeability of membranes. Influence of the size of their interstices. (Mlle.) Choucroun (Compt. rend., 1927, 185, 502—505; cf. A., 1924, ii, 155).—The diffusion-potential set up between differently concentrated solutions of an electrolyte is modified by the presence of a membrane. In the case of potassium chloride (zero diffusion-potential), an " acid " gel produces an *E.M.F.* owing to the repulsion of the potassium ions by the positively charged walls of the interstices, whilst an " alkaline " gel is negatively charged, and produces an opposite potential owing to the repulsion of the chlorine ions. The potential increases with the strength of the gelatin solutions, since the interstices are then smaller and

their stopping powers greater. Analogous results are obtained with hydrochloric acid and sodium hydroxide solutions. J. GRANT.

Formation of Liesegang rings in serological precipitation. L. REINER and H. KOPP (Kolloid-Z., 1927, **42**, 335—338).—Periodic structures of the nature of Liesegang rings may be produced in the mutual precipitation of antiserum and antigen solutions. The best effect is obtained by allowing the antiserum to set in an agar gel on which the antigen solution is poured. The rings form after a few days. The effect is related to the fact that the antiserum and antigen precipitate each other only when present in certain concentration ratios, an excess of either producing peptisation. E. S. HEDGES.

Density of ammonium chloride solutions. H. JESSEN-HANSEN (Compt. rend. Lab. Carlsberg, 1927, **16**, No. 11, 1—6).—The density of solutions of ammonium chloride containing 32·9867—0·9992 g. per 100 g. of water has been measured at 18°. The results are in good agreement with those of Dijken (Z. physikal. Chem., 1897, **24**, 107). E. A. LUNT.

Density of green solutions of potassium chromium alum. M. A. RAKUZIN and A. ROSENFELD (Chem.-Ztg., 1927, **51**, 638).—The saturated solution of green potassium chromium alum at 20° was found to contain 114·19 parts per 100 of water, the density of the saturated solution being 1·6683. These figures differ from those obtained by Gerlach and by Franz. The density of the alum solutions does not increase proportionally with the concentration and solutions of the same strength made from two different samples of alum have different densities. These anomalies are probably due to the varying extent to which the green modification has changed to the violet in different solutions. F. R. ENNOS.

Viscosity of alum solutions. M. BOBTELSKY and MALKOVA-JANOWSKAJA (Z. anorg. Chem., 1927, **165**, 249—252).—The viscosities of potassium sulphate, aluminium sulphate, and sulphuric acid solutions and of solutions of binary equimolar solutions of these compounds have been determined by the Ostwald method at temperatures between 15° and 55°, and at concentrations between 0·049 and 0·3655*M*. The viscosity of an equimolar solution of potassium and aluminium sulphates may be calculated additively from the viscosities of the components, and is identical with that of a solution of potassium alum of the same concentration. No evidence for complex ion formation is shown by the viscosity of mixed solutions of sulphuric acid and aluminium sulphate up to a concentration of 0·1960*M*. H. F. GILLBE.

Sodium perchlorate [solutions]. E. CORNEC and J. DICKELY (Bull. Soc. chim., 1927, [iv], **41**, 1017—1027).—See this vol., 723.

Dielectric constants of dilute aqueous solutions of electrolytes. R. SKANCKE and E. SCHREINER (Physikal. Z., 1927, **28**, 597—604).—Two methods are described for measuring the dielectric constants of dilute aqueous solutions of electrolytes by means of the Wheatstone bridge. Measurements have been made with lithium, potassium, and barium chlorides, lanthanum nitrate, magnesium sulphate, and potassium ferrocyanide between 0·001*N* and 0·005*N* with a frequency of 868,200±100 per sec. The bridge must be screened from capacity and induction effects, and if it is not symmetrical a correction must be applied, proportional to the fourth power of the current and independent of the frequency. C. W. GIBBY.

Light scattering of aqueous salt solutions. C. W. SWEITZER (J. Physical Chem., 1927, **31**, 1150—1191; cf. this vol., 510; Gans, Z. Physik, 1924, **22**, 44).—The relative light scattering and depolarisation factors have been measured for dust-free, aqueous solutions of various salts, and data are given for solutions of sodium, potassium, and ammonium chlorides and nitrates, sodium and ammonium sulphates, potassium iodide, barium, calcium, and hydrogen chlorides, calcium and lead nitrates, and for nitric and sulphuric acids. The orientation scattering is approximately proportional to the molar concentration of the salt, and decreases in the order sulphates, nitrates, chlorides. The order of cations within each group is the same, viz., potassium<sodium< ammonium. The relative scattering of a solution containing two salts is approximately additive, and differs little from the value calculated by the Einstein formula. Water and salt solutions show fluorescence which, in the latter case, is due to impurities. This fluorescence invalidates the preliminary results of the author (Trans. Roy. Soc. Canada, 1924, **18**, 125). Acid solutions show practically no fluorescence. The compressibilities and refractive indices of solutions of certain of the above-mentioned salts have been measured. L. S. THEOBALD.

Synthesis of red gold sols by means of aqueous extracts from fresh leaves. E. IWASE (Bull. Chem. Soc. Japan, 1927, **2**, 187—190).—Stable and reproducible sols are obtained by reducing hydrochloroauric acid solution with a freshly-prepared extract of cherry, pine, maple, bamboo, or camellia leaves, according to von Weimarn's method. The colour of the sols varied from ruby-red to purple. F. S. HAWKINS.

Preparation of silver hydrosols free from protective colloids and with particles of a uniform size. I. J. VOIGT and J. HEUMANN (Z. anorg. Chem., 1927, **164**, 409—419).—Silver hydrosols with particles of a uniform size may be prepared by reduction, in presence of nuclei, of silver oxide solutions, which must be carefully purified and contain about 0·001% of silver. Silver nuclei may be obtained by reduction of a similar solution of silver oxide with an ethereal solution of phosphorus, with subsequent addition of a little ammonia or sodium carbonate. Better results are, however, obtained by using gold nuclei prepared in a similar manner, the amount required being less. As reducing agents, hydrazine hydrate, formaldehyde, hydrazine sulphate, and hydrogen peroxide may be used, but ethereal solutions of phosphorus are not satisfactory, as the tendency for spontaneous formation of nuclei is too pronounced. R. CUTHILL.

Colloid syntheses with the aid of titanium trichloride. III. Colloidal copper. A. GUTBIER and B. OTTENSTEIN (Z. anorg. Chem., 1927, **164**, 274—280; cf. this vol., 620).—Red copper sols may

be obtained by adding a suspension of cupric oxide or a 0·1% solution of copper sulphate to an excess of a dilute solution of titanium trichloride which has previously been boiled so as to produce some titanic hydroxide. The sols are fairly resistant to freezing and boiling, but are very sensitive to electrolytes, and the particles are positively charged. Their properties are dependent on their titanic oxide content.

R. CUTHILL.

Colloid syntheses with the aid of titanium trichloride. IV. Colloidal rhodium. A. GUTBIER and E. LEUTHEUSSER (Z. anorg. Chem., 1927, **164**, 281—286).—Stable black rhodium sols may be prepared by adding a 10% solution of a rhodium salt to the theoretical amount of a solution of titanium trichloride to which sodium hydroxide has been added until the precipitate of titanium trihydroxide just dissolves, then dialysing. Such sols contain titanium dioxide, and are less resistant to the effect of electrolytes and changes of temperature than sols prepared by reduction with hydrazine hydrate in presence of gum arabic. The particles are positively charged.

R. CUTHILL.

Colloid syntheses with the aid of titanium trichloride. V. Colloidal bismuth and colloidal antimony. A. GUTBIER, B. OTTENSTEIN, and F. ALLAM (Z. anorg. Chem., 1927, **164**, 287—296).—By adding a 1% suspension of bismuth hydroxide to a large excess of a previously boiled mixture of a 17% titanium trichloride solution with four times its volume of a 5% sodium acetate solution, black sols of bismuth are obtained, which may be considerably purified by dialysis, and can be preserved for some time unchanged out of contact with air. These sols are not coagulated by boiling or freezing, and contain positively-charged particles. It is not possible to obtain colloidal bismuth in a pure aqueous medium.

Reduction of an aqueous suspension of antimonious chloride with a titanium trichloride solution, to which sodium acetate has been added to reduce the acidity, and which has been boiled, gives a blackish-brown sol of antimony, which must be dialysed out of contact with air, owing to the readiness with which it is oxidised. The properties of such sols are largely influenced by the large amount of hydrated titanic oxide which they contain. They can be preserved for months in sealed tubes. R. CUTHILL.

Disperse systems of lead iodide, lead bromide, and lead chloride. P. P. VON WEIMARN, T. L. CHEN, Y. KIDA, and K. YASUDA (Kolloid-Z., 1927, 42, 305—309).—Photomicrographic observations have enabled the authors to determine the absolute size of the crystals of lead halide which are produced by mixing at various concentrations solutions of lead nitrate and calcium halide. The results are in agreement with von Weimarn's precipitation laws. At certain concentrations of the reagents, it was possible to record photographically the primary production of a colloid system, changing after a short time to a crystalline precipitate. E. S. HEDGES.

Sols of barium sulphate in methyl alcohol. P. C. L. THORNE and C. G. SMITH (Kolloid-Z., 1927, 42, 328—331).—Sols of barium sulphate were prepared in methyl alcohol–water mixtures by pouring baryta water and dilute sulphuric acid simultaneously into methyl alcohol with stirring. Baryta was kept in excess, since it was found that excess of sulphuric acid precipitates the sol irreversibly. Concentrations of 0·83 g. of barium sulphate per 100 c.c. of sol were reached, and the properties of the sols vary with the relative amounts of the three components: those rich in water are stable for some months, whilst those of low water content are unstable. The sols evaporate at the ordinary temperature to a residue of the consistency of an ointment, but, on warming, an irreversible coagulation occurs; the temperature of coagulation depends on the composition of the sol. The particles are positively charged, probably as a result of dissociation of the barium sulphate micelle, since the ultrafiltrate gave a reaction for sulphate ions. Precipitation by electrolytes follows the usual rules for aqueous sols, except that an excess of a tervalent or quadrivalent ion produces stabilisation. In the latter case, the sol becomes negatively charged. The viscosity of the sols differs only slightly from that of the corresponding dispersion media, but increases slightly with age. E. S. HEDGES.

Physico-chemical properties of mercurisulphosalicylates. I, II. S. BERKMANN and H. ZOCHER (Kolloid-Z., 1927, 42, 309—322, 322—328).—I. Mercurisulphosalicylic acid forms a colloidally disperse phase in water. The potassium salt is characterised by the turbidity which appears on shaking the sol—a change which takes place in the sodium salt when the sol is kept for some months. The particles of these turbid sols are thread-like. The anisotropy caused by mechanical stirring differs from other cases in that the least force produces strong double refraction, which disappears immediately on cessation of the movement. The phenomena suggest a strong cohesion of the particles, so as to resemble a delicate gel. The gels obtained at higher concentrations are permanently doubly refractive after deformation. The double refraction becomes positive in an electric field or in a magnetic field. It is suggested that the particles arrange themselves with their long axes perpendicular to the lines of force, in opposition to the behaviour of most sols with non-spherical particles. The sols have a considerable electrical conductivity, and the colloid migrates to the anode. The appearance of dichroism on mixing the sols with colouring matters is due to an adsorption of the latter. The stream-double refraction increases strongly with increasing concentration of sol. The nature of the cation is of influence on the anisotropy of sols of the alkali salts of mercurisulphosalicylic acid, in accordance with the following series: $Li > NH_4 > Na > K$. The double refraction decreases on raising the temperature. Addition of chlorides in small amounts at first increases the double refraction, and later diminishes it.

II. The stream-double refraction of sols of mercurisulphosalicylic acid and its salts increases with increasing velocity of flow. The double refraction is less in old sols, which is contrary to the behaviour of sols previously investigated. The double refraction is also reduced by mechanical agitation of the sol; it is increased by addition of colouring matters, the

amount depending on the nature of the colouring substance. The elasticity and viscosity of both colourless and coloured sols are parallel with the double refraction. It is claimed that these sols are the prototype of a new class of colloids. In general, they are hydrophilic and belong to the class of colloidal electrolytes. Addition of electrolytes has a different effect from that usually observed. The influence of the cation does not follow the Hofmeister series, but depends on the solubility relations of the salts.

E. S. HEDGES.

Dependence of the Avogadro number on size of particles. S. RAY (Z. physikal. Chem., 1927, **128**, 182—188).—Theoretical. It is suggested that the reason why Perrin's method of determining the Avogadro number from measurements of the density of colloidal solutions gives uniformly higher values than Millikan's method is to be found in the dependence of the number on the size of the particles, an effect which is eliminated in the latter method. An examination of the results of Porter and Hedges (A., 1923, ii, 743) lends support to this view.

R. CUTHILL.

Interference microscopical method for the measurement of small particles of 150 $\mu\mu$ diameter. U. GERHARDT (Z. Physik, 1927, **44**, 397—402).—The technique developed by the author (*ibid.*, 1926, **35**, 697—717) has been extended to the measurements of particles of 150 $\mu\mu$ diameter. Examples of photographic records are described and discussed. R. W. LUNT.

Determination of dispersion of protected metal sols. F. HEBLER (Pharm. Ztg., 1927, **72**, 1013—1014).—The colour and metal content of an ultrafiltrate do not afford conclusive evidence relative to the degree of dispersion of a sol; the ultramicroscope is trustworthy for single determinations, and for a large number a nephelometric method can be recommended. S. I. LEVY.

Density and specific optical rotation of solutions of albumin. H. JESSEN-HANSEN (Compt. rend. Lab. Carlsberg, 1927, **16**, No. 10, 1—20).—The density of crystalline egg-albumin in ammonium sulphate solutions has been derived from the density of these solutions on the assumption, justified by experiment, that egg-albumin in aqueous or salt solution may be regarded as a two-phase system miscible without volume change, the hydrated protein constituting the disperse phase. The results show that the density of the hydrated protein in a solution of ammonium sulphate of given concentration decreases slightly as the concentration of ammonium sulphate is increased. Data are also given referring to the density of hydrated egg-albumin in ammonium sulphate solution as a function of the p_H in the range p_H 4·1—5·4.

The specific optical rotation of solutions of egg-albumin in solutions of ammonium sulphate has been determined for the *C*, *D*, *E*, and *F* lines. The specific rotation does not appear to depend on the concentration of ammonium sulphate, but it increases slightly as the concentration of the protein is diminished. Unless bacterial decomposition sets in the specific optical rotation is practically constant between 11·5° and 29°. The optical rotation of various samples of crystalline egg-albumin in solution in ammonium sulphate varied from $[\alpha]_D$ +31·64° to 29·92°. E. A. LUNT.

Viscosimetry in the study of colloidal clay. A. DEMOLON and G. BARBIER (Compt. rend., 1927, **185**, 542—545).—Viscosimetric measurements on colloidal suspensions of clay are of value only when made under comparable conditions. The suspensions (prepared by dialysis of decalcified and washed brick-earth) do not obey Poiseuille's law. The viscosity increases as a hyperbolic function of the concentration, but diminishes rapidly with rise of temperature. The effect of a flocculating electrolyte increases rapidly to a maximum with the amount added, and falls off slowly, the curve showing no anomaly at the flocculation point. Nitrates and chlorides have the same flocculation effect, sulphates less, and sodium salts the least influence. The permeability of the coagulum increases continuously with the concentration of electrolyte. The phenomena are explainable by the production in the colloidal clay of aggregates of variable size, the greater aggregates having the maximum permeability. J. GRANT.

Viscosity and hydration of dye solutions. S. LIEPATOV (J. Russ. Phys. Chem. Soc., 1926, **58**, 1321—1333).—See A., 1926, 903.

Viscosity and gel-formation of ceric hydroxide sols. D. N. CHAKRAVARTI, S. GHOSH, and N. R. DHAR (Z. anorg. Chem., 1927, **164**, 63—68).—Dialysis of solutions of ceric ammonium nitrate prepared in the cold yields sols of ceric hydroxide which are readily transformed into gels by electrolytes. These sols have the properties characteristic of hydrophilic colloids, viz., with increasing age the conductivity diminishes and the viscosity increases, and the viscosity increases rapidly with increasing concentration. If the ceric ammonium nitrate solutions are boiled before dialysis, the resulting sols will not pass into the gel state, and are of a distinctly hydrophobic character. For both kinds of sol, the coagulative power of the fluoride ion is very much greater than that of the chloride ion, being approximately equal to that of the sulphate ion, which would seem to indicate that the fluoride ion is bivalent.

R. CUTHILL.

Influence of gum acacia on the specific conductance of some binary electrolytes and the effect of binary electrolytes on the viscosity of gum acacia solutions. J. F. SPENCER and (MISS) R. DRUMMOND (Kolloid-Z., 1927, **42**, 332—335).—The experiments differ from most others on the influence of colloids on the specific conductance of electrolytes in that gum acacia itself has a considerable conductivity. Measurements were made of the viscosity of solutions of gum acacia at various concentrations, and of the effect of progressive addition of hydrochloric acid, sodium chloride, and barium chloride. In all cases, the viscosity was reduced by the presence of the electrolyte. With solutions of gum acacia under 10%, a minimum viscosity was obtained in presence of 0·2*N*-hydrochloric acid. For stronger solutions of the colloid, the viscosity fell continuously with increasing concentration of hydrochloric acid. All concentrations

of gum acacia showed a minimum of viscosity in presence of 0·1*N*-sodium chloride and also in presence of 0·2*N*-barium chloride. Measurements of the conductivities of gum acacia mixed with each of the same electrolytes gave in all cases a result lower than the sum of the conductivities of the colloid and the electrolyte. In presence of hydrochloric acid weaker than 0·5*N*, the change of conductivity with increase of concentration of the colloid passes through a minimum value, the position of which depends on the concentration of acid. The results suggest that a certain amount of the solvent is bound. Ageing of the gum acacia solution caused no appreciable difference in the effect of electrolytes on the viscosity or conductivity.

E. S. HEDGES.

Action of *X*-rays on colloids. J. A. CROWTHER and J. A. V. FAIRBROTHER (Phil. Mag., 1927, [vii], 4, 325—335).—The effects of -radiation on iron, copper, silver, and gold sols have been studied. It has been found that positively-charged iron and copper sols are coagulated by irradiation, whilst the negatively-charged gold and silver sols are further dispersed and their stability is increased. The effect has been studied numerically for a copper sol prepared by Bredig's method and the results suggest that the coagulation is due to ionisation produced in the diffuse double layer surrounding the particles.

A. E. MITCHELL.

Influence of colloids on the reaction of a solution of electrolytes. Hydrolysis of glucosides by animal membranes. J. LOISELEUR (Bull. Soc. Chim. biol., 1927, 9, 785—801).—When animal membranes are introduced into a solution of sucrose containing an electrolyte, hydrolysis of the sugar takes place. This is attributed to the preferential adsorption of one type of ion on the surface of the membrane, the alteration of p_H which results causing the hydrolysis of the sugar. W. O. KERMACK.

Drop number and emulsifiability. R. C. SMITH and (MISS) I. C. DOW (J. Physical Chem., 1927, **31**, 1263—1266).—The relation between drop number and emulsifiability has been investigated for various oils and water. Emulsifiability implies ease of emulsification and also stability of the resulting emulsion, and the drop number measures only the first factor and hence is not a true indication of emulsifiability.

L. S. THEOBALD.

Phenomena associated with the hydration of myelin. G. FRIEDEL (Compt. rend., 1927, **185**, 330—332).—The phenomena associated with the hydration of purified myelin have been examined by polarised light, and found to be similar to those characterising the hydration of soaps.

E. A. LUNT.

Vibrating soap jelly. E. H. BUCHNER (Nature, 1927, **120**, 367).—Soft soap appears to crystallise on keeping to a network of crystal fibres sufficiently rigid to permit sound vibration. A. A. ELDRIDGE.

Structure of gels. Crystallisation of *l*-arabinosazone. P. THOMAS and (MLLE.) M. SIBI (Compt. rend., 1927, **185**, 540—542; cf. A., 1926, 303).—By the addition of a suitable foreign gummy substance, the crystallisation of arabinosazone has been modified in such a way as to lead to the formation of a pseudo-gel. The general nature of this phenomenon is indicated. Concentrations of gum exceeding 1% of the sugar present gradually tend to change the crystals from radiating tufts of short non-flexible needles to very long hair-like filaments, which hold the liquid in their interstices and produce a gel effect. J. GRANT.

Function of water present in silicic acid gel. Structure of silicic acid gel. H. A. FELLS and J. B. FIRTH (J. Physical Chem., 1927, **31**, 1230—1236).—The state of combination of the water contained in a silicic acid gel has been followed by desiccation over sulphuric acid. The amount of water withdrawn in this way, before crystals of sodium chloride appear, increases as the gel increases in age, indicating that the water available as solvent for this salt is increasing. These results lead to the conclusion that the water in the gel exists as (i) " fixed " water, which is associated with the silica of the gel, and (ii) " free " water, which is mechanically enclosed and is available as solvent for the sodium chloride. The process of ageing then consists in the change of the ratio of " fixed " to " free " water. A newly-formed gel consists of molecules of heavily hydrated silica which slowly crystallise, liberating water and leaving a loose, mesh-like structure which finally, in the dried gel, becomes of a capillary nature.

L. S. THEOBALD.

Diffusion-potential measurements applied to hydrochloric acid–gelatin systems. I. Equivalent weight of gelatin. A. L. FERGUSON and E. K. BACON (J. Amer. Chem. Soc., 1927, **49**, 1921—1934).—A cell arrangement permitting the approximate determination of static liquid-junction potentials is described and measurements on hydrochloric acid systems, with and without sodium chloride and gelatin, are recorded. The reaction between hydrochloric acid and gelatin is stoicheiometric and purely chemical in nature. From the position of the cusps on the diffusion potential–concentration curves the equivalent weight of gelatin is found to be 1090.

S. K. TWEEDY.

Diffusion-potential measurements applied to hydrochloric acid–gelatin systems. II. Components of hydrochloric acid–gelatin solutions. E. K. BACON [with A. L. FERGUSON] (J. Amer. Chem. Soc., 1927, **49**, 1934—1939).—A consideration of the diffusion-potential curves of hydrochloric acid–gelatin solutions indicates that the components of such solutions must be defined in terms of free acid, combined and uncombined gelatin, and that the solution contains highly-ionised gelatin chloride.

S. K. TWEEDY.

Coagulation of colloidal sulphur solutions. G. ROSSI (Zymologica, 1927, 2, 63—72).—The adsorptive action of colloidal sulphur on the ions derived from stabilising electrolytes varies with the temperature. Since coagulation occurs when the temperature is raised, it would seem that there is a close connexion between the adsorption of ions and the stability of colloidal solutions. Experimental data are given which support this view. T. H. POPE.

Protein coagulation in drops. IX. Synergism of proteins in mixtures. F. BOHM (Biochem.

Z., 1927, 187, 84—91).—Mixtures of an albumin with a globulin show precipitation reactions, with various coagulants, of the type characteristic of globulins. The precipitation number of such a mixture, whether artificial or natural, is the arithmetic mean of the precipitation numbers of the components, provided that allowance is made for the presence of other dissolved substances in the natural mixtures. Egg-white and serum-protein have approximately identical precipitation numbers. The numbers for globulins are in descending order of magnitude for edestin, egg-white, and serum-globulins, whilst serum-albumin has a higher number than egg-albumin.

C. R. HARINGTON.

Thermodynamic necessity of gas degeneration. N. DE KOLOSOVSKI (Physikal. Z., 1927, 28, 475—476).—It is shown that the specific heats of gases at constant pressure and also at constant volume vanish at the absolute zero. Hence, it follows that gas degeneration is a necessary concomitant of the third law of thermodynamics. W. E. DOWNEY.

Nernst's heat theorem. J. J. VAN LAAR (Chem. Weekblad, 1927, 24, 302—311).—The theorem is attacked, and condemned as wholly fallacious, since it is based on the assumption that relations which hold to a reasonable degree of approximation at very low temperatures (Kirchhoff's formula) are valid also at much higher temperatures. The theorem in its original form does not give the correct transformation point of sulphur, for example, and it is shown that only by modifying the theorem, and employing a value for the constant which presupposes the temperature, is it possible to arrive at the correct figure, 96°. S. I. LEVY.

Absolute zero of entropy and internal energy. J. E. VERSCHAFFELT (Phil. Mag., 1927, [vii], 4, 335—337).—The author is in disagreement with Kleeman (this vol., 520) with regard to the axiomatic character of the third law of thermodynamics and the consequences arising from this. A. E. MITCHELL.

Properties of substances and mixtures in the condensed state at the absolute zero of temperature. R. D. KLEEMAN (J. Physical Chem., 1927, 31, 937—947; cf. this vol., 520).—Further relationships are derived. L. S. THEOBALD.

Quantitative treatment of deviations from Raoult's law. J. H. HILDEBRAND (Proc. Nat. Acad. Sci., 1927, 13, 267—272).—For each solute (mol. fraction N_2) most solvents yield a family of curves $\log N_2=f(1/T)$ (cf. Mortimer, A., 1923, ii, 299). Solutions conforming to such a family of solubility curves are termed "regular." In the case of regular solutions the existing solubility data are accounted for by an extension of Raoult's law, viz., $\log_e a_2-\log_e N_2+(bN_1^2/RT)$, where b is a constant which can be calculated from internal pressures or otherwise and a_2 is the activity of the solute. Several corollaries of the equation are deduced, *e.g.*, the partial molal heat of mixing of the solute is $-bN_1^2$. The equation may also be deduced from van der Waals' equation of state. S. K. TWEEDY.

Storch's equation, a general dilution formula, and the validity of the law of mass action at limiting dilutions. A. FERGUSON and I. VOGEL (Phil. Mag., 1927, [vii], 4, 1—17).—Examination of the data for nineteen electrolytes has shown that Storch's equation, in its simple or in a generalised form, represents satisfactorily the relationship between the degree of ionisation and the concentration over a wide range. Ostwald's dilution law holds for only two of the electrolytes examined.

A. E. MITCHELL.

Calculation of activity coefficients from conductivity measurements. C. W. DAVIES (Phil. Mag., 1927, [vii], 4, 244—250).—The mean activity coefficients for a number of uni-univalent acids have been calculated from conductivity measurements. The results vary from 0·35 to 0·44 and include the following: formic acid 0·382, acetic acid 0·393, cyanoacetic acid 0·372. The value for the series of acids is considered to be $0·38\pm0·01$. This is in agreement with the value for hydrochloric acid obtained by Randall and Vanselow (A., 1925, ii, 33) and by Nonhebel (A., 1926, 1006). The value for uni-univalent electrolytes required by Debye and Hückel's theory is 0·5 and by Milner's is 0·37, so that these results tend to support Milner's theory.

A. E. MITCHELL.

Factors determining the dissolution of electrolytes and their condition in solution. I. K. FREDENHAGEN (Z. physikal. Chem., 1927, 128, 1—24).—The electrical properties of solutions of electrolytes in various solvents have been examined. The normal potentials of the halogens in ammonia are: fluorine, 0·77; chlorine, 1·06; bromine, 1·26; and iodine, 1·51 volts; the potential of the nitrate group is greater than that of iodine, whilst that of the hydroxyl group is less than that of fluorine. The value for the nitrate group in ammonia is approximately the same as in water, whilst that for iodine is much greater than, and that for fluorine much less than the corresponding figure in water. The electrolytic solution pressures of the alkali metals are much smaller in ammonia than in water, but the saturation concentration of the alkali halides is influenced markedly only by the solution pressure of the anion.

The preparation of pure hydrogen fluoride is described; its specific conductance is $0·4\times10^{-4}$ mho at 0°, and its dielectric capacity 83·6 at 0°, 110·6 at −27°, 134·2 at −42°, 173·2 at −70°, and 174·8 at −73°. Measurements of the conductivity of methyl alcohol and of water in hydrogen fluoride solution indicate that in this solvent the latter is the stronger acid. The groups OH, NO_3, SO_4, ClO_3, BrO_3, IO_3, ClO_4 exhibit an unusually great solution pressure in hydrogen fluoride, whilst that of the halogens is very small.

Hydrogen cyanide, despite its high dielectric constant, is a less powerfully ionising solvent than water, methyl alcohol, ethyl alcohol, ammonia, or hydrogen fluoride; the solution pressures of all the substances investigated are very small. The solvent and ionising powers of a number of compounds are compared and discussed. H. F. GILLBE.

Factors determining the dissolution of electrolytes and their condition in solution. II. K.

FREDENHAGEN (Z. physikal. Chem., 1927, **128**, 239—265).—It is shown thermodynamically that the electrolytic solution number (electrolytic solution tension/concentration) of an element in a particular solvent is a function of the affinity of the element for the ions resulting from the dissociation of the solvent and of the internal forces. The element assumes a positive or negative charge in the solution according as its affinity for the anion of the solvent is greater or less than its affinity for the cation. These conclusions are in harmony with the data previously obtained (cf. preceding abstract) for the electrolytic solution tension of elements in various solvents. If a compound is in equilibrium with its ions in a solution and with its neutral atoms in the vapour phase, the dissociation constant in the liquid phase, K', is related to that in the vapour phase, K, by the expression where k_1 and k_2 are the distribution ratios of the ions and k_3 is that of the undissociated compound. This equation is found to be applicable with a fair degree of accuracy to aqueous solutions of the hydrogen halides. Other things remaining the same, the dissociation constant in the liquid phase depends on the electrolytic solution numbers, and as these are high for metals the almost complete dissociation of neutral salts is explained. The slight effect of temperature change on electrolytic dissociation is attributed to the opposite effects of temperature on the dissociation constant in the gas phase and on the electrolytic distribution ratios. It appears probable that the above equation is valid even for solutions of the strong electrolytes, deviations from the dilution law in dilute solutions being due to increase in the electrolytic solution numbers with increasing concentration, these numbers depending on the internal forces of the solution. R. CUTHILL.

Boric acids and their alkali salts. I. Free boric acids. II. Alkali borates in aqueous solution. H. MENZEL (Z. anorg. Chem., 1927, **162**, 1—21, 22—62).—I. F.-p. measurements with solutions containing 0·04—0·36 g.-mol. of orthoboric acid per 1000 g. of water give a value of unity for van 't Hoff's coefficient, i, over the whole concentration range. The solubility of boric acid in water at 18° decreases continuously with the addition of increasing amounts of hydrogen peroxide, and the acidity of the solutions is increased. There is, however, no indication of compound formation. Concentrated mixed solutions have a conductivity greater than the sum of the conductivities of solutions containing each component alone, but no quantitative deductions can be made from the experimental data.

II. The equivalent conductivity of a solution of potassium monoborate exceeds that of a solution of ıe diborate of the same normality by an amount w ich increases with increasing concentration (cf. ʌ., 1 756). The conductivities of pentaborate so'utıons are less than those of either of the other orates, probably owing to fewer hydroxyl ions being ormed by hydrolysis. From f.-p. determinations, e va ues of i for solutions of sodium and lithium ' ates equal concentrations are found to be sensibly the same, whilst those for the potassium salt are higher. As a whole, however, the values show these monoborates to be binary electrolytes, and give no evidence of a ternary dissociation corresponding with formulæ of the type $M_2B_2O_4$. Concentrated solutions of the corresponding diborates apparently contain B_4O_7'' ions rather than univalent diborate ions. For more dilute solutions, the experimental data are compatible with a decomposition of the diborate into monoborate and free boric acid. In concentrated solutions, the perborates are to be regarded as ternary electrolytes, giving the ion $2BO_2,2H_2O_2''$, whilst dilute solutions apparently contain the ion BO_2,H_2O_2'. The pentaborates give unusually high values for i, which is to be ascribed to a very considerable decomposition of the pentaborate ion, B_5O_8', into less complex ions and boric acid, this not being absent even when considerable excess of boric acid is added. Ammonium di-, penta-, and per-borates exhibit the same osmotic behaviour as the other borates examined. Concentrated solutions corresponding in composition with the monoborate resemble solutions of the diborates of the metals, the boric acid produced by hydrolysis forming complexes with the monoborate ions. R. CUTHILL.

Importance of buffering capacity in biochemistry. H. MOSER (Koll.-Chem. Beih., 1927, **25**, 69—126).—Previous work on buffered biochemical systems is discussed, and a form of hydrogen electrode for the electrometric titration of small quantities of liquid is described. A study was made of the buffering capacity of blood sera by determining the titration curves of horse serum (dialysed and undialysed), horse serum mixed with carbamide, and human serum in pregnancy and in rickets. The dissolution of precipitated euglobulin on the addition of carbamide is a colloid-chemical and not an ionic process. Eclamptic serum has less buffering capacity than normal serum in pregnancy: also the buffering capacity of rachitic serum is less than that of normal suckling children. A distinct difference was found in the buffering effect of the serum and urine of rabbits after feeding on oats and on green food. A similar study was made of the urine after administration of milk or acid, and the effect of ammoniacal decomposition was determined. The influence of the buffering capacity of foods on digestion is considered, and milk was studied as an example. The buffering capacity of cow's milk is very high, that of human milk is very low, whilst goat's milk occupies an intermediate position. This is discussed with respect to the feeding of infants. The buffering capacity of various milk fractions and preparations was also determined. E. S. HEDGES.

Buffering capacity and plant juices. F. LEUTHARDT (Koll.-Chem. Beih., 1927, **25**, 1—68).—In characterising biological liquids, it is not sufficient to consider only the hydrogen-ion concentration, but the buffering capacity also, for two solutions of the same hydrogen-ion concentration, but with different buffering capacities, may behave differently towards an acid-producing culture. An expression, $d(S-S_0)/dh$, is derived for the buffering capacity, where S is the amount of acid added to unit volume of the

solution, and S_0 is the amount of acid which would have to be added to water to give the same hydrogen-ion concentration, h. The buffering capacity of water is therefore zero, and provision is made for "negative buffering." This latter effect has been realised in the action of certain non-electrolytes (glycerol, sugars, alcohols). For example, addition of dextrose or sucrose to buffered solutions of malic acid or tartaric acid produces a rise in the hydrogen-ion concentration. It was found that, in alkaline solution, dextrose and sucrose have themselves a strong buffering effect, and that they bind considerable quantities of alkali. Formulæ are derived showing the buffering effect of mixtures of polybasic acids with their salts. A study was made of the buffering capacity of the expressed juice of apples, grapes, lemons, tomatoes, and some succulent plants by following their titration curves. The conclusion was reached that the buffering power is almost entirely due to the organic acids mixed with their salts (mainly potassium). The slight deviations of the curves from the theoretical were probably due to the sugar content. Examination of the expressed juice of *Mesembryanthemum* showed a large content of glutamin. The importance of organic acids in metabolism is discussed, especially the possibility of their formation from carbohydrates or higher fatty acids by oxidation at the β-carbon atom. It is suggested that glyoxalic acid may be the first step in the oxidation.

E. S. HEDGES.

Transitions of silver–zinc alloys in the crystalline state. G. I. PETRENKO (Z. anorg. Chem., 1927, **165**, 297—304).—The cooling curves of silver–zinc alloys containing from 21·5 to 48% of zinc indicate the existence of a transition temperature at about 251°, corresponding with the breaking down of a solid solution. The transition at 242° is due to the separation of the β-solid solution, containing 35·5% of zinc, into two saturated solid solutions α and β_1, containing 24% and 36·5% of zinc respectively, whilst that at 262° corresponds with a reaction between the compound Ag_2Zn_3 and a solid solution containing 39% of zinc, which results in the production of a new crystalline phase containing 41% of zinc. The times of transition of alloys containing from 35·5 to 39% of zinc indicate that the compound AgZn is dimorphic. At temperatures below 300° zinc dissolves up to 4% of silver, and at 440°, 10%. Photomicrographs of a number of the alloys are given and discussed. At ordinary temperatures nine groups of silver–zinc alloys are recognised: 0—24% zinc, α solution; 24—35%, α and solution; 36·5—41%, solution; 41—47·61%, γ and solution; 47·61—51%, γ solution; 51—60%, γ+δ solution; 60—80%, δ solution; 80—96%, δ and ε solution; 96—100%, ε solution. The compounds AgZn, Ag_2Zn_3, and Ag_2Zn_5 exist.

H. F. GILLBE.

Changes in solid crystalline organic substances on heating. B. GARRE (Z. anorg. Chem., 1927, **164**, 81—85).—By determining the heating (time–temperature) curves of ammonium cyanate and maleic acid, it is found that the transformation of these substances into carbamide and fumaric acid, respectively, commences below the m. p. Similarly, with mixtures of quinol and *m*-phenylenediamine, pyrocatechol and *o*-phenylenediamine, and *p*-phenylenediamine and quinol or resorcinol, but not with many other mixtures in which compounds are formed in the molten state, there is evolution of heat below the lowest eutectic temperature.

R. CUTHILL.

Vapour pressure of the saturated aqueous solutions of certain salts. H. G. LEOPOLD and J. JOHNSTON (J. Amer. Chem. Soc., 1927, 49, 1974—1988).—The vapour pressures over the temperature range 20—50° of saturated solutions of sodium and potassium chlorides (separate and mixed), sodium and potassium sulphates, and potassium dichromate were determined with an accuracy of 0·05 mm. The regularity of vapour-pressure data is no criterion of their accuracy since the presence of a constant error is not indicated; a sensitive criterion is the graph of the relative molal lowering of vapour pressure, $\Delta(=(p_0-p)/p_0M)$, against M, the molality. Within the accuracy of existing data Δ is independent of T (Babo's law), so that the method enables results from various sources to be correlated. In this way the "best" curves for the vapour pressures of the above salt solutions are constructed and the interpolated pressures for a series of molalities are tabulated. The rate of increase of Δ with concentration is higher the greater the degree of hydration of the solute. The curves show that a saturated solution (and presumably some unsaturated solutions) attains its final vapour pressure only after being maintained at constant temperature for 24 hrs.

S. K. TWEEDY.

Calcium nitrate. I. Temperature–composition relations of the binary system calcium nitrate–water. W. W. EWING, N. L. KREY, H. LAW, and E. LANG (J. Amer. Chem. Soc., 1927, 49, 1958—1962).—Investigation of the above system by the f.-p. method reveals the existence of a metastable region between the concentrations of 70 and 78% and the temperatures 20° and 51° in which there are metastable eutectic mixtures of tetra- and di-hydrate, of tetrahydrate and anhydride, and of trihydrate and anhydride. The saturated solutions in this region are supersaturated with respect to various modifications and their solid constituents are in metastable conditions.

S. K. TWEEDY.

Calcium nitrate. II. Vapour pressure–temperature relations of the binary system calcium nitrate–water. W. W. EWING (J. Amer. Chem. Soc., 1927, 49, 1963—1973).—The vapour pressure–temperature relations of the above system were determined by the dynamic method of Smith and Menzies between 20° and the b. p. for concentrations varying between 20% and saturation. The results at concentrations above 50% are uniformly higher than those of Gerlach (A., 1887, 1012). For mixed crystal systems and for solutions below 60° $\log p$ is proportional to $1/T$. The temperature–composition diagram previously described (cf. preceding abstract) can be constructed from the vapour-pressure measurements here recorded.

S. K. TWEEDY.

Probable combinations of acetylsalicylic acid with products of pharmaceutical use: cryoscopic researches. A. ANGELETTI (Annali Chim. Appl., 1927, **17**, 313—320; cf. Oliveri-Mandala, this vol.,

303).—Thermal analysis of mixtures of acetylsalicylic acid (aspirin) with acetanilide is impossible, owing to decomposition of the former; similarly mixtures of pyramidone containing more than 35% of aspirin decompose when heated to the m. p. The depression of the f. p. of acetic acid by mixtures of aspirin with acetanilide and with phenacetin, and that of acetophenone by aspirin–pyramidone mixtures has been examined. Although the solubility of aspirin is unaffected by acetanilide, the magnitude of the depression indicates some complex-formation. Similarly a molecular complex of aspirin with phenacetin is indicated.

The solubility of aspirin in acetophenone is increased slightly when pyramidone is present and the depression of the f. p. indicates complex-formation, which increases with concentration.

E. W. WIGNALL.

Reciprocal displacement of sodium and potassium from their chlorides. L. HACKSPILL and E. RINCK (Compt. rend., 1927, **185**, 463—465).—The equilibrium $KCl+Na \rightleftharpoons NaCl+K$ has been studied by heating one metal with the chloride of the other at 900° in an iron tube. The mass-action constant is about 11 at 900°, in agreement with Jellinek and Tomoff (A., 1924, ii, 658), but increases with fall of temperature. C. W. GIBBY.

Systems $AgNO_3$–$LiNO_3$ and $AgNO_3$–$RbNO_3$. A. P. PALKIN (J. Russ. Phys. Chem. Soc., 1926, **58**, 1334—1338).—Silver nitrate (m. p. 208°) and lithium nitrate (m. p. 249°, not 245° as usually given in Landolt's tables) afford a simple f.-p. diagram with a eutectic at 171·5°, containing 75% of silver nitrate. With rubidium nitrate (m. p. 306°) silver nitrate forms a compound, $AgNO_3,RbNO_3$, m. p. 139·5°, and the two eutectic points at which this coexists with silver nitrate and rubidium nitrate respectively are at 128°, 67·5% $AgNO_3$ and 136°, 40% $AgNO_3$.

E. ROTHSTEIN.

Composition of crystals obtained from solutions containing sodium sulphate and iodides. (SIGNA.) E. FABRIS (Annali Chim. Appl., 1927, **17**, 321—335; cf. this vol., 518).—The composition of the products obtained by crystallisation has been determined. E. W. WIGNALL.

Carbon dioxide–carbon monoxide equilibrium over copper. E. BRODY and T. MILLNER (Z. anorg. Chem., 1927, **164**, 86—95).—The equilibrium constant of the reaction $2Cu+CO_2 \rightleftharpoons Cu_2O+CO$ has been calculated from available data for the reactions $2CO_2 \rightleftharpoons 2CO+O_2$ and $4CuO \rightleftharpoons 2Cu_2O+O_2$, since at equilibrium the partial pressure of the oxygen produced by the dissociation of the carbon dioxide must be equal to the dissociation tension of the cuprous oxide, which is probably nearly the same as that of cupric oxide. At 600° the value of $[CO]/[CO_2]$ is 10^{10}, and at 400° 10^{-13}, so that between these temperatures carbon dioxide, either alone or diluted with inert gases, is not reduced to any appreciable extent by copper. Wohler and Balz's figures for the dissociation tension of cuprous oxide (A., 1921, ii, 633), on the other hand, would indicate that measurable quantities of carbon monoxide are formed, but experients have failed to confirm this. R. CUTHILL.

Combustion of carbon monoxide and methane over cupric oxide (Jager's method of analysis). E. BRODY and T. MILLNER (Z. anorg. Chem., 1927, **164**, 96—100).—The calculated values of the equilibrium constant of the reaction $2Cu+CO_2 \rightleftharpoons Cu_2O+CO$ (cf. preceding abstract) show that at 200—600° the oxidation of carbon monoxide by copper oxide is practically complete when equilibrium has been attained. Computation of the equilibrium constant of the reaction $CH_4+2O_2 \rightleftharpoons CO_2+2H_2O$ from data for the reactions $CO_2+4H_2 \rightleftharpoons CH_4+2H_2O$ and $2H_2+O_2 \rightleftharpoons 2H_2O$ shows the same to be true for methane at 250—800°. The difficulty in obtaining complete oxidation experienced by Terres in his investigation of Jager's method of analysis of mixtures of hydrogen, carbon monoxide, methane, and nitrogen (B., 1915, 214) must consequently be ascribed to delay in reaching equilibrium. The use of suitable catalysts is therefore indicated. R. CUTHILL.

Equilibria in reduction, oxidation, and carburation of iron. I. R. SCHENCK [with F. KRAGELOH, F. EISENSTECKEN, and H. KLAS] (Z. anorg. Chem., 1927, **164**, 145—185).—The decomposition of methane in presence of iron, CH_4 $C+2H_2$, and the cementation of iron by methane, according to the equation CH_4+3Fe Fe_3C+2H_2, have been studied between 300° and 900°. By starting with pure iron and adding to the methane so much hydrogen that the composition of the gas phase is a little below the equilibrium composition for the cementation system, the equilibrium in the former system may be observed. Up to 720°, the cementation equilibrium corresponds with lower hydrogen concentrations than the other equilibrium, but at 720° the composition of the gas phases in the two systems becomes the same, so that at this point carbon, ferrite, and ferrite–cementite mixed crystals co-exist in equilibrium. Above about 695°, the equilibria cementite–concentrated mixed crystals–gas, and ferrite–dilute mixed crystals–gas can be observed. By means of the van 't Hoff isochore, the heat of the reaction $CH_4=C+2H_2$ is calculated to be −21,045 g.-cal., and that of the reaction $3Fe+CH_4=Fe_3C+2H_2$ to be −36,450 g.-cal., giving −15,405 g.-cal. for the heat of formation of cementite. The present results are not in complete agreement with those of Johansson and von Seth (B., 1926, 826), probably because the iron used by these authors contained manganese. From the new data and those available for the equilibrium 2CO $C+CO_2$, the equilibrium in the system $3Fe+2CO$ Fe_3C+CO_2 has been calculated. R. CUTHILL.

Equilibria in the reduction, oxidation, and carburation of iron. II. R. SCHENCK [with F. KRAGELOH and F. EISENSTECKEN (Z. anorg. Chem., 1927, **164**, 313—325).—The system cobalt–methane has been studied between 350° and 720°. Primarily, the catalysed decomposition of methane, $CH_4 \rightleftharpoons C+2H_2$, is observed, equilibrium being established more rapidly than when iron is used as catalyst (cf. preceding abstract), but if the metal has previously been treated with pure methane there is set up after some time another equilibrium, presumably due to the formation of carbide. With rise in temperature, the two equilibria approach each other, and above 680° the

former only can be observed under ordinary conditions. The observed values of the equilibrium constant for the decomposition of methane into its elements are, in general, in excellent agreement with those obtained using iron as catalyst. At 683°, the curve for this equilibrium intersects that of the carbide equilibrium, the resemblance to the effects observed with iron being such as to suggest that cobalt carbide may be able to form mixed crystals with cobalt. From the experimental data, the heat of the reaction $n\text{Co}+\text{CH}_4=\text{Co}_n\text{C}+2\text{H}_2$ is calculated to be −32,650 g.-cal., and the heat of formation of cobalt carbide from its elements to be −11,282 g.-cal. The equilibrium $2\text{CO}\rightleftharpoons\text{C}+\text{CO}_2$ over cobalt has been examined at 618°, 668°, and 718°. A comparison of the heat of the reaction calculated from the experimental figures with the accepted value shows that at 618° the observed equilibrium constant is not that of the monoxide–dioxide equilibrium. The deviation could be explained on the assumption that dilute cobalt carbide–cobalt mixed crystals play a part in the establishment of equilibrium. R. CUTHILL.

System $\text{Fe(NO}_3)_3$–$\text{Al(NO}_3)_3$–H_2O at 25°. G. MALQUORI (Atti R. Accad. Lincei, 1927, [vi], 5, 801—802).—The system is characterised by the absence of double salt formation, the solid phases in equilibrium with the saturated solutions being $\text{Al(NO}_3)_3,9\text{H}_2\text{O}$ and $\text{Fe(NO}_3)_3,9\text{H}_2\text{O}$. When both are present the saturated solution contains 15·21% $\text{Al(NO}_3)$ and 29·98% $\text{Fe(NO}_3)_3$. R. W. LUNT.

Ternary system formic acid–sodium formate–water. Acid sodium salts of formic acid. E. ELOD and K. TREMMEL (Z. anorg. Chem., 1927, 165, 161—170).—Isothermal solubility data at 13°, 23·4°, and 45° for the system formic acid–sodium formate–water, together with dilatometric measurements of the binary system sodium formate–water, indicate the existence of anhydrous, di- and tri-hydrated sodium formate, and of the two acid salts $\text{H·CO}_2\text{Na,H·CO}_2\text{H}$ and $3\text{H·CO}_2\text{Na,H·CO}_2\text{H}$. The transition temperature of the dihydrate to the anhydrous salt is 27·9°, and of the trihydrate to the dihydrate 15·3°.

H. F. GILLBE.

System ferric oxide–arsenic acid–water at low concentrations of arsenic acid. N. H. HARTSHORNE (J.C.S., 1927, 1759—1768).—Measurements at 25° over the range 2·6—23·1% of arsenic acid indicate the existence of a normal salt $\text{Fe}_2\text{O}_3,\text{As}_2\text{O}_5,x\text{H}_2\text{O}$, in which x is less than 8 (probably 6), as well as a metastable acid salt $\text{Fe}_2\text{O}_3,2\text{As}_2\text{O}_5,8\text{H}_2\text{O}$. No basic salts appear to be formed. Equilibrium is reached very sluggishly, and in some cases was not attained even after prolonged stirring. F. S. HAWKINS.

Heat of formation of ammonium carbamate from ammonia and carbon dioxide. K. G. CLARK and H. C. HETHERINGTON (J. Amer. Chem. Soc., 1927, 49, 1909—1915).—The heat of the reaction $2\text{NH}_{3\text{gas}}+\text{CO}_{2\text{gas}}=(\text{NH}_3)_2\text{CO}_{2\text{solid}}$ was directly determined to be 36,300 g.-cal. at constant volume at 21°, in agreement with the indirect determination of Lecher (Sitzungsber. Preuss. Akad. Wiss. Berlin, Abt. II, 1878). S. K. TWEEDY.

Free energy of formation of phosphine. D. H. DRUMMOND (J. Amer. Chem. Soc., 1927, 49, 1901—1904).—The thermal dissociation of phosphine between 573° and 613° was determined by a streaming method. For the evaporation of white phosphorus, $4\text{P(l.)}\longrightarrow\text{P}_4\text{(g.)}$, $\Delta F=58{,}871{\cdot}7+15{\cdot}4T\log_e T+0{\cdot}00033T^2-0{\cdot}0000008T^3-203{\cdot}7T$, whilst for fusion $\Delta F=-70-0{\cdot}8T\log_e T+4{\cdot}87T$. For the reaction $\frac{3}{2}\text{H}_2\text{(g.)}+\frac{1}{4}\text{P}_4\text{(g.)}=\text{PH}_3\text{(g.)}$, $\Delta F=-16{,}486{\cdot}5+3{\cdot}72T\log_e T+0{\cdot}0004T^2+0{\cdot}0000007T^3+2{\cdot}52T$; the values −20,200 and −19,711 g.-cal. are calculated for the heat of this reaction. The standard entropies of phosphine and white phosphorus are 52·4 and 9·95 g.-cal. per degree, respectively. S. K. TWEEDY.

Heat of dilution of electrolyte solutions. P. GROSZ (Monatsh., 1927, 48, 243—250).—According to the new theory of strong electrolytes the free energy of solution at sufficient dilution should be independent of the nature of the electrolyte, for the same valency type. Hence individual differences between the heats of dilution of similar electrolytes should diminish with decreasing concentration, but experimental results show that this is not so, the heat of dilution being determined by individual properties—the ionic radius, change of dielectric constants and their temperature coefficients. A footnote added subsequently states that new measurements reveal the decrease of individual differences with increasing dilution as demanded by theory. S. J. GREGG.

Calculation of combustion temperatures. P. DROSSBACH (Z. Elektrochem., 1927, 33, 349—350).—The theoretical temperatures of combustion of carbon monoxide and hydrogen have been calculated from published thermal data and from values for the degree of dissociation of carbon dioxide and steam at high temperatures. The values obtained are: for carbon monoxide 2811° (burning in oxygen) and 2237° (burning in air); for hydrogen, 3527° (oxygen) and 2410° (air). The considerably lower values calculated by a different method by Pollitzer (A., 1923, ii, 11) are criticised. H. J. T. ELLINGHAM.

Deviation from Ohm's law for electrolytes. M. WIEN (Ann. Physik, 1927, [iv], 83, 327—361).—For certain electrolytes the conductivity increases with increasing voltage at a rate greater than is to be expected on the basis of the increased temperature when the temperature-coefficient is normal. The increase in conductivity ($\Delta\lambda$) is made up of two separate effects, the Joule heat effect ($\Delta\lambda_w$) and an increment ($\Delta\lambda_v$) which is proportional to the voltage. $\Delta\lambda_v$ increases rapidly with increasing valency of the ions and corresponds with a departure from Ohm's law. If the deviation were due to a heat effect the form of the current curve would not influence the result and also $\Delta\lambda$ would be proportional to V^2 (V voltage). The experiments indicate a marked variation of $\Delta\lambda$ with the wave-form and are only consistent with the relations $\Delta\lambda=\Delta\lambda_w+\Delta\lambda_v$ and $\Delta\lambda=AV+BV_2$ (A and B being constants). Increases in conductivity as large as 50% have been measured. Over the range $\Delta\lambda_v=1-10\%$, for calcium ferrocyanide, $\Delta\lambda_v$ is proportional to the voltage (1—40 kilovolts); similarly for beryllium sulphate and sulphuric acid the straight-line relationship holds. When, however, the voltage is very high or the concentration very low $\Delta\lambda_v$ approaches a limiting value. The

valency of the ions exerts a marked effect on the appearance of this limit, since both increasing concentration and higher valencies shift the limit in the direction of higher values. The initial increase of conductivity with increasing voltage varies as $v_1^2 v_2^2$, where and v_2 are the valencies of the ions in the solution, and falls as the concentration increases. At great dilution the equation $\Delta\lambda=\lambda_0(1+4{\cdot}0v_1^2v_2^2\times 10^{-5}F)$, in which F is the field strength (in kilovolts per cm.), expresses the results for six salts of different types with reasonable accuracy. R. A. MORTON.

Calculation of the equivalent conductivity of strong electrolytes. Aqueous solutions. II. Application of data at 0°, 18°, and 25°. III. Mobilities of the hydrogen and hydroxyl ions. A. FERGUSON and I. VOGEL (Phil. Mag., 1927, [vii], 4, 233—242, 300—305).—II. The constants n and B in the equation $\Lambda_0=\Lambda+BC^n$ vary from one electrolyte to another. These constants have been determined from the data for a large number of electrolytes and the values of Λ_0 have been calculated. Where sufficient data exist the calculated values are much more constant than those obtained by Lorenz and Michael (A., 1921, ii, 482) and by others. The constant B appears to vary irregularly with temperature, whilst n appears to decrease with increasing temperature except for solutions of potassium bromide and sodium acetate.

III. From calculations of the conductivities at infinite dilution of solutions of hydrochloric and of iodic acid made according to the method previously described by the authors (A., 1925, ii, 1163) the most probable value of the mobility of the hydrogen ion at 25° is found to be 349·05. Similar calculations for sodium hydroxide solutions lead to the value of 175·4 as the mobility of the hydroxyl ion at 18°.

A. E. MITCHELL.

Electrode potentials of beryllium, magnesium, calcium, strontium, and barium from thermal data. W. M. LATIMER (J. Physical Chem., 1927, 31, 1267—1269).—The electrode potentials, E_0, at 25°, calculated from the equation $E_0nF=\Delta H-T\Delta S$, where ΔH is the heat of dissolution of the metal in acid and ΔS is the entropy change of the aqueous ions, are beryllium −1·69, magnesium −2·40, calcium −2·87, strontium −2·92, and barium −2·90 volts.

L. S. THEOBALD.

Potential of the gold–auric oxide electrode. R. H. GERKE and (MISS) M. D. ROURKE (J. Amer. Chem. Soc., 1927, **49**, 1855—1858).—From measurements of the *E.M.F.* of the cell $Hg(l),Hg_2SO_4(s.)|H_2SO_4$soln.$|Au_2O_3,Au(cryst.)$ at 25° the standard potential of the gold–auric oxide electrode, $Au(cryst.),Au_2O_3(s.)|H^{\cdot}$, is found to be −1·362 volt, the free energy of formation of the oxide thus being 18,810 g.-cal. All attempts to prepare aurous oxide were unsuccessful and it is doubtful if the pure oxide has ever been obtained (cf. Buehrer, Wartman, and Nugent, this vol., 629). S. K. TWEEDY.

Free energy of auric oxide as determined from measurements of the gold–auric oxide electrode. . . BUEHRER and W E ROSEVEARE (J. Amer. Chem. Soc., 1927, **49**, 1989—1991).—The *E.M.F.* of the cell $H_2(gas)|H_2SO_4(xM)|Au_2O_3(sol.),Au(cryst.)$ is 1·364±0·001 volt at 25°; this is practically independent of the value of x between 1·024 and 0·010. Assuming the mean value −1·363 volt for the standard potential of the gold–auric oxide electrode (cf. preceding abstract) the free energy change of formation of the oxide is +19,100 g.-cal. at 25°, and the entropy change −108·4 g.-cal. per degree. The calculated dissociation pressure is $2{\cdot}13\times10^9$ atm. S. K. TWEEDY.

Effect of hydrochloric acid on the electrode potential between mercury and mercurous chloride. S. R. CARTER, F. M. LEA, and R. A. ROBINSON (J.C.S., 1927, 1906—1911).—*E.M.F.* measurements for the cell $Hg|Hg_2Cl_2,xN$-HCl$|N$-HCl$|N$-KCl$|N$-KCl,$Hg_2Cl_2|Hg$ with acid concentrations ranging from 0·0027*N* to 10·0*N* are recorded, corrections being applied for the diffusion potentials. The effect of the addition of mercuric chloride to the element $Hg|Hg_2Cl_2,xN$-HCl caused a small increase in the *P.D.* The potentials given by such solutions in combination with an inert platinum electrode were also measured at different concentrations of hydrochloric acid and mercuric chloride. F. S. HAWKINS.

Oxidation–reduction potentials of mercurous and mercuric chlorides in hydrochloric acid solution. S. R. CARTER and R. A. ROBINSON (J.C.S., 1927, 1912—1923).—The potentials were measured by means of a cell of the type $Pt|Hg_2Cl_2,xM$-$HgCl_2,yN$-HCl$|yN$-HCl$|N$-HCl$|N$-KCl$|N$-KCl,$Hg_2Cl_2|Hg$, with acid concentrations from 0·01*N* to 10*N*, and mercuric chloride concentrations from 0·0001*N* to 3·8*N*. The results indicate the formation of complex ions, probably $HgCl_4''$, in concentrated solutions of mercuric chloride. The reduction and oxidation of mercury salts by sulphur dioxide are shown to be in general agreement with the electrochemical properties of the system.

F. S. HAWKINS.

Overvoltage. II. Oxygen overvoltage. III. Relationship between hydrogen overvoltage and concentration and surface tension of the solution. T. ONODA (Z. anorg. Chem., 1927, **165**, 79—92, 93—136).—II. A study of the overvoltage of oxygen at electrodes of platinum, gold, copper, and nickel shows it to be but little influenced by changes in the surface of the electrode. The values in volts at 20° are: nickelised nickel, 1·399; polished nickel, 1·405; platinised platinum, 1·441; polished platinum, 1·663; copper, 1·465; gold, 1·693. The temperature coefficient of the overvoltage between 0° and 60° is very small for platinised platinum and for nickelised nickel; for polished platinum the coefficient is −0·0045 and for gold −0·00388, whilst for nickel the relationship $v_t=1{\cdot}3880+0{\cdot}0019t-0{\cdot}000039t^2$ is valid, v_t being the overvoltage at temperature $t°$. It has been established that the oxygen–hydrogen element is irreversible between 0° and 60°.

III. The hydrogen overvoltage at a mercury electrode in solutions of hydrogen chloride and of sulphuric acid containing various concentrations of inorganic salts or of organic compounds such as mannitol, α-aminohexoic acids, or glycerol, has been determined. The change $\delta-$ of the hydrogen overvoltage with alteration of concentration is related to the change $\delta\gamma$ of the surface tension between the

mercury electrode and the solution by the relation $\delta\pi=-0{\cdot}0065\delta\gamma$. From the expression $\pi_a=\pi_0+(\gamma_a-\gamma_w)\delta\pi/\delta\gamma$, the true overvoltage π_0, corrected for the surface-tension change, may be calculated from the apparent value π_a; γ_a is the surface tension between mercury and the acid employed, and γ_w that between mercury and water. The relationship between the hydrogen-ion concentration C_H and π_0 is $\pi_0 C_H^{0{\cdot}1358}=0{\cdot}5018$. The equation connecting surface tension and overvoltage is valid for amalgams of gold, silver, lead, and tin, employed in solutions of hydrochloric or sulphuric acid with and without added salts. H. F. GILLBE.

Influence of hydration on the mechanism of the generation of *E.M.F.* N. A. ISGARISCHEV (J. Russ. Phys. Chem. Soc., 1926, **58**, 1175—1186).—See A., 1926, 802.

Passivity of metals. F. MEUNIER (Bull. Soc. chim. Belg., 1927, **36**, 435—447).—A lecture.

Passivity of chromium. W. J. MULLER and E. NOACK (Monatsh., 1927, **48**, 293—313).—The passivity of Goldschmidt chromium in *N*-sulphuric acid has been investigated electrometrically. So long as the current density was below a certain critical value (i_c) which varied from sample to sample according to treatment, the metal remained active, and dissolved with the evolution of hydrogen. On exceeding this critical value, a fall of density immediately set in, during which the log. of the density varied inversely as the time since the commencement of the fall, and after sufficient time complete passivity resulted. Log i_c was inversely proportional to the temperature between 0° and 35°. Activity of the chromium was characterised by a potential of −0·34 volt, and passivity by zero potential, so that during the time of falling density, the metal remained active. These facts agree with Muller's theory of passivity (A., 1924, ii, 743) as suggested originally for iron, according to which the metal dissolves in the acid, but owing to the high mobility of the hydrogen ions, the anodic solution becomes impoverished in these; hence basic ferrous salt is formed and deposits on the electrode when the solution becomes saturated, thus increasing the resistance and decreasing the current, causing complete passivity only when the covering is complete. With chromium, the chromous salt first formed by dissolution of the metal in the acid rapidly oxidises to chromic salt (hydrogen being evolved), which hydrolyses much more rapidly than the iron salts; with high current densities (*e.g.*, 1400 milliamp. per cm.^{2}), the time required for passivity is only 0·3 sec., but by using an oscillograph, the curve connecting time and current density was shown to be entirely analogous to the much slower iron curve, *i.e.*, of the logarithmic form mentioned above. With perfectly clean metal the fall of current density would often be suspended for a time and then occur suddenly; this is easily explained by the supersaturation of the solution with regard to hydroxide, which would be possible only in the absence of impurities. S. J. GREGG.

Electro-capillary phenomena and ions. W. KOPAZEWSKI and M. ROSNOWSKI (Compt. rend., 1927, **185**, 450—453).—The effect of ions on the electro-capillary phenomena accompanying the rise of colloids in filter-papers has been investigated in concentrations of 0·001*M*. In general, cations diminish the capillary rise of negative colloids and sometimes suppress it entirely, before any visible coagulation takes place. The capillary rise of positive colloids is increased, particularly by Fe^{+++} and Th^{++++}. Anions have the reverse effect, and suppress completely the rise of positive colloids. In the action of acids, the effect of the hydrogen ion is considerable, but is sometimes equalled by that of the anion. C. W. GIBBY.

Becquerel effect. J. LIFSCHITZ and S. B. HOOGHOUDT (Z. physikal. Chem., 1927, **128**, 87—109).—It is shown that the Becquerel effect in solutions of dyes is not due to changes of hydrogen-ion concentration. In solutions of electrolytes the effect at platinum electrodes may be ascribed to the after-effects of a photochemical change in the electrolyte. With simple electrolytes both positive and negative effects are observed; these are dependent on the nature of the ions present in the solution, whilst for photosensitive substances the effect apparently vanishes.

The magnitude of the Becquerel effect is greatly influenced by impurities in the substance under investigation, and for mixtures the additive law is not valid. The effect is not present at reversible metal–metal ion electrodes nor at the hydrogen electrode, but is exhibited only at polarisable electrodes and at the interfaces between phases. H. F. GILLBE.

General equation of chemical kinetics and its significance. Rate of hydrolysis of "organic oxides." A. SKRABAL (Z. Elektrochem., 1927, **33**, 322—348).—The velocities of many reactions in aqueous solutions can be represented by the equation, $dx/dt=(k_w+k_a[H^\cdot]+k_b[OH^\cdot])(a-x)=k(a-x)$, where k_w is the velocity constant of the uncatalysed reaction, k_a that of the catalysis by hydrogen ions, and k_b that of the catalysis by hydroxyl ions. The manner in which the total velocity constant, k, varies, according to this equation, with changing acidity or alkalinity of the system is shown by plotting log k on p_H, the curves assuming various forms according to the relative magnitudes of k_w, k_a, and k_b. Examples of reactions giving curves of the various types are quoted. No entirely satisfactory theory of the mechanism of the catalytic action of hydrogen and hydroxyl ions has yet been put forward. The theory developed by Euler (cf. A., 1921, ii, 498; 1926, 580) has not been completely verified experimentally in any single case and in most cases is incapable of such verification, since for the crucial tests impossibly high hydrogen- or hydroxyl-ion concentrations are needed; moreover, several established facts are not in harmony with the theory. The above general kinetic equation can be applied to the velocity of hydrolysis of substances containing "ether oxygen ("organic oxides"). It has been shown that for the hydrolysis of esters, k_w, k_a, and k_b depend on the chemical constitution of the component alcohols and carboxylic acids. To each aldehyde or ketone and each alcohol can be attributed a factor from which the rate of hydrolysis of all acetals in acid solutions

can be calculated. A relation has been developed connecting the velocity coefficient of saponification of a mixed organic oxide, XOY, with those of the corresponding simple oxides, X_2O and Y_2O, where X and Y represent alkyl or acyl groups (cf. A., 1926, 681, 1010). H. J. T. Ellingham.

Thermal decomposition of ozone. O. R. Wulf and R. C. Tolman (Proc. Nat. Acad. Sci., 1927, **13**, 272—275).—See this vol., 631, 834.

Least energy required to ignite mixtures of air and vapour of ethyl ether. Y. Nagai and M. Furihata (Proc. Imp. Acad. Tokyo, 1927, **3**, 352—354).—The minimum amount of energy in the form of a spark from a condenser necessary to fire mixtures of air and ether vapour has been determined. With increase in the concentration of ether, the necessary energy with a *P.D.* of 100 volts first decreases up to a concentration of about 4% of ether, then remains constant for a little, rapidly rises and again remains constant, and finally rises continuously again. Increase in voltage results in an extension of the concentration range of the first region of constancy and ultimate disappearance of the second. Reduction in the pressure causes the minimum energy to increase throughout. R. Cuthill.

Effect of ethyl bromide on the least energy required to ignite mixtures of air and vapour of ethyl ether. Y. Nagai and M. Furihata (Proc. Imp. Acad. Tokyo, 1927, **3**, 355—360; cf. preceding abstract).—Addition of ethyl bromide to air–ether vapour mixtures raises the minimum amount of energy required to effect ignition, except with mixtures containing less than about 3% of ether, when the reverse effect occurs because the lower limit of inflammability is lowered. With increase in the amount of bromide, the second horizontal portion and then the first of the minimum energy curve contracts and finally disappears, because the upper limit of inflammability is depressed. With a mixture containing 4% of ether, the minimum energy increases with increase in the amount of bromide up to a concentration of about 0·75% of the latter, above which it remains nearly constant. This can be accounted for by supposing that the bromide raises the flame propagation temperature of the ether until a temperature is reached at which its own molecules are activated for combustion. R. Cuthill.

Combination of nitrogen and hydrogen activated by electrons. A. Caress and E. K. Rideal (Proc. Roy. Soc., 1927, **A**, **115**, 684—700).—Experiments have been performed on the rate of formation ammonia from hydrogen and nitrogen as a function of the energy of thermions used to activate molecules and atoms. Previous work is reviewed. A triode valve with a tungsten emitter was used and the reaction vessel was immersed in liquid air; the rate of formation of the ammonia was determined by measurements of the decrease in pressure. At the emission used, a high rate of pressure decrease was observed with no applied voltage, both with nitrogen–hydrogen mixtures and with pure hydrogen, even when retarding potentials were applied. In the latter case, this is shown to be due to the production and freezing out of hydrogen atoms. The rate of pressure decrease due to this cause is proportional to the difference between the pressure and the final pressure, and this difference is proportional to the area of surface not covered by hydrogen atoms. With nitrogen–hydrogen mixtures this saturation pressure was not observed, the reaction proceeding until all the mixture was used up. Some experiments were also made with an oxide emitter, and the electron-efficiency of the process has been calculated. The mechanism of the process is discussed, and it is shown that synthesis can occur due to the following reactions: N_2+H at the surface of platinum or nickel; N_2+H′ in the bulk at 13 volts. The following molecular species are shown to be chemically reactive: N_2^+ in the bulk at 17 volts; N^+ in the bulk at 23 volts. L. L. Bircumshaw.

Kinetics of the intramolecular transformation of ammonium thiocyanate into thiocarbamide and thiocarbamide into ammonium thiocyanate. A. N. Kappanna (J. Indian Chem. Soc., 1927, **4**, 217—228).—Study of the kinetics of the reaction, $NH_4CNS \rightleftharpoons CS(NH_2)_2$, over the range 140—180° shows that the velocity is unaffected by the presence of air, by glass or platinum surfaces, or by traces of water or alcohol. The reaction is perfectly reversible and unimolecular. From determinations of the equilibrium between the two components over the same range, it is found that the heat of reaction equals the difference between the heats of activation of the two molecules. The Dushman–Rideal equation gives values in approximate agreement for the direct reaction, $CS(NH_2)_2 \longrightarrow NH_4CNS$, but not for the reverse reaction. The active life values of the two molecules are calculated to be $7{\cdot}24 \times 10^{-12}$ and 8×10^{-14} sec. respectively. G. A. C. Gough.

Decomposition of nitrous acid in aqueous solution. T. W. J. Taylor, E. W. Wignall, and J. F. Cowley (J.C.S., 1927, 1923—1927).—The rate of decomposition of aqueous solutions of nitrous acid is considerably reduced if the surface is covered with a layer of medicinal paraffin. A critical concentration (0·2*N* at 25°) exists, above which the rate of decomposition is higher. The unimolecular velocity coefficient for the slower reaction diminishes as the reaction proceeds. An explanation is suggested. C. W. Gibby.

Oxidation of a mixture of stannous chloride and sodium sulphite in alkaline solution with air. S. Miyamoto (Bull. Chem. Soc. Japan, 1927, **2**, 191—196; cf. this vol., 525).—Air was passed through the mixture, and the extent of the oxidation measured by titrating with iodine and thiosulphate. When the concentration of stannous chloride was large, the velocity of reaction was independent of the concentration, and smaller than that of either salt. When it was small, the velocity was slow, but increased with time. F. S. Hawkins.

Kinetics of reaction in crystal powders. K. Fischbeck (Z. anorg. Chem., 1927, **165**, 46—54).—Theoretical. H. F. Gillbe.

Reaction between silver and sulphur in crystalline powder mixtures. K. Fischbeck and W. Jellinghaus (Z. anorg. Chem., 1927, **165**, 55—

58).—The rate of formation of silver sulphide from finely-divided silver, prepared by precipitation from silver nitrate solution by zinc, and sulphur, precipitated from solution in carbon disulphide by the addition of petroleum, has been studied at 22—55°. The percentage of reaction product formed is proportional to the square root of the time; the velocity of the reaction increases 5·47 times per 10° rise of temperature, whilst the diffusion constant increases 1·65 times, indicative of the diffusion taking place solely in the solid phase. H. F. GILLBE.

Dehydration of gypsum. R. STUMPER.—See B., 1927, 676.

Calcium sulphate. II. [Velocity of hydration.] III. Analysis and use of plaster. L. CHASSEVENT.—See B., 1927, 676, 722.

Influence of reaction rate on operating conditions in contact sulphuric acid manufacture. II. W. K. LEWIS and E. D. RIES.—See B., 1927, 700.

Mechanism of the steam-carbon reactions. E. W. THIELE and R. T. HASLAM (Ind. Eng. Chem., 1927, **19**, 882—887).—The effect of varying pressure on the reactions between steam and incandescent carbon was determined, activated vegetable charcoal, electrode carbon, natural graphite, and retort carbon being used. With the first three the weight of steam decomposed per min. was independent of the pressure. With retort carbon the weight decomposed increased with reduction of pressure. Reduction of the partial pressure by dilution with nitrogen produced similar results. The reaction may therefore be described as of "zero" or "negative" order according to the type of carbon used. In the first case variation in pressure produces little alteration in the composition of the resulting gas mixture; in the second, increase in pressure lowers the carbon monoxide concentration. These results may be explained by the assumption that the most rapid reaction is the formation of a surface complex C_xO_y. The (slower) decomposition of this yields carbon dioxide, whilst carbon monoxide can be produced only in absence of the complex. C. IRWIN.

Reactivity of coke [and carbon]. S. W. PARR and W. D. STALEY.—See B., 1927, 672.

Oxidation of charcoal with sulphuric acid. E. PHILIPPI and R. SEKA [with H. SEDLATSCHEK, O. SCHMIDT, and K. SEKORA] (Monatsh., 1927, **48**, 375—389).—The oxidation of charcoal (carbo ligni depuratus of specified composition) with sulphuric acid, d 1·83, has been studied. Time-temperature diagrams for the reaction are reproduced, and the amounts of liquid and solid products formed determined. The gases liberated during the reaction, sulphur dioxide, carbon dioxide, and carbon monoxide, were determined by standard methods, and the results are expressed diagrammatically. Sulphur trioxide is not formed in any appreciable quantity during the course of the reaction. H. BURTON.

Influence of boundary films on corrosive action. L. H. CALLENDAR.—See B., 1927, 724.

Rate of dissolution of ultra-light magnesium alloys. A. PORTEVIN and E. PRETET.—See B., 1927, 657.

Hydrolysis of proteins by acids and alkalis. I. S. YAITSCHNIKOV (J. Russ. Phys. Chem. Soc., 1926, **58**, 1377—1383).—Gelatin, casein, keratin, and silk have been hydrolysed by 0·2N-hydrochloric acid and 0·2N-sodium hydroxide. A 1% solution of the protein at 10° took several days for complete hydrolysis, but at higher temperatures, only a few hours were necessary. Alkalis always hydrolyse the proteins faster than acids of the corresponding concentration. Casein is less easily hydrolysed than gelatin. In ease of hydrolysis keratin and silk lie between casein and gelatin. The formula $K_s=x/\sqrt{t}$ applies in the following cases: acid hydrolysis of gelatin, casein, and keratin at 100°; alkaline hydrolysis of the same three proteins at 10°, 37°, and 70°, and of casein at 100°; alkaline hydrolysis of silk at 70°. E. ROTHSTEIN.

Decomposition of glycylglycine by alkalis. I. S. YAITSCHNIKOV (J. Russ. Phys. Chem. Soc., 1926, **58**, 1373).—0·05N-Glycylglycine in 0·1N-sodium hydroxide solution is completely hydrolysed at 100° in 7 hrs. The velocity of the reaction agrees with the formula $K=(1/t)\log[a/(a-x)]$. E. ROTHSTEIN.

Hydrolysis of peptone, albumin, and casein by N-alkali solution. I. S. YAITSCHNIKOV (J. Russ. Phys. Chem. Soc., 1926, **58**, 1374—1376).—Peptone, albumin, and casein (1%) are completely hydrolysed by N-sodium hydroxide at 10° in 25 days. At higher temperatures only 9—12 hrs. are required. The rate of hydrolysis of peptone agrees with the formula: $K_s=x/\sqrt{t}$, where x=amount of hydrolysis. That of albumin agrees best with $K_p=x/t$. At 37° and 70°, K_s for casein is practically constant but at 10° and 100° it decreases with time. This is the case with K_p at all temperatures. E. ROTHSTEIN.

Mechanism of oxidative processes. XII. Activation of hydrogen peroxide by iron. H. WIELAND and W. FRANKE (Annalen, 1927, **457**, 1—70; cf. A., 1926, 806).—The activation of hydrogen peroxide by ferric salts is generally small, but ferrous salts are very effective. Ferric salts become equally active if the substance to be oxidised, or its primary oxidation product, is capable of reducing ferric to ferrous ions. Oxidation of iron ions by hydrogen peroxide to a peroxide stage must therefore play only a very subordinate part in the activation. The primary oxidation impulse, very marked in the case of formic acid and all the aliphatic hydroxy- and amino-acids investigated, less marked in the case of keto-acids, far exceeds that possibly due to an iron peroxide, and indicates that the formation of a complex between ferrous ions and the substrate delays the oxidation of the ferrous ions and enables them to catalyse the oxidation of the substrate.

In the oxidation of formic acid, 20—30% of the iron remains in the ferrous state at the end of the reaction even when 7—10 times the amount of hydrogen peroxide necessary for its oxidation to the ferric condition is present. The ferrous iron is determined colorimetrically by means of potassium ferricyanide, and the co-existence of ferrous ions and hydrogen peroxide is placed beyond doubt.

Ferric salts have practically no effect on a mixture of hydrogen peroxide and lactic acid, but in the

presence of ferrous salts the amount of peroxide reduced is 15—17 times the ferrous equivalent. Determination of lactic and malic acids presents difficulties, but glycollic acid is readily determined by means of hot acid permanganate. The activation in the case of glycollic acid is greatest at p_H 3·6, increases proportionally with the concentration of ferrous salt and of glycollic acid, and decreases greatly with increased hydrogen peroxide concentration; the temperature effect is small for the initial activation and normal for the subsequent reaction.

Tartaric acid, which is unattacked in presence of ferric salts, is rapidly oxidised when ferrous salts are present, the dihydroxymaleic acid first formed being immediately oxidised by ferric salts to mesoxalic semi-aldehyde, $CHO{\cdot}CO{\cdot}CO_2H$, so that only ferrous iron is found in the reaction product. The effect is most marked in moderately acid solution (p_H 2·4—5·8). Data are also given for mucic acid and dihydroxymaleic acid. With the latter substance activation is independent of the anion of the iron salts. Pyruvic and phenylpyruvic acids behave similarly to dihydroxymaleic acid. Ferric salts do not induce the oxidation of ethyl acetoacetate or lævulic acid; with ferrous salts the primary oxidation effect is independent of the peroxide concentration.

The oxidation of α-amino-acids to the next lower aldehydes by hydrogen peroxide and iron salts (Neuberg and Kansky, A., 1909, i, 690; Dakin, *ibid.*, 293) shows a similar marked primary oxidation impulse followed by a small peroxidative action superimposed on a much greater catalytic action due to ferrous complex compound with the amino-acid. The oxidation of glycine, alanine, histidine, tyrosine, and dihydroxyphenylalanine is investigated.

With *p*-phenylenediamine, quinol, pyrocatechol, pyrogallol, phloroglucinol, and hydroxyquinol the marked primary effect is absent, and ferric salts are as active as ferrous salts. The action is most rapid in moderately strong acid solution (p_H 2) and is almost non-existent at p_H 4. Hydrogen cyanide has no effect in acid solutions, but potassium cyanide is an active catalyst in neutral media. *o*-, *m*-, and *p*-Hydroxybenzoic acids, 3-hydroxyphthalic, 1 : 2- and 2 : 1-hydroxynaphthoic, gentisic, protocatechuic, and gallic acids are affected like the aliphatic hydroxy-acids. Ferric salts have little or no action; ferrous salts produce an initial impulse followed by a strong catalytic effect.

A parallel is drawn between these results and oxidations in the plant cell, which are also associated with an iron complex catalyst (cf. Madelung, A., 1911, i, 411; Harrison and Thurlow, A., 1926, 641; Wolff and de Stoecklin, A., 1908, i, 746; 1909, i, 347, 862). C. HOLLINS.

Neutral salt effect in ionic reactions. I. Specific ionic effects. A. VON KISS and V. BRUCKNER (Z. physikal. Chem., 1927, **128**, 71—86).—Brönsted's law of neutral salt action is in agreement with the influence of neutral salts on the ionic reaction between persulphates and the iodine ion. The reaction has been studied in presence of chlorides, nitrates, and sulphates. The activity of the hydrogen ion is increased by the presence of neutral salts. Specific anion and cation effects have been discovered; of univalent cations potassium has the greatest effect and lithium the smallest, whilst for univalent metals the sulphates have the greatest salt effect and the chlorides the smallest. No specific effect is evidenced by the nitrates and sulphates of the alkali metals. For a large number of binary salts it has been shown that the relationship between the concentration and the neutral salt effect is neither linear nor logarithmic up to $2N$. Among univalent ions the greatest salt effect is exhibited by those of greatest ionic volume. There is a qualitative relationship between the ionic effect of salts of the alkalis and the viscosity of the solutions, the effect being smaller in the more viscous solutions. H. F. GILLBE.

Activation of chemical reactions by neutral salts. I. Activation of reaction between marble and acids by neutral salts. N. ISGARISCHEV and F. S. SCHAPIRO (Z. physikal. Chem., 1927, **128**, 230—238).—The effect of various chlorides and potassium salts on the reaction between marble and acetic or nitric acid has been studied. For about the first half-hour, the reaction velocity can be represented satisfactorily by Boguski's equation, $kFt/2{\cdot}303 = \log\{c/(c-x)\}$, where F is the surface of the solid, k is a constant, c is the initial concentration of acid, and x is the decrease in acid concentration after a time t. Ultimately, however, k tends to rise, possibly owing to an increase in the surface of the solid as a result of the reaction. A few salts retard the reaction, but most of them accelerate it, increase in k running parallel with a slight rise and then a fall in the p_H of the solution, but there is no definite relation between k and the ionic volumes. The neutral salt effect is more pronounced with nitric than with acetic acid. R. CUTHILL.

Active surface of catalysts. B. KUBOTA (J. Fuel. Soc. Japan, 1927, **6**, 5—6).—A discussion of the relation between the reducing temperature of a nickel catalyst and the amount of active nickel present. C. W. GIBBY.

Stability of the catalytic properties of the palladium magnet. L. VALLERY (Compt. rend., 1927, **185**, 538—540).—By application of the differential equation representing the speed of a bimolecular reaction, it has been shown that the use of a palladium catalyst for the determination of hydrogen in a gas is not affected by ageing of the catalyst, or by the poisoning effects of stibine and arsine in concentrations of 10^{-5}. Catalysts of the same commercial origin may have very different activities. J. GRANT.

Effect of continued small additions of poisonous substances on the velocity of gaseous catalytic reaction in closed vessels. F. H. CONSTABLE (Proc. Camb. Phil. Soc., 1927, **23**, 832—837).—Theoretical. The results of Pease and Stewart (A., 1925, ii, 691) on the poisoning of the hydrogenation of ethylene (copper as catalyst) by increasing quantities of carbon monoxide are used to show that the mean life of the carbon monoxide molecule is very much greater on the centres which are most active in hydrogenation than on the rest of the surface. It is concluded that there are enhanced fields on the most active spots on a surface. W. E. DOWNEY.

Catalytic decomposition of ammonia. G. M. SCHWAB (Z. physikal. Chem., 1927, **128**, 161—181).—Progressive measurements of the decomposition of ammonia on the surface of platinum at 1050—1150° and under low pressures indicate that the order of the reaction is higher than the first, whereas the percentage of ammonia undecomposed after a given time is approximately a linear function of the initial concentration, which would require a lower order than the first. These results can, however, be reconciled if the reaction is opposed by the resultants, and this is found to be so. The experimental data at low pressures agree satisfactorily with the equation $-dc/dt=kc/(\delta n+\varepsilon h)$, where c is the pressure of the ammonia, n that of the nitrogen, and h that of the hydrogen, and δ and ε are constants. Since argon also exerts a retarding influence, it is presumably adsorption effects rather than purely chemical effects which come into play. This view receives further support from the fact that the above equation can be deduced from Langmuir's theory of reaction at solid surfaces, the constants δ and ε being adsorption coefficients. This theory is not, however, capable of accounting for the experimental results at higher pressures, when the opposing effect of nitrogen disappears (cf. Hinshelwood and Burk, A., 1925, ii, 691). Under these conditions, it is necessary to suppose that the surface becomes saturated with nitrogen sooner than it does with hydrogen, which may be explained by assuming either that the hydrogen is able to form surface layers more than one molecule thick or that it is adsorbed by the whole surface, whereas the nitrogen is adsorbed only by peculiarly sensitive regions of the surface. With further increase in pressure the reaction velocity would then be expected to become independent of the hydrogen pressure, and ultimately of the ammonia pressure, all adsorptions then having attained saturation. Hinshelwood and Burk's observation that the reaction is of zero order when tungsten is used as catalyst at the ordinary pressure is probably to be ascribed to this effect rather than to the absence of adsorption of the products of decomposition, since at low pressures the experimental results resemble those obtained with platinum as catalyst. R. CUTHILL.

Temperature and activity of nickel catalysts. II. F. THORÉN (Z. anorg. Chem., 1927, **165**, 171—191).—The relationship between temperature and activity of a nickel catalyst has been investigated by passing a mixture of ethylene and hydrogen over the catalyst maintained at constant temperature, and measuring the change in volume. At −18°, 10°, 41°, 61°, 81°, 100°, 120°, 139°, and 163° there are sharp increases in the activity of the catalyst. The changes in the catalyst are reversible, the activity falling sharply as the temperature decreases.

H. F. GILLBE.

Depressing action of rhodium and of iridium on platinum in the catalysis of sulphur trioxide. G. R. LEVI and M. FALDINI.—See B., 1927, 651.

Camphor series. XII. Catalytic activity of various reduced coppers on *l*-menthol. T. HIRAIDZUMI (Mem. Coll. Sci. Kyōtō, 1927, **10**, 255—261).—According to its mode of preparation, reduced copper oxide may catalyse either the dehydration or the oxidation of *l*-menthol. The oxide preparations were reduced at 200° by means of hydrogen, and *l*-menthol was passed over them at 250°. With oxide obtained from copper hydroxide gel heated at 250—300°, no hydrogen was evolved, but some water was formed together with 49% of menthene, whilst 45·8% of menthol was recovered. Using oxide prepared by ignition of copper nitrate, hydrogen was liberated freely but not continuously and 92·6% of menthone was obtained. Basic copper nitrate of a grey colour gave an oxide which was the basis of the least active copper preparation tried. The catalyst prepared from copper oxide obtained with basic copper nitrate and excess of dilute ammonium hydroxide, gave menthene (6%), menthone (77%), and hydrogen. Copper nitrate and 20% ammonia solution gave a black oxide which on reduction yielded menthene (2·6%), menthone (50%), menthol (31%), and hydrogen. Crystalline copper hydroxide prepared from basic copper nitrate gave a catalyst which yielded menthene (2%), menthone (80%), and thymol (2%), whilst amorphous copper hydroxide on reduction yielded a catalyst which resulted in the formation of water, menthene (46%), menthol (25%), and thymol (14%). The use of colloidal copper hydroxide favours the catalytic dehydration, whereas the copper oxide prepared by direct ignition of the nitrate gives a catalyst favouring the oxidation reaction. The remaining preparations exhibit both catalytic actions to varying extents. R. A. MORTON.

Behaviour of various metals (as electrodes) in the electrolysis of water by alternating current. A. P. ROLLET (Compt. rend., 1927, **185**, 457—460).—The current density and voltage necessary for the decomposition of solutions of sodium hydroxide and of sulphuric acid, by alternating current, between electrodes of various metals, have been determined at various concentrations. The electrodes were polished, and examined under magnification for the appearance of bubbles of gas. The initial values were taken, since the critical current density increased as the electrodes became coated with reduced metal. The critical current density is independent of the applied voltage, of which there is also a minimum permissible value. With increase of concentration the critical current density rises to a maximum limiting value.

C. W. GIBBY.

Anodic formation of powdered copper and passivity of the anodes. E. DENINA.—See B., 1927, 656.

Elementary mechanism of photochemical reactions. V. HENRI and R. WURMSER (J. Phys. Radium, 1927, [vi], **8**, 289—310).—A theoretical paper in which the primary processes of photochemical reactions are discussed. The photochemical reaction as a whole does not obey Einstein's law of photochemical equivalence, but, in general, the primary process of such a reaction, consisting of activation, predissociation, or dissociation of the molecule, does so. The study of the fluorescence, the absorption spectra, and other conditions for a reaction in the gaseous state makes it possible to decide in which of these three ways the elementary process takes place. In

other cases, the quantum efficiency of a photochemical reaction increases with the frequency of the light used owing to the different modes of activation produced by radiations of increasing frequency.

L. S. THEOBALD.

Increase in translational energy of the products of a gaseous photochemical decomposition. T. R. HOGNESS and J. FRANCK (Z. Physik, 1927, **44**, 26—31).—If a molecule suffers photochemical decomposition, associated with a work term D, due to the absorption of a quantum $h\nu$, then the excess energy, $h\nu-D$, should appear as excess translational energy of the atoms or molecules of the decomposition. The photochemical decomposition of sodium iodide vapour at 650° has been examined from this point of view, and the magnitude of the Doppler effect characterising the sodium D light emitted by the excited ($2p_2^1$ state) sodium atoms produced has been used as a measure of the excess translational energy. The low wave-length limit for the decomposition is 2450 Å. Three sources of excitation were used: a silver arc giving effective intense radiation only in the neighbourhood of 2450 Å., a cadmium arc emitting effective lines in the range 2923—2144 Å., and a zinc arc giving a group between 2139 and 2026 Å. The Doppler effect was measured by the relative transmission of the sodium D light by sodium vapour at a temperature of 200—300°; the amounts absorbed were 80%, 76%, and 50% respectively. The Doppler effect thus increases as the frequency of excitation is increased beyond the limit corresponding with 2450 Å. in agreement with theory. From the data obtained it is computed that the half width of the sodium D line excited by the zinc arc is 0·1 Å., whilst that corresponding with the thermal agitation of sodium at 650° is only 0·03 Å.

R. W. LUNT.

Reaction between chlorine, hydrogen, and oxygen in light. E. CREMER (Z. physikal. Chem., 1927, **128**, 285—317).—Bodenstein and Dux's investigation of the formation of hydrogen chloride from its elements in light in presence of oxygen (A., 1913, ii, 1039) has been extended to higher oxygen concentrations. The formula $d[2HCl]/dt=k[Cl_2]^2/[O_2]$ expresses the results satisfactorily if the range of oxygen concentration considered is not too wide, but the expression $d[2HCl]/dt=k[Cl_2]^2[H_2]/([Cl_2]+0{\cdot}02[H_2][O_2])$ is valid over the whole concentration range. The amount of water formed is so small as not to affect the oxygen concentration to any appreciable extent, the rate of formation being represented by the equation $d[H_2O]/dt=k_w[Cl_2]$, where k_w is a constant. It is suggested that the formation of hydrogen chloride is brought about by the following chain of reactions: (1) $Cl_2+h\nu=Cl^a+Cl$; (2) $Cl^a+Cl_2=Cl_3^a$; (3) $Cl_3^a+H_2=2HCl+Cl^a$; (4) $Cl^a+O_2=O_2^a+Cl$; (5) $Cl_3^a+O_2=O_2^a+Cl_2+Cl$; (6) $Cl_3^a=Cl_2+Cl$; (7) $Cl^a=Cl$. The formation of water occurs by (4) and (5), followed by: (8) $O_2^a+2H_2=2H_2O$. From reactions (1)—(4), which are mainly decisive for the rate of reaction, Bodenstein and Dux's formula for the rate of formation of hydrogen chloride follows, and, if (8) is taken into account, the above expression or the rate of formation of water. Reactions (5)—(7) be regarded as side reactions, and according to which predominates over the others the following special cases are considered. By neglecting (5) and (7) in comparison with (6), the above more general expression for the rate of formation of hydrogen chloride may be derived. Assuming this mechanism for the reaction, the length of the chain is calculated to be 18 members, which agrees with the value derived from an experimental determination of the yield of hydrogen chloride per quantum. If (5) is the predominating side reaction, corresponding with Thon's experiments with more than 0·2 mm. of oxygen (this vol., 323), an expression analogous to Thon's formula, $dx/dt=k[Cl_2]^2[H_2]/\{([H_2]+n[Cl_2])[O_2]\}$, may be derived. The non-agreement between this expression and Chapman's results (J.C.S., 1909, **95**, 959; 1923, **123**, 3062) seems to be due to reaction (6) being catalysed by the walls of the containing vessel, the value of the velocity coefficient being zero only under the experimental conditions of Thon. Taking (7) and (5) as the predominating side reactions, it may be shown that n in Thon's expression is of the form $K[H_2]/([O_2][Cl_2])+K'$, where K and K' are constants. For oxygen concentrations above about 0·17 mm. this expression is appreciably constant, and below this concentration the modified velocity formula is in excellent agreement with Thon's results. Porter, Bardwell, and Lind's observation (A., 1926, 1111) that the temperature coefficient is the greater the greater is the sensitivity of the mixture of gases can be accounted for by supposing that the velocity coefficient of reaction (6) decreases with increasing temperature. It is calculated that when the oxygen concentration is zero, the maximum yield of hydrogen chloride per quantum is $7{\cdot}6\times10^6$ molecules.

R. CUTHILL.

Action of light on concentrated aqueous solutions of ammonium thiocyanate. S. S. BHATNAGAR, H. B. DUNNICLIFF, and M. ALI (J. Indian Chem. Soc., 1927, **4**, 229—238; cf. A., 1926, 920).—That the production of colour and precipitates in concentrated solutions of ammonium thiocyanate is due to oxidation by oxygen of the air catalysed by light, is shown by the following facts: (i) no colour appears in an atmosphere of carbon dioxide or hydrogen or in a vacuum; (ii) the same colour is produced by the addition of hydrogen peroxide, the absorption spectra of the solutions and the carbon and hydrogen contents of the precipitates being the same in each case. It is suggested that the red colour is due to cyanogen sulphide, formed by the oxidation of thiocyanic acid produced by hydrolysis of the ammonium salt. This cyanogen sulphide polymerises to pseudocyanogen sulphide, which is precipitated. Analyses of the precipitates agree with this view.

G. A. C. GOUGH.

Photosynthesis with malachite-green. D. BURK (J. Amer. Chem. Soc., 1927, **49**, 1819—1825).—When solutions of malachite-green chloride (0·005%) are exposed to condensed sunlight, there are formed, in addition to formaldehyde (cf. Baly, Heilbron, and Barker, J.C.S., 1921, **119**, 1032; Baur and Büchi, A., 1924, ii, 82; Baly, Ind. Eng. Chem., 1924, **16**, 1016), and in greater concentration, amines. Under alkaline, aerobic conditions, nitrites are also formed. It is concluded that, as the order of magnitude of the formaldehyde concentration is extremely low, and

can be controlled particularly by variation of p_H, the production of formaldehyde need not prejudice the interpretation of photosynthetic experiments with malachite-green solutions. F. G. WILLSON.

Absorption spectrum of ergosterol in relation to the photosynthetic formation of vitamin-*D*. R. A. MORTON, I. M. HEILBRON, and E. D. KAMM (J.C.S., 1927, 2000—2005).—Maxima in the absorption spectrum of ergosterol are found at 293·5, 281·5, and 270 μμ, corresponding with almost identical values previously found for cholesterol. Ergosterol is $2—4\times10^3$ times as active as cholesterol. The ergosterol bands disappear linearly with time when an alcoholic solution is irradiated, and a new maximum appears at 247 μμ, which itself disappears on further irradiation. This is in agreement with the view that it is due to vitamin-*D*. The bearing of the results on the industrial preparation of vitamin-*D* is discussed. C. W. GIBBY.

Radiation and collision in gaseous chemical reactions. J. H. HIBBEN (Proc. Nat. Acad. Sci., 1927, **13**, 626—631).—The mechanism of the process of activation in homogeneous gaseous systems has been studied in the light of the radiation and collision hypotheses. No change in reaction velocity could be detected in the decomposition of nitrous oxide exposed to infra-red radiation at different temperatures and with different frequencies. As in the decomposition of ozone no such change was observed, it was concluded that if there is activation by collision, it is more complex than simple absorption of one or more activating frequencies. The bimolecular decomposition of nitrous oxide at low pressures is entirely heterogeneous. The unimolecular decomposition of nitrogen pentoxide between the pressures 0·2 and 0·002 mm. shows no alteration in the rate of reaction such as was found by Hirst and Rideal, but follows exactly the rate determined by Daniels and Johnson at high pressures. No diminution of the reaction velocity was observed. R. A. MORTON.

Disproof of the radiation theory of chemical activation. G. N. LEWIS and J. E. MAYER (Proc. Nat. Acad. Sci., 1927, **13**, 623—625).—The discovery of a very high absorption coefficient at wave-lengths longer than the limit of Daniels' work (8 μ) might in the case of nitrogen pentoxide still permit the retention of the radiation hypothesis. By dispensing with windows, using a black body at 100—150° and a thermopile to receive the radiation, it has been shown that the coefficient of total absorption for an interposed layer of nitrogen pentoxide is but little greater than at 8 μ. Whilst the experiment seems to disprove the hypothesis of activation of nitrogen pentoxide by radiation, it is open to criticism in certain directions. Accordingly, the reaction of a molecular stream passing through an exhausted enclosure which is permeated by radiation corresponding with a temperature that would be sufficient in ordinary circumstances to produce chemical reaction was studied. The gas is at so low a concentration in the molecular stream that the number of collisions is negligible. In order to avoid the complications involved in dissociation, the racemisation of pinene, a satisfactory unimolecular reaction, was used. At 800° Abs. the racemisation should from the temperature coefficient of the reaction amount to 10%, and at 1000° Abs. only 10^{-6} should remain unracemised. An experiment was set up in which the density of energy was in no part of the spectrum less than that which would be present in a Hohlraum at 800° Abs. Over the greater part of the spectrum the energy density was greater than in a Hohlraum at 1000° Abs. No racemisation whatever was detected, and it is claimed that, at least for this one reaction, the radiation hypothesis is definitely disproved. R. A. MORTON.

Topochemical reactions. V. KOHLSCHUTTER (Kolloid-Z., 1927, **42**, 254—268).—Topochemical reactions are defined as those which take place in the inner or outer fields of force of crystalline matter. The significance of such a classification is discussed, and examples of many different types of topochemical reaction are given, including electrode processes (separation of metals), cases of polymorphism (sulphur and mercuric iodide), ageing processes, such as the formation of crystals in metal sols and the formation of aggregates, the appearance of somatoid forms etc. The mechanism and causes of the localisation of these processes are considered. L. L. BIRCUMSHAW.

Dehydration of metal salt hydrates. V. Theory of the mode of combination of water of crystallisation. M. A. RAKUZIN (Z. angew. Chem., 1927, **40**, 967—973).—From the results of dehydration experiments on various salt hydrates and from tensimetric data the hydrates are classified and their behaviour on exposure to the air is explained. Hydrates in which the water of crystallisation, calculated as a percentage of the anhydrous salt, exceeds 100% are classified as perhydrates and are characterised by the fact that they lose water in a current of dry air at 20°. Hydrates containing from 70 to 100% of water of crystallisation are stable or normal hydrates and those containing less are extraordinarily stable. Sodium carbonate and sodium sulphate decahydrates belong to the first-named class, the heptahydrates of zinc, nickel, and cobalt sulphates to the second, and the pentahydrate of copper sulphate to the third. Sodium sulphate monohydrate and nickel sulphate hexahydrate are considered to be subhydrates. Only the true water of crystallisation is responsible for the vapour tension of crystal hydrates, which is not always identical with the dissociation pressure. Most sulphates are converted into monohydrates in a current of air at 100° but alum under these conditions gives the tetrahydrate. The stability of sodium carbonate monohydrate in a current of dry air at 20° suggests that this compound should be formulated as sodium hydrogen orthocarbonate, $Na_2H_2CO_4$. The stable dihydrate would then be $Na_2H_2CO_4,H_2O$ and the unstable decahydrate, $Na_2H_2CO_4,9H_2O$. Potassium carbonate monohydrate would similarly be formulated as $K_2H_2CO_4$ (see also B., 1926, 1011). A. R. POWELL.

Conversion of alkali chlorides into nitrates with simultaneous production of chlorine. V. DOMINIK.—See B., 1927, 700.

Sodium monometaphosphate and its acid hydration. H. T. BEANS and S. J. KIEHL (J. Amer.

Chem. Soc., 1927, 49, 1878—1891).—The reaction $NaPO_3+H_2O \rightleftharpoons NaH_2PO_4$ was investigated by direct methods. When the initial hydrogen-ion concentration exceeds that due to the end-product, it decreases as the reaction proceeds; otherwise, it increases. Sodium pyrophosphate is formed as an intermediate product. The hydration is more affected by change in the concentration of the hydrogen ion than of the monometaphosphate. The *hydrate*, $NaH_2PO_4,2H_2O$, was prepared by precipitation at 0° of an aqueous solution of monosodium phosphate with 95% alcohol. Some properties of sodium monometaphosphate are recorded.

S. K. TWEEDY.

Reduction of silver compounds in alkaline solution. W. FARMER and J. B. FIRTH (J.C.S., 1927, 1772—1780).—The reduction in ammoniacal solution of certain silver salts in presence of aluminium and alkali hydroxide has been investigated. The extent of the reduction is determined by the conditions of the experiment, and there is no stoicheiometric connexion between the amount of aluminium used and the amount of silver deposited. In the presence of aluminium the intermediate deposition of silver nitride and the evolution of nitrogen are inhibited. In the absence of aluminium the amount of silver deposited is equivalent to the amount of nitrogen evolved. The yield of silver produced in presence of aluminium is the cumulative effect of two reactions: (1) the deposition of silver equivalent to the aluminium used, (2) the reduction of more silver, the necessary increment of energy being supplied by the finely-divided metal already precipitated. Freshly precipitated silver, if activated by heating in a vacuum, can cause the reduction of ammoniacal solutions in the absence of aluminium. Prolonged contact of the reduced metal with the solution causes the grey coherent masses to break down into a powder, with a simultaneous diminution in activity.

C. W. GIBBY.

Decomposition of crude [calcium] phosphate with sulphurous acid and with ammonium sulphite. W. STOLLENWERK.—See B., 1927, 652.

Gaseous reduction of zinc [oxide]. C. J. MAIER and O. C. RALSTON.—See B., 1927, 680.

Aluminium nitrate hydrates. G. MALQUORI (Atti R. Accad. Lincei, 1927, [vi], 5, 892—896; cf. this vol., 628).—The system $Al(NO_3)_3$–H_2O was studied in the interval between the cryohydric temperature, −27°, and the temperature (130°) at which the salt decomposes with elimination of nitric acid. The f.-p. curve and the solubility up to the m. p. of the nonahydrate were determined in the usual manner; above this temperature the solubility data were obtained by heating a mixture, of carefully determined composition, of the nona- and hexa-hydrates in a sealed tube and noting the temperature at which crystallisation

From the cryohydric point to 73·5° (the m. p. of the nonahydrate), the nonahydrate alone is in equilibrium with the saturated solution. Above this temperature the solubility curve shows a discontinuity with the existence of the octahydrate the hexahydrate, the latter being produced by partial fusion of the octahydrate into hexahydrate and solution.

M. CARLTON.

Double sulphates of the rare-earth metals and the alkali metals. VIII. Double sulphates of cerous cerium and sodium. F. ZAMBONINI and S. RESTAINO (Atti R. Accad. Lincei, 1927, [vi], 5, 828—832; cf. A., 1925, ii, 222, 315; 1926, 137, 255, 696, 1015; this vol., 112).—The existence of the following *compounds* is indicated by the determination of the 25° isotherm of the system $Ce_2(SO_4)_3$–Na_2SO_4–H_2O: $Ce_2(SO_4)_3,Na_2SO_4,2H_2O$, stable in contact with solutions containing from 0·14% to about 7% of sodium sulphate and 0·35% of cerous sulphate; $4Ce_2(SO_4)_3,5Na_2SO_4,8H_2O$, stable in contact with solutions practically free from cerium but containing from about 7·5% to 15% of sodium sulphate. Both salts are white, microcrystalline powders and are completely dehydrated at 400°.

M. CARLTON.

Double sulphates of the rare-earth metals and the alkali metals. X. Sulphates of neodymium and ammonium. F. ZAMBONINI and A. STOLFI (Atti R. Accad. Lincei, 1927, [vi], 5, 832—837; cf. preceding abstract).—Investigation of the system $Nd_2(SO_4)_3$–$(NH_4)_2SO_4$–H_2O at 25° indicates the existence of the *compound* $Nd_2(SO_4)_3,(NH_4)_2SO_4,8H_2O$, stable at 25° in contact with solutions containing 2·5—0·58% of neodymium sulphate and 1—44% of ammonium sulphate. The violet crystals have d 2·590 and belong to the monoclinic system.

M. CARLTON.

Decomposition of glass by water at high temperatures and pressures. G. W. MOREY and N. L. BOWEN.—See B., 1927, 654.

Stability of titanium sulphate solutions. H. WILKINSON and A. G. TYLER.—See B., 1927, 652.

Titanium sesquioxide. G. LUNDE (Z. anorg. Chem., 1927, **164**, 341—344).—Small amounts of titanium sesquioxide can be obtained by heating titanic oxide in a mixture of hydrogen and titanic chloride vapour, although the method is not suitable for the preparation of the substance. The oxide so obtained is probably pure, and is isomorphous with the other sesquioxides of the corundum type.

R. CUTHILL.

Differences of stability of similarly constituted hafnium and zirconium complexes. J. H. DE BOER (Z. anorg. Chem., 1927, **165**, 1—15).—The complexes formed by hafnium and zirconium in oxalic, sulphuric, phosphoric, nitric, and hydrochloric acid solutions have been studied; those of the former metal are in every case less stable. Hafnium phosphatofluoric acid and its salts are more readily decomposed than the corresponding zirconium compounds, and the same is true of the complexes formed when a salt of the metal is precipitated by ammonium carbonate and the precipitate dissolved in excess of the reagent, and when the phosphates are dissolved in α-hydroxy-acids and in alcohols. The density of hafnium has been re-determined and found to be 13·07, whilst that of zirconium is 6·53, giving for the atomic volumes 13·66 and 13·97, respectively.

H. F. GILLBE.

Gaseous nature of carbon reduction of tin concentrates. C. J. FINK and C. L. MANTELL.—See B., 1927, 680.

Reduction of tin oxide and cassiterite concentrates. E. F. KERN.—See B., 1927, 680.

Action of hydrogen on tin salts at high temperatures and pressures. V. IPATIEV and V. NIKLAEV (Compt. rend., 1927, **185**, 462—463).—Stannic hydroxide can be reduced to the stannous state by hydrogen at 300° and 38 atm., and to the metal at 350° and 50 atm. Stannic sulphate at 302° and 162 atm. gives, successively, stannous sulphate and stannous sulphide. The reductions are retarded by the presence of sulphuric acid or a sulphate. Stannic chloride is reduced to stannic oxide at 280—300° and 110 atm., and to metallic tin at higher temperatures. Addition of silver chloride gives, at 380° and 260 atm., mainly OH·SnCl.

C. W. GIBBY.

Complex compounds of stannic and stannous iodides. T. KARANTASSIS (Ann. Chim., 1927, [x], **8**, 71—119).—Stannic iodide does not dissolve in concentrated hydriodic acid, but its aqueous solution is stabilised by the presence of 2*N*-hydriodic acid, although some hydrolysis to oxyiodide occurs. In contrast to the other alkali metals, rubidium and cæsium iodides, when added to this solution, afford complex black iodostannates, Rb_2SnI_6 and Cs_2SnI_6. These iodostannates are decomposed by water and alcohol, less readily by ether, chloroform, carbon disulphide, and carbon tetrachloride. When heated above 140° they afford stannic iodide and the alkali iodide, but the residue becomes white only at 275—280°, hence rubidium periodide is not a cause of the dark colour of the complex salt. Similar compounds, $(AsMe_4)_2SnI_6$ and $(NMe_4)_2SnI_6$, are formed with tetramethylarsonium iodide and tetramethylammonium iodide respectively, whilst aniline and stannic iodide in chloroform yield indefinite products. The stability of these complex salts is attributed to the pronounced electropositive character of the cation, and to the tendency of the electropositive radical to form periodides. Although potassium and ammonium do not form iodostannates in the above way, mixed crystals of the bromoiodostannates are obtained by mixing solutions of stannic bromide and potassium or ammonium iodide. Mixed crystals of the same type are also obtained by the action of hydrobromic acid (47%) on rubidium iodostannate. Hydrochloric acid does not behave in this way and no mixed crystals were obtained from stannic ammonium chloride and ammonium iodide. Other quadrivalent elements such as titanium, zirconium, and thorium do not afford analogous complex compounds, probably because solutions of the oxyiodides of these metals on evaporation in excess of hydriodic acid afford the normal iodide and not the tetraiodide, as in the case of tin. Ceric chloride showed a tendency to form complexes with rubidium chloride and with tetramethylarsonium chloride, but the tendency of ceric compounds to pass into cerous, with loss of halogen, rendered the results imperfect.

With stannous iodide, rubidium and cæsium iodides afford iodostannites of a known type, $RbSnI_3$ and $CsSnI_3$, and in addition the orange-yellow compounds of a new type, $RbSn_2I_5$ and $CsSn_2I_5$. Tetramethylammonium iodide, tetramethylarsonium iodide, aniline, and pyridine hydriodides afford iodostannites of the former type, $XSnI_3$. Evidence of the existence of a well-defined stannous chloroiodide, SnClI, is adduced (cf. Young and Adams, A., 1898, ii, 338). Thermal analysis in the case of stannous iodide–stannous bromide merely established the existence of mixed crystals with a tendency to form the bromoiodide, SnBrI. With stannous chloride and stannous bromide, a considerable volume change occurs in the solidus at a point corresponding with the composition Sn_2ClBr_3.

In double decomposition (by distillation) of the halogen compounds of tin, arsenic, antimony, bismuth, phosphorus, silicon, zirconium, titanium, and thorium, the iodine combines with the element possessing the more pronounced metallic character. Thus a mixture of antimony trichloride and stannic iodide affords stannic chloride and antimony tri-iodide: phosphorus tri-iodide and arsenious chloride afford arsenious iodide and phosphorus trichloride; phosphorus tri-iodide and stannic chloride afford stannic iodide and phosphorus trichloride, stannic chloride and titanium tetraiodide give titanium tetrachloride and stannic iodide, etc. The reverse reactions do not occur. With arsenic tri-iodide and stannic chloride a certain equilibrium appears to obtain, although with arsenic trichloride and stannic iodide double decomposition takes place. Repetition of Gramp's experiments (Ber., 1874, **7**, 1723) afforded no evidence of the formation of an additive compound between arsenious chloride and iodide.

R. BRIGHTMAN.

Soluble metatungstates. E. F. SMITH (Chem. News, 1927, **135**, 129—131).—In order to prepare pure crystals of lead metatungstate, the aqueous solution should be allowed to evaporate at the ordinary temperature, as hydrolysis occurs if heat is applied. The sodium and ammonium salts are best obtained by adding tungstic acid to a solution of the corresponding paratungstate at 70—75°.

R. CUTHILL.

Besson's supposed phosphorus suboxide, P_2O. L. J. CHALK and J. R. PARTINGTON (J.C.S., 1927, 1930—1936; cf. A., 1897, ii, 370).—The supposed phosphorus suboxide produced by the action of phosphorus trichloride on phosphorous acid is shown to be a variable mixture of finely-divided amorphous phosphorus with adsorbed phosphorous acid. The oxygen present is insufficient for the formula P_2O.

C. W. GIBBY.

Reduction of arsenic compounds in acid and in alkaline solution by sodium hyposulphite. Production of sodium arsenohyposulphite. W. FARMER and J. B. FIRTH (J.C.S., 1927, 2019—2021).—In the reduction of sodium arsenate by sodium hyposulphite in cold aqueous solution, sodium arsenohyposulphite, $Na_3As(S_2O_4)_3$, is formed. When this decomposes in presence of sodium sulphite, sodium arsenothiosulphate is produced as an intermediate compound, the final product containing arsenious sulphide (cf. A., 1926, 256).

C. W. GIBBY.

Double sulphates of bismuth and the alkali metals. I. Sulphates of bismuth and potassium. V. Caglioti and A. Stolfi (Atti R. Accad. Lincei, 1927, [vi], **5**, 896—901).—A relationship is sought between the double sulphates of bismuth with the alkali metals and those of the rare earths (cf. Zambonini and others, this vol., 949). Crystals which separated from solutions of bismuth nitrate in nitric acid to which potassium sulphate solution (1 : 1 and 1 : 3) had been added were identical and homogeneous, having the composition $Bi_2(SO_4)_3,3K_2SO_4$. A systematic study of the system $Bi_2(SO_4)_3$–K_2SO_4–H_2O at 25° indicated the existence of the compound $K_3Bi(SO_4)_3$ only. It is stable over a wide range, being in equilibrium in solutions containing 5·32—12·8% of potassium sulphate. Evidence suggesting the formation of a basic bismuth sulphate was obtained. M. Carlton.

Reaction of tellurium [with thiocarbamide]. P. Falciola (Annali Chim. Appl., 1927, **17**, 359—360; cf. this vol., 952).—Tellurium in hydrochloric acid solutions is not precipitated in the free state by thiocarbamide. A yellow colour is, however, produced at a concentration of 2 in 10^6, and at higher concentrations a yellow *substance*, m. p. 165° (decomp.), containing carbon, nitrogen, chlorine, sulphur, and tellurium, separates. On adding ether and potassium xanthate, a red ethereal solution is obtained, from which tellurium separates as a black solid; a red crystalline substance is also obtained.

E. W. Wignall.

Complex chromium salts. A. del Campo, F. Manzano, and A. Mallo (Anal. Fís. Quím., 1927, 25, 186—193).—Hexa-aquochromic chloride may be obtained by the action of hydrogen chloride on a solution of violet chromic sulphate at a low temperature. Weinland's violet chromic chlorosulphate may be obtained by the action of hydrogen chloride on a cold concentrated solution of the violet chromic sulphate. Penta-aquochromic chloride may be obtained by saturating with hydrogen chloride an aqueous-ethereal solution of Recoura's green chromic chlorosulphate, $Cr[Cl(H_2O)_5]SO_4,H_2O$. The third non-electrolytic member of Werner's series, $[CrCl_2(H_2O)_3]$, is obtained by the action of hydrogen chloride on a solution of the green chromic chloride, $[CrCl_2(H_2O)_4]Cl,H_2O$, at 90—100° under pressure. The new *compound* is very hygroscopic.

G. W. Robinson.

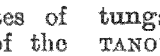
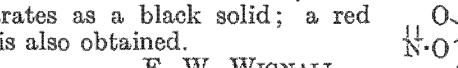
Gaseous reduction of tungsten and molybdenum oxides. E. W. Engle.—See B., 1927, 680.

Reaction of incandescent tungsten with nitrogen and with water vapour. C. J. Smithells and H. P. Rooksby (J.C.S., 1927, 1882—1888).—The dark brown deposit, d 5·0±0·5, formed in high-wattage gas-filled incandescence lamps does not contain the oxides WO_3, W_2O_5, WO_2, or metallic tungsten, but consists of the nitride WN_2 (cf. Langmuir, A., 1913, ii, 859). It burns in air to tungstic oxide and when heated evolves nitrogen and oxygen.

In the reaction with water vapour a black deposit is formed, which was shown by *X*-ray examination to consist of metallic tungsten only. This confirms Langmuir's conclusion (B., 1926, 550) that atomic hydrogen produced at the surface of the hot metal reduces the oxides of tungsten at a lower temperature.

C. W. Gibby.

Action of gaseous hydrogen chloride on tungsten compounds. V. Spitzen and L. Kaschtanov (J. Russ. Phys. Chem. Soc., 1926, **58**, 1230—1251).—See this vol., 33.

Complex nitric oxide compounds and so-called univalent iron. H. Reihlen and A. von Friedolsheim (Annalen, 1927, **457**, 71—82).—The reaction between ferrous hydroxide, nitric oxide, and ethyl mercaptan (Hofmann and Wiede, A., 1895, ii, 317, 451) may be written: $2Fe(OH)_2 + 2NO + EtSH = Fe(OH)_3 + H_2O +$  . Hofmann and Wiede's yield (25%) is increased to 82% by carrying out the reaction in a closed vessel under special conditions, but a quantitative yield is prevented by oxidation of some of the mercaptan to disulphide by the ferric hydroxide. By using excess of mercaptan and nitric oxide according to the equation: $2Fe(OH)_2+4NO+4EtSH=2(N_2O_2)Fe{\cdot}SEt+Et_2S_2+4H_2O$, a yield of 93% is obtainable. The ethyl bishyponitritoferrisulphide, m. p. 78°, is isolated by extracting the water-insoluble products with alcohol and ether, the residue being ferric hydroxide free from ferrous compounds. The compound is bimolecular and has probably the structure,  , which accounts for its non-formation from hyponitrites, since these have an *anti*-configuration. Manchot's suggestion (Manchot and Gall, A., 1926, 694, 698; Manchot and Linckh, *ibid.*, 452, 453) that the nitric oxide complex is always null-valent is rejected, and Roussin's salt, $Fe_4(NO)_7S_3K$, is formulated

$$[(N_2O_2)_2Fe_2'''S_2{=}Fe''(NO){-}S_2Fe_2'''(N_2O_2)_2{-}Fe''(NO){-}S_2Fe_2'''(N_2O_2)_2]K_2.$$

The formation of Hofmann and Wiede's compound according to the second of the above equations would, on Manchot's view, involve the reduction of bivalent to univalent iron by ethyl mercaptan.

C. Hollins.

Application of a general method for the synthesis of silicates to iron and neodymium. A. Dubois (Compt. rend., 1927, **185**, 416—417).—Silicates of neodymium and of iron have been prepared by fusion of the respective oxides with normal or acid potassium fluoride and silica. Crystalline compounds of the formulæ $Nd_2O_3,3K_2O,9SiO_2$ and $Nd_2O_3,2K_2O,7SiO_2$ (containing potassium chloride and fluoride) have been isolated. C. W. Gibby.

Cyanogen compounds of the platinum metals. F. Krauss [with G. Schrader] (Z. anorg. Chem., 1927, **165**, 59—72).—The following *cyanoruthenites*, in which ruthenium is bivalent, have been prepared: $Cu_2[Ru(CN)_6],xH_2O$, $Cu_2[Ru(CN)_6],4NH_3$, $Ag_4[Ru(CN)_6],xH_2O$, $Ag_4[Ru(CN)_6],3NH_3$, and the brucine and strychnine salts of the acid $H_4[Ru(CN)_6]$. The compound $K_4[Ru(CN)_6]$ and its trihydrate have been further investigated. H. F. Gillbe.

***cis–trans*-Isomerism among metallic salts of the type $R_2M^{IV}X_6$.** F. Krauss and F. Brodkorb

(Z. anorg. Chem., 1927, **165**, 73—78).—The *cis*- and *trans*-forms of the compounds $C_5H_5N,PdCl_2$, $(NH_2Et)_2,PdCl_2$, and $(NH_3)_2,PdCl_2$ have been prepared, and, with the exception of *trans*-diamminodichloropalladium, which is decomposed by water, are shown to exist as single molecules in aqueous solution. H. F. GILLBE.

Preparation of electrically pure water. E. F. KRAUSE and A. V. NOVOSSELOV (J. Russ. Phys. Chem. Soc., 1926, **58**, 1222—1229).—A simple method of preparing pure water in the laboratory is described, whereby a tin still containing 60 litres of ordinary distilled water yields 20—25 litres of water having an electrical conductivity of $0{\cdot}7$—$0{\cdot}9\times10^{-6}$ ohm^{-1}. No chemicals are used in this method. When air free from carbon dioxide is passed through the water, the conductivity falls to $0{\cdot}2$—$0{\cdot}3\times10^{-6}$ ohm^{-1}, and this value remains constant for 10—12 days. Dissolved nitrogen does not raise the conductivity of the water. When contained in a glass flask, oxygen raises the conductivity to an indeterminate value, but in quartz the conductivity is not raised. Pure hydrogen, whatever the source, raises the conductivity to a constant value. E. ROTHSTEIN.

Chlorination of ilmenite. Y. F. KRIEGER. **Chlorination of titanium carbide.** M. S. MAKSIMENKO and A. ELISEEV. **Production of titanium carbide.** M. S. MAKSIMENKO. **Production of titanium dioxide, carbide, and tetrachloride.** V. S. SUIROKOMSKII.—See B., 1927, 701.

Preparation of titanium tetrachloride. (*a*) K. F. BELOGLAZOV, (*b*) S. I. ORESHKIN.—See B., 1927, 652.

[Preparation of] vanadium. J. W. MARDEN and M. N. RICH.—See B., 1927, 657.

Apparatus for microanalysis. C. VAN ZIJP (Pharm. Weekblad, 1927, **64**, 916—919).—Apparatus for filtering, subliming, receiving and measuring distillates, testing for carbonates, extraction with warm solvents, extraction with ether, and distillation is described. S. I. LEVY.

Nitrometer for small volumes of gas. A. KLEMENC and E. HAYEK (Z. anorg. Chem., 1927, **165**, 157—160).—A nitrometer for determining the quantity of nitrogen present in very dilute solutions of nitric and nitrous acids is described. H. F. GILLBE.

Determination of the gas content of molten metals. A. WÜSTER and E. PIVOVARSKY.—See B., 1927, 681.

Determination of p_H value. K. WOLF (Collegium, 1927, 370—397).—Experiments were performed with various electrodes, viz., glass electrodes of the original Haber type, glass drawn over smooth metallic wires, smooth metal electrodes, and bimetallic electrode systems. Glass electrodes and smooth metal electrodes proved more suitable for extrapolation measurements and for obtaining titration curves. An easily worked soda glass of low m. p. is more suitable than potash or lead glass. Highly sensitive quadrant or binant electrometers were not satisfactory with these electrodes and a specially constructed electrode valve was therefore used for measuring the *P.D.* D. WOODROFFE.

[Apparatus for microchemical] methods. VII. L. PINCUSSEN (Biochem. Z., 1927, **186**, 28—35).—A quinhydrone micro-electrode and a micro-titration burette are described, and the Barcroft differential manometer as modified by Verzar (A., 1925, i, 178) is further modified. P. W. CLUTTERBUCK.

Use of chromate solutions as comparison solutions in colorimetric measurements. H. JØRGENSEN (Biochem. Z., 1927, **186**, 485—489).—Dilute aqueous chromate or dichromate solutions have no definite colour, since the tone is dependent on the p_H of the solution. It is incorrect, therefore, to use these solutions directly as comparison solutions for colorimetric determinations or as standards in the indicator methods for p_H determination. If a buffer solution is used to dissolve the chromate or dichromate, the solution has a definite hue, and suitable tints between red and yellow can be obtained by varying the p_H of the solution. A. WORMALL.

Determination of hardness and alkalinity of water. H. VIGNAL.—See B., 1927, 670.

Colorimetric determination of perchlorate. JUNCK and KUPPER.—See B., 1927, 701.

Separation and determination of mixtures of iodide, bromide, and chloride. O. CHICK.—See B., 1927, 651.

Analysis of mixed acid. LORIETTE and JOVINET.—See B., 1927, 700.

Detection [and determination] of selenium. P. FALCIOLA (Annali Chim. Appl., 1927, **17**, 357—358).—Selenium contained in a hydrochloric acid solution gives with thiocarbamide a red colour at a concentration of 1 in 10^6, and at higher concentrations separates in the free state and may be weighed and quantitatively determined. Other elements do not react, except copper, which gives with thiocarbamide an insoluble compound, soluble, however, in a large excess of the reagent. By rapid filtration, selenium may be separated from tellurium if this is present (see this vol., 951). E. W. WIGNALL.

Determination of nitrogen by the Davis-Lunge method. A. PINKUS and J. JACOBI (Bull. Soc. chim. Belg., 1927, **36**, 448—468).—The determination of the nitrogen content of nitrates and nitrites by measuring the volume of nitric oxide evolved on shaking the substance with sulphuric acid and mercury invariably yields low results, the absolute error increasing with the amount of nitrate or nitrite present and with the concentration of the sulphuric acid employed. With acid of concentration greater than 90% very erratic results are obtained, probably due to adsorption of nitric oxide by the mercurous sulphate formed in the reaction. Errors are also caused by the varying solubility of the nitric oxide in the acid liquor and by neglecting the appreciable vapour tension of the liquid phase. Comparable results are obtained by the process only when a blank determination is carried out under precisely the same conditions as the analysis proper, using a quantity of pure potassium nitrate containing about the same quantity of nitrogen as the sample and making allowance for the deficiency found. A. R. POWELL.

Determination of very small amounts of yellow phosphorus in red phosphorus. R. H. KRAY.—See B., 1927, 701.

Titration of the ammonium phosphomolybdate precipitate (Lorenz method) with sodium hydroxide in the presence of formaldehyde. F. SCHEFFER (Landw. Versuchs-Stat., 1927, **105**, 335—343).—The precipitate is washed on a Gooch crucible with 0·5—1% sodium sulphate solution, until the washings are neutral to litmus. The crucible and precipitate are placed in a flask with excess of 0·04*N*-sodium hydroxide solution. The flask is shaken until all the precipitate is dissolved, 5 c.c. of 40% formaldehyde solution are added, and the liquid is titrated immediately with 0·1*N*-hydrochloric acid using phenolphthalein as indicator. A. G. POLLARD.

Determination of silicon in ferrosilicon. L. DEUTSCH.—See B., 1927, 703.

Electrolytic determination of alkali. P. DROSSBACH (Z. anorg. Chem., 1927, **165**, 149—156).—Hildebrandt's method for the electrolytic determination of alkalis yields accurate results. A convenient form of apparatus is described. H. F. GILLBE.

Conversion of alkali chlorides into carbonates by the action of oxalic acid. L. N. MURAVLEV (Z. anorg. Chem., 1927, **165**, 137—141).—In view of the incomplete conversion of alkali chlorides into carbonates by oxalic acid the method cannot be employed for the determination of the alkalis. H. F. GILLBE.

Analysis of the simpler glasses. W. H. WITHEY.—See B., 1927, 654.

Analysis of glasses. V. DIMBLEBY.—See B., 1927, 654.

Analysis of refractories. W. J. REES.—See B., 1927, 654.

Analysis of silicate slags. T. P. COLCLOUGH.—See B., 1927, 654.

Electrolytic determination of zinc in solutions acid with sulphuric acid. R. BELASIO and E. MELLANA (Annali Chim. Appl., 1927, **17**, 336—346).—Zinc can be accurately determined electrolytically in the presence of dilute sulphuric acid if an anode of lead peroxide is used. The latter may be supported on a platinum spiral or deposited (by electrolysis of a 40% lead nitrate solution by a 0·2 amp. current) on a cylinder of platinum gauze. The zinc is deposited using such an anode, a Winkler copper cathode, or, better, a cathode of amalgamated brass, and a current of 0·4—0·5 amp. at 3·5 volts, as a compact crystalline mass; no measurable quantity of lead is deposited, and deposition is successful in presence of sodium or ammonium sulphate, or of disodium phosphate. The method has been tested on metallic zinc, brass, bronzes, German silver, and zinc minerals. E. W. WIGNALL.

Sensitive microchemical reactions for cadmium salts. A. MARTINI (Anal. Asoc. Quim. Argentina, 1927, **15**, 52—56).—To a drop of 1% cadmium chloride solution on a slide an equal quantity of saturated sodium bromide solution is added. On adding a little concentrated brucine acetate solution by means of a gold pen a white precipitate is formed consisting of characteristic crystals. If quinine acetate is substituted for brucine acetate, a characteristic crystalline precipitate is also obtained. Photomicrographs of the crystalline compounds are given. G. W. ROBINSON.

Confirmatory test for aluminium. W. J. ALLARDYCE (J. Amer. Chem. Soc., 1927, **49**, 1991).—The washed aluminium hydroxide, free from chromium and zinc, is dissolved in hydrochloric acid and reprecipitated with a slight excess of ammonia solution. One drop of a saturated solution of alizarin in concentrated acetic acid is then added. The aluminium hydroxide settles out carrying the pink colour with it and leaving the solution colourless. S. K. TWEEDY.

Thioglycollic acid as a colour test for iron. E. LYONS (J. Amer. Chem. Soc., 1927, **49**, 1916—1920).—To about 5 c.c. of neutral or slightly acid solution, free from oxidising agents, 1 drop of thioglycollic acid is added and 0·5 c.c. of strong aqueous ammonia solution. If ferrous or ferric iron is present in a concentration of 1 part in 5×10^6 or greater, a purple or pink colour immediately develops; at lower concentrations (down to 1 part in 10^7) the colour develops within 5 min. A test with thiocyanate may be made first, and the above test afterwards applied to the same solution. Contrary to the views of Andreasch (A., 1880, 236) and Claesson (A., 1881, 646) the mechanism is probably: (i) $2Fe^{\cdot\cdot\cdot}+2HS\cdot CH_2\cdot CO_2H \longrightarrow 2Fe^{\cdot\cdot}+(\cdot S\cdot CH_2\cdot CO_2H)_2''$; (ii) $Fe^{\cdot\cdot}+(\cdot S\cdot CH_2\cdot CO_2H)_2'' \longrightarrow Fe(S\cdot CH_2\cdot CO_2H)_2 \longrightarrow Fe(S\cdot CH_2\cdot CO_2)_2''$. When ferric iron is present, reaction (i) takes place; ferrous ion forms the colourless ferrous thioglycollic acid complex, which gives a coloured ion on addition of alkali. The method may be applied quantitatively; its delicacy is unaffected by the presence of most salts. S. K. TWEEDY.

Titanous chloride for the determination of iron and of chloric acid. P. S. BRALLIER.—See B., 1927, 652.

Detection of chromium by oxidation with chlorine or bromine in presence of silver nitrate. E. POSNER (Z. anorg. Chem., 1927, **164**, 407—408; cf. this vol., 37).—Chromium may be detected, even in presence of considerable amounts of iron and manganese, by adding to 0·5 c.c. of the solution 5 c.c. of 2*N*-silver nitrate and 0·5 c.c. of bromine water or, preferably, 1 c.c. of chlorine water, boiling for 1 min., adding a slight excess of 2*N*-ammonia solution, filtering, and precipitating silver chromate from the filtrate with nitric acid. If the result is negative, the precipitate should be treated with ammonia, and the solution neutralised with nitric acid, as the precipitate sometimes carries down with it the whole of the chromium. R. CUTHILL.

Separation of chromium, tungsten, molybdenum, and vanadium. E. CREMER and B. FETKENHEUER.—See B., 1927, 704.

Potentiometric titration of molybdenum. H. BRINTZINGER and F. OSCHATZ (Z. anorg. Chem., 1927, **165**, 221—224).—The optimum conditions for the potentiometric titration of molybdenum are obtained as follows: to 20 c.c. of the (sodium)

molybdate solution are added 50 c.c. of hydrochloric acid and 50 c.c. of water; the hot solution is saturated with potassium chloride, and the dissolved oxygen removed by boiling the solution, through which is passing a slow current of carbon dioxide, rendered free from oxygen by passage through chromous chloride solution. The solution is then titrated with 0·1*N*-chromous chloride solution, employing a platinum wire as electrode. A sharp fall in potential indicates the total conversion of Mo^{VI} into Mo^{V}, whilst a second sharper fall occurs when molybdenum is converted completely into the tervalent state. H. F. GILLBE.

Determination of tungsten in ferro-tungsten and tungsten steels. L. MOSER and K. SCHMIDT.—See B., 1927, 656.

Separation of hafnium and zirconium by precipitation of the phosphates from sulphuric acid solutions. J. H. DE BOER (Z. anorg. Chem., 1927, **165**, 16—20).—The mixture of hafnium and zirconium phosphates is converted into hydroxide by dissolution in acid and precipitation with potassium hydroxide. The washed precipitate is dissolved in concentrated sulphuric acid and a solution in concentrated sulphuric acid of a quantity of the phosphate mixture equal to that employed in the first operation is added. On dilution of the solution with twice its volume of water a precipitate of the mixed phosphates is obtained and is treated in the same manner as the original mixture. The zirconium and hafnium remaining in the solution are precipitated as phosphates by the addition of phosphoric acid. From a mixture of phosphates containing hafnium to the extent of 20% of the total content of metal a first fraction can be obtained containing 30% of hafnium. After about eight fractionations pure hafnium phosphate is obtainable. When the phosphate mixture contains only 2% of hafnium 12—15 operations are required, whereas by the earlier method of precipitation of phosphates from oxalic acid solution 26 fractions were necessary. H. F. GILLBE.

Separation of hafnium and zirconium by fractional decomposition of the complex phosphatofluoro-hafnates and -zirconates. J. H. DE BOER and P. KOETS (Z. anorg. Chem., 1927, **165**, 21—30).—To a mixture of zirconium and hafnium phosphates dissolved in a solution of hydrogen chloride and ammonium hydrogen fluoride containing free phosphoric acid, sufficient borax is added to precipitate as phosphate about half of the metal present. The precipitate is redissolved and reprecipitated in the same manner. After eight operations, starting from a mixture containing hafnium to the extent of 20% of the total metal present, the precipitate contains 85% of hafnium. H. F. GILLBE.

Analysis of antimony alloys. H. VIGNAL.—See B., 1927, 725.

Rontgen apparatus for crystallographical investigations in the chemical laboratory. J. BOHM (Kolloid-Z., 1927, **42**, 285—287).—A simple and easily manipulated apparatus for rontgenographical investigations consists of three separate parts: the source of high tension, the *X*-ray tube, and the camera. The *X*-ray tube is of chromium steel and glass, and may be used with either gas cathode or heated cathode. Various types of Debye–Seherrer camera may be used, adapted for the investigation of streaming sols, thin films, or fibres, for working in dry air or in air with constant water-vapour pressure. L. L. BIRCUMSHAW.

Hot wire vacuum gauge. A. M. SKELLETT (J. Opt. Soc. Amer., 1927, **15**, 56—58).—A modified form of Pirani hot wire gauge, allowing changes in pressure to be automatically plotted against time, is described. W. E. DOWNEY.

Absolute manometer for low pressures. W. H. RODEBUSH and C. C. COONS (J. Amer. Chem. Soc., 1927, **49**, 1953—1955).—A graphite disc, ground to fit on to the end of a glass tube leading to the vacuum pump, is suspended from a piece of soft iron enclosed in glass and attached to a quartz arm. The whole is enclosed in a glass vessel, which has a coil of wire wound round that portion enclosing the soft iron, and is attached to the apparatus. The coil current necessary to raise the disc from its seat is a measure of the gas pressure on the disc. The pressure range is about the same as that of the MacLeod gauge, against which the manometer is conveniently calibrated. It can also be calibrated absolutely by placing weights on the disc. It is unsuitable for use where escape of gas from the apparatus must be avoided. S. K. TWEEDY.

Low-pressure value. M. F. PETERS and E. H. KLEIN (J. Opt. Soc. Amer., 1927, **15**, 59—61).—Lead solder is melted in a pyrex glass U-tube and allowed to solidify. By taking advantage of the comparatively wide difference in the coefficients of expansion of the glass and of the solder, the opening between the solder and the glass may be varied. This variable opening may be used as a gas valve at low pressures. W. E. DOWNEY.

Differential dilatometer for the determination of volume changes during solidification. C. J. SMITH (Proc. Roy. Soc., 1927, **A**, **115**, 554—570).—Measurements have been made with a new dilatometer, which is described, of the volume change on freezing of the lead–tin and bismuth–tin eutectics, and it is found that the contraction on solidification for the lead–tin eutectic is 2·5%, and the expansion on solidification for the bismuth–tin eutectic is 0·8%. The volume changes associated with the freezing of pure tin are also recorded. L. L. BIRCUMSHAW.

Rotating adiabatic calorimeter. Surface energy and heat of dissolution of sodium chloride. II. S. G. LIPSETT, F. M. G. JOHNSON, and O. MAASS (J. Amer. Chem. Soc., 1927, **49**, 1940—1949).—The calorimeter previously described (this vol., 520) is modified so that the salt is not exposed to water vapour before dissolution occurs. The heats of dissolution of sodium chloride at 20° were determined at concentrations up to saturation. An indirect, but accurate, method of calculating the specific heats of solutions from the temperature coefficients of the heats of dissolution is described, values are tabulated for the complete concentration

range of sodium chloride. The mean value of the surface energy of this salt is 386 ergs/cm.^{2} at 25°.
S. K. TWEEDY.

[Prevention of bumping during] high vacuum distillation. E. S. WEST (J. Amer. Chem. Soc., 1927, **49**, 2118).—Sufficient glass wool is placed in the distillation flask to extend slightly above the surface of the liquid or syrup. S. K. TWEEDY.

Purification of toluene for thermo-regulators. G. D. BEAL and B. L. SOUTHER (J. Amer. Chem. Soc., 1927, **49**, 1994).—The toluene is boiled with a 1% sodium amalgam under a reflux condenser, decanted, washed, and distilled. S. K. TWEEDY.

Ultra-filter. R. S. AITKEN and H. D. KAY (J. Physiol., Proc. Physiol. Soc., 1927, **62**, xxix).—The apparatus is designed for the ultra-filtration of 3—5 c.c. of undiluted serum or plasma through cellophane at pressures up to 6 atm., giving 0·5 c.c. or more of protein-free ultra-filtrate in 2 hrs.
A. A. ELDRIDGE.

Colorimeter lamp. H. D. KAY (J. Physiol., Proc. Physiol. Soc., 1927, **62**, xxxi).—A simple form of lamp, in which the light is reflected from a white paper surface, is described. A. A. ELDRIDGE.

Laboratory apparatus for the electrolytic preparation of oxygen and of ozone. O. R. WULF (J. Opt. Soc. Amer., 1927, **15**, 119—124).—An apparatus for the electrolytic preparation of oxygen from alkaline solutions at a high rate and in a reasonable state of purity is described. A convenient form of electrolytic ozone generator using dilute sulphuric acid as electrolyte and a lead anode is also described. R. A. MORTON.

Proportion of nitrous vapours in the neighbourhood of arc lamps. J. DADLEZ (Compt. rend., 1927, **185**, 420—422).—The concentrations of nitric acid in the air at various distances from an arc lamp have been determined. Quantities sufficient to produce irritation of the mucous membrane are found only in the absence of efficient ventilation.
C. W. GIBBY.

Mineralogical Chemistry.

Rare gases of some thermal springs of Bulgaria. N. P. PENTCHEV (Compt. rend., 1927, **185**, 511—513).—Three thermal springs in Bulgaria were found to contain nitrogen (95·15—98·3% by volume), helium (0·064—0·25%), argon (1·336—1·56%), and traces of carbon dioxide and oxygen. The total rare gases varied from 1·40 to 1·81% by volume and their densities varied from 1·711 to 1·564 g./litre. The combustible gases (calculated as hydrogen) ranged from 0·3 to 3·21%, and the radioactivities from $5·6\times10^{-10}$ to 560×10^{-10} curie per litre of water, or 50×10^{-10} to 6100×10^{-10} curie per litre of gas. The proportions present of the various gases were in accord with the astrophysical theory of Moureu and Lepape. J. GRANT.

Diffusion of several gases and salts. Application in biology and industry. M. YEGUNOV (Visti Odeskogo Sil'skogo-Gospodars'kogo Inst., 1925—1926, No. 1, 81—90; 1926, No. 2, 49—60).—The water of the Black Sea below 120—150 m. is undisturbed. Below 200 m. the salinity, temperature, *d*, and high hydrogen sulphide content are constant; it is held that above this zone sulphur bacteria accumulate which oxidise the hydrogen sulphide to sulphuric acid. Diffusion experiments discredit the view that the hydrogen sulphide is formed at the sea bottom and diffuses upwards. It is probably formed throughout the whole thickness of the water column, but accumulates only where it cannot be oxidised.
CHEMICAL ABSTRACTS.

Arsenic content of East Prussian waters. GOY and W. RUDOLPH (Z. angew. Chem., 1927, **40**, 945—948).—Samples of Baltic water contain 1 g. of arsenic per 1000 cubic metres; water from the brackish shore lakes contains from one to four times as much, but this is natural, and not due to effluents of pulp factories which discharge into them. The muds from the lakes are very much richer in arsenic, containing from 2 to 30 g. per ton of dry weight; this enrichment is attributed to the extraction of arsenic from the water by the minute water organisms.
S. I. LEVY.

Occurrence of iodine in nature. XI. Geochemistry of iodine. II. T. VON FELLENBERG (Biochem. Z., 1927, **187**, 1—6).—Iodine was detected in various meteorites and in sulphide ores; bromine was sometimes found in the meteorites but not in the ores. C. R. HARINGTON.

Mineralogical composition of some soils of the Netherlands. J. H. DRUIF (Proc. K. Akad. Wetensch. Amsterdam, 1927, **30**, 365—367).

Effect of radon on the solubility of lead uranate. K. C. BAILEY.—See this vol., 928.

Composition of crocidolite (Cape blue asbestos). C. J. N. JOURDAN (J. Chem. Met. Min. Soc. S. Afr., 1927, **27**, 287—289).—The complete analysis of eight samples of crocidolite from different localities in the Cape Province, South Africa, is given together with details of colour and texture of fibres. Seven of the samples were remarkably concordant in composition although coming from widely separated districts, the figures for the different constituents varying within the following limits: SiO_2 50·5—52·9, Fe_2O_3 17·5—21·0, FeO 13·1—18·7, CaO 0·65—0·9, MgO 2·3—4·5, Na_2O 4·0—4·5, H_2O 3—4%. The colour varied from light blue to dark lavender-blue and the texture of the fibres from rather harsh to soft and silky. A. R. POWELL.

Zeolites of the natrolite group. A. CAVINATO (Mem. R. Accad. Lincei, 1927, [vi], **2**, 320—350).—The percentage loss of water suffered by natrolite, scolecite, and mesolite has been determined for temperatures up to 800°, and crystallographic data are

given for these minerals and for the corresponding metazeolites thus formed. Natrolite loses water slowly to 260° and then rapidly, dehydration being practically complete at 330°; scolecite loses approximately one third of its water between 150° and 190°, and most of the residue between 330° and 350°; the curve for mesolite shows slight inflexions only, at 200° and 390°. The rate and amount of absorption of water vapour at 8—10 mm. and at the ordinary temperature characterising the substances produced by heating these minerals at temperatures from 50° to 800° have also been determined. Up to 500° natrolite absorbs an amount approximately equal to that lost; at higher temperatures of calcining the amount absorbed diminishes rapidly. When heated at temperatures below 300°, scolecite absorbs approximately all the water lost, but above 350° practically no water is absorbed by the product. The product obtained by heating mesolite below 250° absorbs the water lost; above 310° practically no water is absorbed. The loss of water in 2 hrs. at 250° is suggested as a convenient method of identifying these minerals; natrolite loses 1·5%, scolecite 4·5%, and mesolite 6·4% of the initial weight. R. W. LUNT.

Dehydration of apophyllite. A. CAVINATO (Atti R. Accad. Lincei, 1927, [vi], 5, 907—910).—The diversity of results of previous authors on the dehydration of apophyllite on heating is attributed, not to the different sources of the mineral, but to insufficient duration of heating (cf. preceding abstract; Colombo, A., 1907, ii, 705; Zambonini, A., 1909, ii, 154, etc.). The dehydration curve now obtained shows that the water from the apophyllite is evolved almost entirely between 200° and 300°, recalling some of the zeolites in this respect. It differs, however, from the zeolites in the slowness of dehydration and also in not returning to its previous water content on exposure to moist air. M. CARLTON.

Pyromorphites of Braubach (Nassau). G. CAROBBI and S. RESTAINO (Rend. Accad. Sci. Fis. Mat. Napoli, 1926, [iii], 32, 17—27).—The possibility of isomorphic substitution of lead by the rare earths in pyromorphites, vanadinites, and mimetites has already been demonstrated (cf. A., 1926, 811).

A sample of pyromorphite from Braubach (Nassau) (Bowman, Min. Mag., 1903, 13, 324) contained La_2O_3, Nd_2O_3, Sm_2O_3, 0·019; Ce_2O_3 0·002; Y_2O_3 etc. 0·024%. For the exact identification of the rare-earth elements photographs of the arc spectrum were taken between 3200 and 4900 Å. The elements present were: yttrium, lanthanum, cerium, neodymium, samarium, europium, gadolinium, dysprosium, erbium, and yttrium.

The total amount of the rare-earth elements is small, but this is not surprising since it has been shown that the possibility of substitution of lead by lanthanum in the pyromorphites etc. is strictly limited.

M. CARLTON.

Solubility of cassiterite. H. C. BOYDELL (Bull. Inst. Min. Met., Aug., 1927. 15 pp.).—From a review of the literature on the solubility of tin oxide in various solvents an attempt has been made to account for the alleged secondary enrichment in depth of tin deposits in Bolivia. Two theories are advanced, one based on the possibility of the formation of colloidal solutions of tin oxide by mechanical means involving fine grinding of the particles, and the other on the formation of colloidal solutions of stannic hydroxide by hydrolysis of sulphate or phosphate solutions derived from the action on cassiterite of ferric sulphate solutions formed by the oxidation of pyrites with or without the intermediate formation of phosphoric acid from phosphate minerals in the vicinity.

A. R. POWELL.

Pleochroic haloes in cordierite. C. MAHADEVAN (Indian J. Physics, 1927, 1, 445—456).—A number of sections of cordierite gneiss from South India, when studied under the polarising microscope, were found to display all the recognised types of pleochroic halo, including embryonic rings and normal, emanation, over-exposed, bleached, and dwarf haloes. Contrary to the observations of Joly and Fletcher (Phil. Mag., 1910, 19, 630), the radii of these haloes agree closely with the calculated values for the α-range of the members of the uranium and thorium series in the mineral, the discrepancies between observed and calculated values being no greater for the haloes of cordierite than for those of biotite. M. S. BURR.

Merua meteorite. G. H. TIPPER (Rec. Geol. Survey India, 1925, 56, 345—351).—Analyses are recorded. CHEMICAL ABSTRACTS.

Organic Chemistry.

Oxidation of *n*-triacontane. F. FRANCIS and N. E. WOOD (J.C.S., 1927, 1897—1902).—Synthetic *n*-triacontane, b. p. 304° (corr.)/15 mm., m. p. 66·5° (Petersen, A., 1906, i, 331), is oxidised by air in the presence of 5% of turpentine in a manner similar, both in the nature of the products formed and in the velocity of the reaction, to that of paraffin wax, m. p. 55—56°, or the pure hydrocarbons derived therefrom. Triacontane contains 12·1% of oxygen after oxidation at 95° for 1009 hrs. and gives (from 100 g.) unchanged hydrocarbon (21 g.), carbon dioxide (4·3 g.), formic acid (0·6 g.), other acids (64 g.), and inert compounds. The following acids were isolated: succinic acid; cerotic acid, $C_{26}H_{52}O_2$, identical with that prepared from beeswax; a small amount of an acid, $C_{24}H_{48}O_2$, identical with that formed in the oxidation of paraffin; acids, $C_{20}H_{40}O_2$(?), m. p. 63°, $C_{16}H_{32}O_2$ (?), m. p. 53·4°, and $C_{22}H_{44}O_2$, m. p. 68°. The last three substances were isolated by conversion into their methyl esters followed by fractional distillation and hydrolysis. The inert products include a ketonic alcohol (? dihydroxy-compound), $C_{30}H_{60}O_2$, m. p. 69°, and a ketone, $C_{30}H_{60}O$, m. p. 62·5°. *X*-Ray analysis of the latter substance shows that the oxygen is probably attached to the fourth carbon atom.

It is suggested that triacontane is first attacked by

oxygen at the fourth (or third) carbon atom and yields secondary alcohols which are progressively oxidised to ketones and to acids, and are simultaneously oxidised to polyoxy-compounds, which in turn pass to a mixture of monobasic and oxy-acids of still smaller carbon content. G. A. C. GOUGH.

Activity of halogens in organic compounds and their characteristic behaviour. B. V. TRONOV (J. Russ. Phys. Chem. Soc., 1926, **58**, 1278—1301).—Various organic halogen derivatives (68 in all) have been allowed to react with pyridine and piperidine in sealed tubes, at 16—18° generally, but in the more difficult cases at 220°. The speed of the reaction is taken to be directly proportional to the amount of halide converted, there being very little error at the beginning of the reaction. The quantities of the components of the reaction were as 1 : 1, and chloroform and chlorobenzene were taken as standards for the speed of reaction with pyridine and piperidine respectively. It was found that iodo-compounds are the most reactive, those of chlorine the least, the difference between the speeds of chloro- and bromo-compounds being much greater than between the latter and iodo-compounds. The differences are much smaller in the case of electronegative radicals. A long carbon chain is found to decrease the speed of reaction, especially if the chain is branched in close proximity to the halogen atom. A phenyl radical and an unsaturated radical raise the reactivity, unless, in the case of the latter, the double linking is in the αβ-position to the halogen atom. Oxygen raises the reactivity in the order hydroxyl, ether, and acid, especially when the halogen is in the α-position. An exception to this is ethyl chloromalonate, in which the speed is one twentieth, probably due to the enolisation of the carbonyl group. Nitro-groups cause the halogen atom to be more reactive than even carboxyl groups. In compounds of the type CH_2X_2 and CH_2MeX, where X is halogen, the entry of further halogen atoms first lowers the reactivity and then raises it. This is not to be observed in the case of aromatic halogen compounds. Moreover, αγ-dibromopropane and α-chloro-γ-bromopropane are more reactive than their corresponding monobromo-derivatives. The author discusses these results, and draws deductions partly based on the theories put forward by Ingold and Ingold (A., 1925, i, 657) and by Holmes and Ingold (A., 1925, i, 1142).

E. ROTHSTEIN.

Activity of fluorine in organic compounds. B. V. TRONOV and E. A. KRUGER (J. Russ. Phys. Chem. Soc., 1926, **58**, 1270—1277).—The ease of elimination of fluorine in *iso*amyl fluoride and fluorobenzene has been compared with that of the corresponding compounds of the other halogens. The reactivity of these compounds with piperidine (with- a solvent) and sodium methoxide in methyl alcohol was measured by sealing the substances in a tube and warming when necessary. The reactivity was found to rise with rising atomic weight, fluorine emg the least reactive, and the differences between e halogens being least in the case of their phenyl compounds. It is considered that the reactivity of uorine depends on the electronegative character of the radical to which it is attached, and if the latter becomes sufficiently negative, then fluorine will become more reactive than the other halogens when in combination with an organic residue. *iso*Amyl fluoride had b. p. 46·7—47°/755 mm. (lit. 72—92°), *d* 0·69945. Attempts to prepare benzyl fluoride by the action of silver fluoride on benzyl bromide failed, the only product isolated being toluene.

E. ROTHSTEIN.

Substitution and addition. J. MEISENHEIMER (Annalen, 1927, **456**, 126—151).—In agreement with Werner's views (A., 1912, i, 74; cf. Pfeiffer, A., 1911, i, 788) the primary action of, for instance, chlorine on methane is probably the formation of an additive compound, $\cdots CH_3\text{–}H\cdots Cl_2$ (I). An auxiliary valency directed away from the chlorine molecule is thus developed on the carbon atom, which may then give a compound, $Cl_2\cdots CH_3\text{–}H\cdots Cl_2$ (II). The substance (I) will ultimately yield a normal substitution product, whilst in (II) the chlorine will enter a position diametrically opposite to that vacated by the hydrogen. Thus, if the carbon atom is asymmetric, type (II) is the precursor of a Walden inversion. The abnormal behaviour of unsaturated alcohols of the type $CH_2{:}CH\cdot CHR\cdot OH$ towards hydrogen bromide (Ziegler, A., 1925, i, 395; Straus and Ehrenstein, *ibid.*, 534) is similarly explained by the formation of a compound, $HCl\cdots CH_2{:}CH\cdot CHR\cdot O(H)\cdots HCl$. Simultaneous addition of 1 mol. of bromine to each of two doubly-linked carbon atoms accounts in the same way for *trans*-addition. The formation of intermediate compounds of this type in solutions containing bromine and an unsaturated compound should render the bromine content determined colorimetrically less than that determined titrimetrically. This appears to be the case with fumaric acid. Although solutions of triphenylethylene dibromide contain free bromine and liberate iodine from potassium iodide forming triphenylethylene and bromotriphenylethylene, the dibromide is probably of normal type since it gives *ethoxytriphenylethylene*, m. p. 135·5°, with boiling alcohol. Bromotriphenylethylene does not react with alcohol; with chlorine it forms *ααβ-trichloro-αββ-triphenylethane*, m. p. 124°. The methyl group in ααβ-triphenyl-β-methyl-Δ^{α}-propene behaves similarly to that in toluene. Bromination gives *γ-bromo-ααβ-triphenyl-β-methyl-*Δ^{α}*-propene*, m. p. 122° (III) (the "dibromide," m. p. 108—113°, of Lévy, A., 1921, i, 861), and, in sunlight, the *γγ-dibromo*-derivative, m. p. 130°, with evolution of hydrogen bromide, resolidifying with m. p. 159°. The constitution of (III) follows from its oxidation by ozone to benzophenone and phenacyl bromide. It is converted by boiling alcohol into *γ-ethoxy-ααβ-triphenyl-*Δ^{α}*-propene*, m. p. 129°, and by the Grignard method using magnesium phenyl bromide into *ααβγ-tetraphenyl-*Δ^{α}*-propene*, m. p. 139°.

H. E. F. NOTTON.

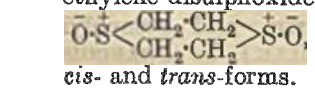
Oleyl alcohol and its derivatives. Preparation of oleicerin, elaidicerin, and stearolyl alcohol. E. ANDRÉ and (MLLE.) T. FRANÇOIS (Compt. rend., 1927, **185**, 387—388; cf. B., 1927, 706).—Oleyl alcohol (*n-trans*-Δ'-octadecen-α-ol) affords a liquid additive compound with bromine which with silver acetate in acetic acid gives a

diacetate, yielding on hydrolysis with alcoholic potassium hydroxide *oleicerin* (n-trans-*octadecane*-αιιx-*triol*), m. p. 126·5°. *Elaidicerin* (n-cis-*octodecane*-αιιx-*triol*), m. p. 92°, is similarly prepared from elaidyl alcohol. The action of alcoholic potassium hydroxide in a sealed tube at 140—150° or of sodamide in toluene or xylene on the dibromo-derivative of oleyl alcohol affords a mixture of alcohols. *Stearolyl alcohol*, m. p. 26° (*phenylurethane*, m. p. 53°; β-*naphthylurethane*, m. p. 71·5°), is obtained in 35% yield by reduction of ethyl stearolate with sodium and alcohol. Concentrated sulphuric acid converts it into ι-*ketostearolic acid*, m. p. 148° (*oxime*). R. BRIGHTMAN.

Decomposition of some halogenated sulphides and the nature of the "polymeric" ethylene sulphides. E. V. BELL, G. M. BENNETT, and A. L. HOCK (J.C.S., 1927, 1803—1809; cf. A., 1926, 1123; this vol., 355).—*γγ-Di-iododipropyl sulphide*, prepared in the crude state by the action of sodium iodide on the corresponding chloro-compound, decomposes on keeping with the liberation of trimethylene di-iodide. ββ′-Dichlorodiethyl sulphide, when heated at 180°, yields ethylene dichloride and dithian (cf. Davies, J.C.S., 1920, **117**, 299). These facts, together with the fact that potassium cyanide reacts with dichlorodiethyl sulphide to give the nitrile, $C_2H_4(S{\cdot}C_2H_4{\cdot}CN)_2$ (Davies, *loc. cit.*), are explained as similar processes involving the formation of sulphonium salts followed by their dissociation into other substances. A scheme on this basis representing the changes undergone by dichlorodiethyl sulphide is supported by the re-formation of dichlorodiethyl sulphide by the action of ethylene dichloride on dithian at 180°. The "polymeric" ethylene sulphides, formed by the action of sodium sulphide on ethylene dichloride, trimethylene dichloride, or dichloroethyl sulphide (Bennett and Whincop, J.C.S., 1921, **119**, 1861; Ray and Bose-Ray, A., 1926, 1023; Staudinger, A., 1925, i, 362), which are converted into dithian on heating only when they contain small amounts of halogen, are shown to be converted into dithian when heated in phenol containing hydrogen bromide. In a similar way, dithian may be obtained from thiodiglycol, ethylenebis-β-hydroxyethyl sulphide, and sulphidobis-β-hydroxyethyl sulphide. These facts support the previously published view as to the constitution of the "polymerides" (Nature, 1926, **118**, 555).

G. A. C. GOUGH.

***cis–trans*-Isomerism of disulphoxides.** E. V. BELL and G. M. BENNETT (J.C.S., 1927, 1798—1803).—The preparation of optically active sulphur compounds containing only three groups attached to the asymmetric sulphur atom (Phillips, A., 1926, 159; Harrison, Kenyon, and Phillips, A., 1926, 1031) precurses *cis–trans*-isomerism in molecules in which two sulphoxyl groups are present. Dimethylethylene disulphoxide and dithian dioxide,



have been found to exist in *cis*- and *trans*-forms.

Oxidation of dithian in glacial acetic acid solution with hydrogen peroxide, followed by crystallisation of the product from aqueous alcohol, yields α-*dithian dioxide* (monoclinic system), decomp. 263°, d_4^{20} (vac.) 1·570. From the mother-liquors, β-dithian dioxide (anorthic system), decomp. 235—250°, d_4^{20} (vac.) 1·554, is obtained. Crystallographic measurements of both forms are given. Considerations of the solubilities indicate that the crude oxidation product contains 89% of the α- and 11·0% of the β-isomeride. Both isomerides yield dithian on reduction with zinc dust and hydrogen chloride in acetic acid solution, but attempts to interconvert them by heating with water or dilute acids were unsuccessful. In a similar manner dimethyldithiolethane yields α-*dimethylethylene disulphoxide*, m. p. 163—164° (obtained in larger proportion), and β-*dimethylethylene sulphoxide*, m. p. 128—130°. The lower-melting β-forms probably correspond, in each case, with the *cis*-isomeride.

The isomeric disulphoxides derived from thianthren (Fries and Vogt, A., 1911, i, 395) probably arise from *cis–trans*-isomerism due to similar causes.

G. A. C. GOUGH.

Silicon tetrachloride as a reagent for the preparation of acid chlorides. R. E. MONTONNA (J. Amer. Chem. Soc., 1927, **49**, 2114—2116).—The following acid chlorides were obtained, in the yields mentioned, by treating the appropriate acids, in an inert solvent, with silicon tetrachloride at about 50°, the mixture being subsequently fractionated: acetyl, 85%; propionyl, 50%; butyryl, 49%; *iso*butyryl, 52%; benzoyl, 77%; phenylacetyl, 61%; and sebacyl chloride, 22%. Maleic, malonic, oxalic, o-nitrobenzoic, and pyruvic acids failed to yield chlorides under these conditions. Acetic anhydride was obtained in 75% yield by treating a suspension of sodium acetate in acetic anhydride with silicon tetrachloride at 50°.

F. G. WILLSON.

Tin salts of organic acids. E. ELOD and F. KOLBACH (Z. anorg. Chem., 1927, **164**, 297—312).—By the action of a solution of an alkali formate in formic acid on stannic chloride, *sodium hexaformatostannate*, $Na_2Sn(HCO_2)_6,5H_2O$, and the corresponding *potassium* ($5H_2O$) and *ammonium* ($5H_2O$) salts may be obtained. Using stannous chloride instead of stannic chloride, the corresponding *tetraformatostannates*, $Na_2Sn(HCO_2)_4,5H_2O$, $(NH_4)_2Sn(HCO_2)_4,5H_2O$, and $K_2Sn(HCO_2)_4,5H_2O$, are obtained. All these salts are hydrolysed by water. Interaction of potassium acetate and stannic sulphate or chloride in acetic acid solution yields a *basic stannic acetate*, $SnO(OAc)_2$. *Sodium hexa-acetostannate*, $Na_2Sn(OAc)_6$, is formed by reaction of sodium acetate with stannic chloride in acetic acid solution. *Ammonium dichlorodioxalatostannate*, $(NH_4O_2C{\cdot}CO_2)_2SnCl_2,H_2O$, may be prepared by the action of ammonium oxalate on stannic chloride or ammonium hexachlorostannate. The analogous potassium and sodium *salts* are formed in a similar manner, the reactions being carried out in acetic acid solution. *Sodium stannic oxalate*, $Sn(O_2C{\cdot}CO_2Na)_4,3H_2O$, is produced by the action of stannic chloride or ammonium hexachlorostannate on sodium oxalate. It appears probable that commercial stannic oxalate is a mixture of stannic acid and oxalic acid.

R. CUTHILL.

Catalytic chlorination of acetic acid [to monochloroacetic acid]. H. BRUCKNER (Z. angew. Chem., 1927, **40**, 973—974).—Glacial acetic acid may be chlorinated to the monochloro-derivative without the action of light in the following manner: 200 g. of the acid are heated at 100° with 2 g. of iodine, 10 g. of phosphorus pentachloride, and 5 g. of red phosphorus and a rapid current of chlorine is passed through for 2 hrs. A further 50 c.c. of glacial acetic acid is added and, after settling, the hot liquid is decanted from the phosphorus. On cooling, practically the whole of the monochloroacetic acid crystallises out and, after sucking dry on a vacuum filter and washing with glacial acetic acid, is obtained in a pure form. The filtrate and washings may be utilised in the preparation of further quantities of the chloro-acid.

A. R. POWELL.

Arylhydrazides of higher fatty acids. V. VESELÝ and J. HAAS (Chem. Listy, 1927, **21**, 351—358).—The following substances have been prepared: *phenylhydrazides* of oleic, m. p. 92—93°, erucic, m. p. 82—83°, brassidic, m. p. 98°, κ-hydroxystearic, m. p. 106—107°, myristic, m. p. 108°, lauric, m. p. 105—106°, elaidic, m. p. 98—99°, and *iso*oleic acids, m. p. 101°, *α-naphthylhydrazides* of stearic, m. p. 132—133°, palmitic, m. p. 134—135°, myristic, m. p. 139°, lauric, m. p. 136°, erucic, m. p. 106—107°, and brassidic acids, m. p. 121—122°, *α-phenyl-α-methylhydrazides* of stearic, m. p. 78·5°, palmitic, m. p. 74°, myristic, m. p. 63°, lauric, m. p. 56°, erucic, m. p. 74°, and brassidic acids, m. p. 69°, *diphenylhydrazides* of stearic, m. p. 122·5°, palmitic, m. p. 124°, oleic, m. p. 83—86°, erucic, m. p. 88°, brassidic, m. p. 106°, and κ-hydroxystearic acids, m. p. 124—125°, *p-ditolylhydrazides* of stearic, m. p. 115—116°, and oleic acids, m. p. 79—80°; *phenyl-m-xylylnitrosoamine*, m. p. 49—50°; *phenyl*-m-*xylylhydrazine*, m. p. 70—71°; *phenyl*-m-*xylylhydrazides* of stearic, m. p. 119—120°, and oleic acids, m. p. 92—93°. By condensation and heating with *dihydrazine* were obtained the *diphenylmethanedimethyldihydrazides* of stearic, m. p. 145—146°, palmitic, m. p. 148°, lauric, m. p. 147—148°, oleic, m. p. 122°, Δ⁴-elaidic, m. p. 126—127°, and *iso*oleic acids, m. p. 136°. *Diphenyldimethyldihydrazine*, m. p. 90—91°, was prepared by the reduction of *diphenyldimethyldinitrosoamine*, m. p. 211—212°; the *diphenyldimethyldihydrazides* of stearic and oleic acids have m. p. 131—132° and 104—105° respectively. The above derivatives are of no value for the quantitative separation of mixtures of fatty acids.

R. TRUSZKOWSKI.

Action of metallic derivatives of ethyl dehydroundecenoate on alkyl halides. W. W. MYDDLETON and R. G. BERCHEM (J.C.S., 1927, 1928—1930).—An attempt to synthesise Δ⁴-stearolic acid by the action of alcoholic heptyl bromide on the silver derivative of ethyl dehydroundecenoate resulted in the formation of silver bromide, ethyl heptyl ether, and free ethyl dehydroundecenoate. The use of an excess of heptyl bromide in the absence of alcohol gave silver bromide, heptene, and ethyl dehydroundecenoate. *n*-Propyl, *iso*butyl, and ethyl bromides and ethyl iodide lead to the formation of corresponding products under each set of conditions. The sodium derivative of ethyl dehydroundecenoate, prepared by refluxing a toluene solution of the ester with sodamide for 2 days, reacts with an excess of heptyl bromide to give sodium bromide and the original ester.

G. A. C. GOUGH.

Salts of α-linoleic acid tetrabromide [θλιτετrabromostearic acid]. A. T. ORETA and A. P. WEST (Philippine J. Sci., 1927, **33**, 169—176).—The following salts of α-linoleic acid tetrabromide, prepared from Philippine lumbang oil (this vol., 540; see B., 1927, 304), are described: *sodium*, m. p. 201·1° (decomp.), *potassium*, *zinc*, m. p. 154·7—158·8°, *calcium*, m. p. 213·4° (decomp.), *strontium*, m. p. 206° (decomp.), *barium*, m. p. 202·5° (decomp.). The solubilities of these salts in numerous organic liquids have been determined qualitatively.

H. BURTON.

Condensation of lactic acid and a dibasic acid under the influence of the combined action of catalysts at high pressures and temperatures. V. IPATIEV and G. RAZUBAIEV (J. Russ. Phys. Chem. Soc., 1926, **58**, 1345—1350).—See A., 1926, 1124.

Action of oxalic acid on some soluble lead salts. (MME.) N. DEMASSIEUX (Compt. rend., 1927, **185**, 460—461).—Conductivity measurements have been made during the addition of oxalic acid to solutions of lead chloride, bromide, iodide, and nitrate. In each case the final product is lead oxalate. The chloride and bromide form intermediate compounds, $Pb_2C_2O_4Cl_2$ and $Pb_2C_2O_4Br_2$.

C. W. GIBBY.

Synthesis of cyclic compounds. I. Ethyl βγ-dimethylbutane-ααδδ-tetracarboxylate and some *cyclo*butane compounds derived therefrom. I. VOGEL (J.C.S., 1927, 1985—1994; cf. this vol., 449).—Reduction of ethyl ethylidenemalonate, b. p. 115—117°/15 mm., $d_4^{17\cdot4}$ 1·01938, $n_D^{17\cdot4}$ 1·43007, with moist aluminium amalgam yields *ethyl βγ-dimethylbutane-ααδδ-tetracarboxylate*, b. p. 225—226°/16 mm., $d_4^{17\cdot0}$ 1·0887, $n_D^{17\cdot0}$ 1·44873. The mixture of isomeric acids, obtained by hydrolysis of this ester, is separated by fractional crystallisation into r- and meso-*βγ-dimethylbutane-ααδδ-tetracarboxylic acid*, m. p. 185—185·5° (decomp.) and 152—154° (decomp.) respectively. The *meso*-acid is the more soluble. When a mixture of the above acids is heated at 200°, a mixture of the isomeric *ββ-dimethyladipic acids*, m. p. 113—117° (mixed *ethyl* esters, b. p. 139—141°/15 mm., $d_4^{19\cdot5}$ 0·98777, $n_D^{19\cdot5}$ 1·43447), is obtained. The *disodio*-derivative of *ethyl βγ-dimethylbutane-ααδδ-tetracarboxylate*, prepared by the interaction of the ester and sodium methoxide, reacts with bromine in ethereal solution to give *ethyl* 2 : 3-*dimethyl*cyclo*butane*-1 : 1 : 4 : 4-*tetracarboxylate*, b. p. 208—210°/16 mm., 1·1216, 1·45573, which yields the corresponding *acid*, m. p. 138—139° (slight softening at 80°), on hydrolysis. When this acid is heated at 180°, it loses carbon dioxide to give a gummy residue of acids which, on esterification, yields the mixed esters, *ethyl* 2 : 3-*dimethyl*cyclo*butane*-1 : 4-*dicarboxylate*, b. p. 138—139°/14 mm., $d_4^{16\cdot8}$ 1·00955, $n_D^{16\cdot8}$ 1·43888. Treatment of the mixture of geometrically isomeric acids, obtained by hydrolysis of these esters, with acetyl chloride yields the cis-*anhydride* of 2 : 3-*dimethyl*cyclo*butane*-1 : 4-*dicarboxylic acid*, m. p. 50—51° (corresponding *acid*, m. p. 87—88°), and trans-2 : 3-

dimethylcyclobutane-1 : 4-*dicarboxylic acid*, m. p. 200—201·5°. No anhydride of the *trans*-acid could be obtained; distillation of the mixed acids yields a mixture of the *cis*-acid and the *cis*-anhydride, whilst treatment of the *trans*-acid with acetic anhydride leads to formation of the *cis*-anhydride.

G. A. C. Gough.

Reaction between formaldehyde and sodium hydroxide : formation of reducing substances resembling sugars. R. Mestre (Bull. Assoc. Chim. Sucr., 1927, **44**, 315—317).—A 40% solution of formaldehyde reacts vigorously with sodium hydroxide solution of *d* 1·5. The products formed include sugars, aldehydes, and formates. By treatment of the cooled reaction liquid with sulphur dioxide crystalline substances may be obtained resembling compounds of aldehydes with hyposulphites.

J. H. Lane.

Biochemistry of the sugars. R. Robinson (Nature, 1927, **120**, 44).—The hydrolysis of phosphoric esters is considered to be in accordance with the scheme $R{-}|{-}O(PO)(OH)_2$; hence if the oxygen atom is directly attached to an asymmetric carbon atom, optical inversion should be observed. Thus it appears that the galactose configuration results from the hydrolysis of a glucosephosphoric acid, which may occur as such or as part of a larger molecule; the hypothesis would be excluded if dextrose contained a butylene oxide ring. Levene's pentosephosphoric acid obtained from vegetable nucleoproteins, and yielding *d*-ribose on hydrolysis, is considered to be *d*-xylosephosphoric acid.

A. A. Eldridge.

Nomenclature of glucides. G. Bertrand (Bull. Soc. Chim. biol., 1927, **9**, 854—856).—The terms oses, osides, homosides, and heterosides are proposed in place of glucoses, glucosides, homoglucosides, and heteroglucosides, suggested by the International Commission for nomenclature in biological chemistry.

W. O. Kermack.

Rotatory dispersion of the penta-acetates of α- and β-glucose and of α- and β-mannose. P. A. Levene and I. Bencowitz (J. Biol. Chem., 1927, **74**, 153—174).—The optical rotations of the penta-acetates of α- and β-glucose and of β-mannose have been determined for ten different wave-lengths; the course of the rotatory dispersion was of the same simple type as that already observed (this vol., 649) for α-mannose penta-acetate. In the case of these derivatives, therefore, determination of the molecular rotation for light of any given wave-length gives as useful information as determination of the dispersion constants.

C. R. Harington.

Companions of cellulose. I. Vegetable cell-membranes. Carbohydrates of ivory-nut seeds. K. Hess and M. Ludtke (Annalen, 1927, **456**, 201—224; cf. Reiss, A., 1889, ii, 687).—Ground ivory-nut seeds (cellulose content 5·5%), after extraction with aqueous acetone, followed by treatment with 0·3% chlorine dioxide and 2% sodium sulphite, contain 7·8% of cellulose. Acetylation of this cellulose yields an acetate, $[\alpha]_D^{21}$ in chloroform −19·3°, and a cellobiose octa-acetate, m. p. 221°, $[\alpha]_D^{18}$ +41·42°. Extraction of the ground seeds with 5% sodium hydroxide solution dissolves mannan-*A* (cf. Baker and Pope, Proc. C.S., 1900, **16**, 72). *Mannan*-B is undissolved, and is purified by successive treatment with ammoniacal copper hydroxide and sodium hydroxide solutions; it is a hygroscopic powder which on acetylation yields an acetate, $[\alpha]_D$ −25·2° in chloroform. Hydrolysis of mannan-*B* with sulphuric acid gives mannose (85—90% yield), identified as the *p*-bromophenylhydrazone. Mannan-*A*, $[\alpha]^{20}$ −44·94° in *N*-sodium hydroxide solution, on acetylation yields an acetate, $[\alpha]_D^{21}$ −29·41°, and on hydrolysis with sulphuric acid gives an 88—91% yield of mannose. Tables giving the rotatory powers of solutions of the cellulose, mannan-*A*, and mannan-*B*, in varying concentrations of ammoniacal copper hydroxide solutions, are given.

Determination of mannose by the hypoiodite method gives varying results, but the method described is satisfactory.

H. Burton.

Synthesis of lactose. A. Pictet and H. Vogel (Compt. rend., 1927, **185**, 332—334).—Lactose has been synthesised by heating, for 30 min., equal weights of β-glucose and β-galactose with a small amount of zinc chloride at 145—150°/15 mm., acetylation of the product, and subsequent hydrolysis of the acetate with sodium methoxide.

E. A. Lunt.

Synthesis of glucosides. I. Synthesis of indican. A. Robertson (J.C.S., 1927, 1937—1943; cf. Perkin, Bloxam, and Thomas, *ibid.*, 1909, **95**, 824; Macbeth and Pryde, *ibid.*, 1922, **121**, 1660).—3-β-Glucosidoxyindole has now been synthesised and is found to be identical with natural indican. *Methyl* 3-*hydroxyindole*-2-*carboxylate*, m. p. 157—158° (prepared by a modification of the method described in G.P. 105495), yields, on treatment with sodium acetate and acetic anhydride, *methyl* 3-*acetoxyindole*-2-*carboxylate*, m. p. 145°, which cannot be further acetylated. The last-named compound reacts with tetra-acetylglucosidyl bromide in aqueous potassium hydroxide to give *methyl* 3-*tetra-acetyl*-β-*glucosidoxyindole*-2-*carboxylate*, m. p. 229—230°, which in turn yields 3-β-*glucosidoxyindole*-2-*carboxylamide*, decomp. 254—256°, on treatment with methyl-alcoholic ammonia at 0° for 14 hrs. Impure *methyl* 3-β-*glucosidoxyindole*-2-*carboxylate* is also formed in the last reaction. Methyl 3-tetra-acetyl-β-glucosidoxyindole-2-carboxylate on treatment with methyl-alcoholic potassium hydroxide at the ordinary temperature yields 3-β-*glucosidoxyindole*-2-*carboxylic acid*, m. p. 215—220°, which decomposes in aqueous solution with the formation of indigotin, and, in the form of the *potassium* salt, yields 1-*acetyl*-3-O-*tetra-acetylglucosidoxyindole* (penta-acetylindican), m. p. 148°, on treatment with sodium acetate and acetic anhydride. The same substance is obtained by the hydrolysis, accompanied by loss of carbon dioxide, of methyl 3-β-glucosidoxyindole-2-carboxylate with barium hydroxide, and is converted in 3-β-*glucosidoxyindole* (indican), m. p. 57—58° when containing 3 mols. of water, and 176—178° when anhydrous. The glucoside is hydrolysed by warm 3% hydrochloric acid with the liberation of dextrose and indoxyl, which in the presence of acids gives "indoxyl brown." The liberated indoxyl may be converted into indigotin by oxidising agents, in

indirubin by isatin, or into *p*-nitrobenzaldehyde-indogenide, m. p. 273—274°, by *p*-nitrobenzaldehyde. G. A. C. GOUGH.

Action of ethylene on pure starch. H. E. REA and R. D. MULLINIX (J. Amer. Chem. Soc., 1927, **49**, 2116—2117).—Dry starch is slowly converted into reducing sugar when kept in an atmosphere of ethylene at 21°, becoming at the same time pale yellow. The same change occurs much more rapidly when the starch is present in aqueous emulsion, and is accelerated by prior boiling of the starch emulsion by an amount increasing with increase in duration of this prior boiling, but is in all cases preceded by an " incubation " period. No absorption of ethylene takes place. F. G. WILLSON.

Lignin. I. Lignin from corn [maize] cobs. M. PHILLIPS (J. Amer. Chem. Soc., 1927, **49**, 2037—2040).—Lignin was isolated from maize cobs by extracting 1 kg. of the latter with 4 litres of alcoholic 2% sodium hydroxide solution, with subsequent neutralisation, concentration, and acidification of the extract. It appears to be either a homogeneous substance or a mixture of closely related isomerides, to which the formula $C_{17}H_{33}O_6(OH)_4(OMe)_3$ is ascribed. It does not yield furfuraldehyde on distillation with 12% hydrochloric acid. A *chloro*-derivative, $C_{40}H_{36}O_{16}Cl_{10}$, was prepared. The results obtained are in accordance with those of Beckmann, Liesche, and Lehmann (A., 1921, i, 546) and of Powell and Whittaker (A., 1924, i, 375; 1925, i, 372). F. G. WILLSON.

Erlenmeyer's amino-acid synthesis. C. R. HARINGTON and W. MCCARTNEY (Biochem. J., 1927, **21**, 852—856).—By using red phosphorus and a mixture of equal parts of hydriodic acid and acetic anhydride in the reduction in Erlenmeyer's synthesis of α-amino-acids much more satisfactory yields can be obtained, and a saving of time is also effected. This modification was applied to a number of syntheses with the following results. β-[3 : 5-Di-iodo-4-(4'-hydroxyphenoxy)phenyl]-α-aminopropionic acid, yield 82%; tyrosine, 60%, phenylalanine, 88%, 3 : 4-dihydroxyphenylalanine, 50%, and deiodothyroxine, 61%. S. S. ZILVA.

Precipitability of diamino-acids by mercuric acetate and sodium hydroxide. G. NAGELSCHMIDT (Biochem. Z., 1927, **186**, 322—326).—*d*-Arginine, *d*-lysine, and *l*-histidine are precipitated with the mercuric acetate–sodium hydroxide reagent of Neuberg and Kerb (A., 1912, i, 540; 1915, ii, 292), addition of alcohol rendering precipitation almost complete. The loss, reckoned as percentage of total nitrogen, is, for histidine, 0·6%, for arginine, 1·2%, and for lysine, 0·8%. P. W. CLUTTERBUCK.

Reducing power of glutathione and cysteine. I. N and H. E. TUNNICLIFFE (Biochem. J., 1927, —851).—Kendall and Nord's view (A., 1926 1129) that in the mechanism of reduction by hol groups an active additive compound of the iol group with oxygen is formed which is capable o reducing indigo-carmine and that this activation is also obtained by the addition of hydrogen peroxide or of sodium disulphide, is not upheld. In spite of ng extreme precautions of excluding all traces of xygen, cysteine or glutathione reduced indigo-carmine. In the presence of fairly large amounts of oxygen there is an acceleration in the rate of reduction of indigo-carmine, but this is most probably due to the formation of hydrogen peroxide, which acts on the indigo-carmine with the production of substances capable of catalysing the reduction. Sodium disulphide reduces indigo-carmine also in the absence of cysteine. Kendall and Nord's experiments with this reagent cannot therefore be considered significant. The technique of their reduction–potential measurements is also criticised and it is held that the conclusion that the ·SH–·S·S· system is reversible is not justified. S. S. ZILVA.

Constitution of thiocarbamide and of thiouronium salts. H. LECHER and W. SIEFKEN (Annalen, 1927, **456**, 192—200).—The formulation of thiocarbamide as a heteropolar ion, +

(cf. A., 1924, i, 1051; 1925, i, 1390, 1392), implies that the amidinium group, which is strongly basic in *S*-methyl-ψ-thiocarbamide, is almost neutralised by the acidity of the thiol radical. If the basicity of the amino-groups is destroyed by acylation the product should be a strong acid. Actually *NN'*-diacetylthiocarbamide (cf. Kohmann, A., 1915, i, 944; Hugershoff, A., 1926, 156) is neutral. Its constitution has been established by its desulphurisation to *NN'*-diacetylcarbamide by freshly-precipitated mercuric oxide in warm acetone. Thiocarbamide is therefore correctly represented by the classical formula. Cryoscopic measurements show that it is unimolecular in aqueous solution, which appears to disprove Hugershoff's bimolecular salt-formula. The constitution of his triacetyl derivative, conveniently prepared by Dimroth and Bamberger's method (Annalen, 1924, **438**, 67), is discussed. H. E. F. NOTTON.

Pentenonitriles. A. CASTILLE and J. GUEURDEN (Ann. Soc. scient. Bruxelles, 1927, **47**, *B*, [i], 56—63; cf. this vol., 652).—Δ^{α}-Pentenonitrile (Henry, A., 1899, i, 568) is separated by repeated fractionation into geometrical isomerides, (*a*), b. p. 127·0—127·2°/769 mm., d_4^{20} 0·8191, n_D^{20} 1·4238, and (*b*), b. p. 144·2—144·4°/769 mm., d_4^{20} 0·8218, n_D^{20} 1·4264. These are isomerised when boiled with sodium phenoxide. They differ from one another in physical properties, and particularly in their ultra-violet absorption spectra in hexane, aqueous alcohol, and 0·02*N*-sodium hydroxide, in the same way as do the isomerides of α-unsaturated nitriles previously examined (A., 1922, i, 817). H. E. F. NOTTON.

Constitution of Grignard's organo-magnesium derivatives. D. IVANOV (Compt. rend., 1927, **185**, 505—507).—In an attempt to differentiate between the formulæ RMgHal and $R_2Mg,MgHal_2$ (Jolibois, A., 1912, i, 753) for organo-magnesium compounds, the author has studied the action of carbon dioxide on magnesium ethyl bromide. The carbonated product is extracted with absolute ether at temperatures from —18° to 28° during 65—240 hrs., the ethereal extract and the residue are hydrolysed with dilute nitric acid, and the bromine and magnesium determined in each part. The results indicate that Jolibois' formula is correct, since magnesium

bromide passes into the ethereal extract apparently from the complex $(R\cdot CO_2)_2Mg,MgBr_2$, whilst the major part of the propionic acid is found in the residue. H. BURTON.

[Constitution of Grignard's organo-magnesium derivatives.] V. GRIGNARD (Compt. rend., 1927, **185**, 507—509).—A criticism of Ivanov's paper (preceding abstract). It is pointed out that at 0° and 28° approximately the same quantity of magnesium bromide was extracted in each case, whilst the solubility of etherated magnesium bromide in ether varies greatly at these temperatures (cf. Menschutkin, A., 1906, i, 131, 552). It is possible that a reversible change $2R\cdot CO_2\cdot MgBr \rightleftharpoons (R\cdot CO_2)_2Mg,MgBr_2$ is taking place, although this last complex should possess great stability. H. BURTON.

Methylmercuric halides and hydroxide. L. E. HINKEL and T. H. ANGEL (J.C.S., 1927, 1948—1950).—An attempt to repeat Marvel and Gould's preparation of methylmercuric chloride by the action of magnesium methyl iodide on an excess of mercuric chloride (A., 1922, i, 329) gave the double *compound*, HgMeCl,2HgMeI, m. p. 129°, which differs from methylmercuric chloride, formed to a small extent in the reaction, in having a more intense odour. The reaction probably proceeds in the following stages: (i) $MgMeI+HgCl_2=HgMeI+MgCl_2$; (ii) $HgMeI+HgCl_2=2HgMeCl+HgI_2$; (iii) $MgMeI+HgI_2=HgMeI+MgI_2$. The last reaction is employed to prepare methylmercuric iodide, m. p. 145°, which yields, on treatment with aqueous methyl alcohol and silver oxide, methylmercuric hydroxide, m. p. 106°, which decomposes and detonates when heated above its m. p. Methylmercuric hydroxide is best purified by crystallisation from chlorobenzene containing alcohol, when it possesses properties differing somewhat from those already described (A., 1923, i, 194). G. A. C. GOUGH.

Mechanism of the Wurtz-Fittig reaction. W. E. BACHMANN and H. T. CLARKE (J. Amer. Chem. Soc., 1927, **49**, 2089—2098).—The action of sodium on boiling chlorobenzene affords benzene, diphenyl, *o-diphenylbenzene*, m. p. 57°, b. p. 332° (cf. Weiler, A., 1896, i, 242), triphenylene (cf. Schultz, A., 1875, 148), and 2 : 2′-*diphenyldiphenyl*, m. p. 118°, b. p. 420°, together with a trace of *p*-diphenylbenzene, and resinous tars. *o*-Diphenylbenzene was synthesised by heating 2-iododiphenyl with iodobenzene and copper powder at 240°, whilst 2 : 2′-diphenyldiphenyl was obtained by heating 2-iododiphenyl with copper powder at 260°. In presence of excess of toluene, sodium and chlorobenzene yield benzene (nearly 50%), diphenylmethane, and 4-methyldiphenyl, but no diphenyl, whilst an analogous reaction, with formation of nitrogenous products, takes place in presence of dimethylaniline. Treatment of mercury di-*p*-tolyl in benzene with metallic sodium in the cold, with subsequent treatment with carbon dioxide, affords benzoic and phenylacetic acids, in addition to *p*-toluic acid, indicating partial migration of the sodium to the benzene and to the side-chain of the toluene. It is suggested that whilst the formation of diphenyl and diphenylbenzene from sodium and chlorobenzene is due to the action of intermediately formed sodium phenyl and sodium diphenyl on the chlorobenzene, there is also produced free phenyl, which then yields benzene and free phenylene. The latter then yields triphenylene by condensation with itself, and diphenylbenzene and diphenyldiphenyl by condensation with more phenyl. The action of sodium on *n*-heptyl bromide affords *n*-heptane, heptylene, tetradecane, and a *heneicosane*, b. p. 340—345°, together with hydrocarbons of high mol. wt. Pentadecane is a by-product in the preparation of *iso*decane from sodium and *iso*amyl bromide. F. G. WILLSON.

Preparation and hydrolysis of the isomeric *p*-tolylethyl bromides. J. B. SHOESMITH and R. J. CONNOR (J.C.S., 1927, 1768—1772; cf. A., 1925, i, 16).—The influence of the methyl group on the reactivity of the halogen atom in the isomeric *p*-tolylethyl bromides is measured by their rates of hydrolysis in aqueous-alcoholic sodium hydroxide at 76°, which are in the descending order, phenylethyl bromide, *m*-, *p*-, and *o*-tolylethyl bromide. In contrast to ω-bromo-*m*- and ω-bromo-*p*-xylene, the isomeric *p*-tolylethyl bromides are stable towards hydrogen iodide in aqueous acetic acid at 100°; they are also stable towards aqueous alcohol at 76°. From these results it is concluded that the transference of general and alternating effects through the α-carbon atom of the side-chain is very weak (cf. Ing and Robinson, A., 1926, 946; Goss, Hanhart, and Ingold, this vol., 236). The tolylethyl alcohols were prepared in improved yields (20—40%) by a modification of Grignard's method (A., 1905, i, 593). The alcohols had b. p.: *o*-, 115—116°/13 mm.; *m*-, 115—117°/13 mm.; *p*-, 116·5—118°/14 mm. Hydrogen bromide is without action on these alcohols; the action of phosphorus pentabromide on benzene solutions of the alcohols, however, yields the corresponding bromides, which have b. p.: *o*-, 99—100°/10 mm.; *m*-, 101—103°/11 mm.; *p*-, 103·5—105°/11 mm. G. A. C. GOUGH.

2-Iodofluorene. P. CHANUSSOT (Anal. Asoc. Quím. Argentina, 1927, **15**, 5—9).—2-*Iodofluorene*, m. p. 126—127°, is obtained by the action of concentrated potassium iodide solution on 2-diazofluorene. Oxidation with sodium dichromate in acetic acid solution yields 2-*iodofluorenone*, m. p. 143—144° (*hydrazone*, m. p. 147—148°; *oxime*, m. p. 180—181°). Nitration of 2-iodofluorene yields (?)2-iodo-7-nitrofluorene, m. p. 235°. G. W. ROBINSON.

Reaction between ethylene oxide and methyl- and ethyl-anilines. G. GABEL (Bull. Soc. chim., 1927, [iv], **41**, 936—940; cf. A., 1925, i, 535).—Ethylene oxide reacts with methyl- and ethyl-anilines in sealed tubes at 100°, giving 15 and 22% yields of β-phenylmethyl- and β-phenylethyl-aminoethyl alcohols, respectively (cf. Laun, A., 1884, 1011). The presence of water has no effect on the reaction. H. BURTON.

Nitro-derivatives of *s*-diphenyldimethyl- and *s*-diphenyldiethyl-carbamides (Centralites). A. APARD (Mém. Poudres, 1926, **22**, 180—190).—Diphenyldimethylcarbamide is nitrated by nitric acid or by nitric–sulphuric acids yielding *di*-p-*nitrophenyldimethylcarbamide*, m. p. 156—157°, which is hydrolysed by sulphuric acid to *p*-nitromethylaniline. *Di-*

2 : 4-*dinitrophenyldimethylcarbamide*, m. p. 192°, and a *hexanitro*-derivative, m. p. above 300°, of the carbamide are described. Hydrolysis of the hexanitro-derivative furnishes a *trinitromethylaniline*, m. p. 180°, not identical with 2 : 4 : 6-trinitromethylaniline. By similar reactions there were obtained from diphenyldiethylcarbamide, *di*-p-*nitrophenyldiethylcarbamide*, m. p. 147°, and *di*-2 : 4-*dinitrophenyldiethylcarbamide*, m. p. 178°. Nitrous fumes convert diphenyldiethylcarbamide into a *dinitro*-derivative, m. p. 144°.

H. BURTON.

Nitration of β-naphthyltrimethylammonium nitrate. B. H. INGHAM (J.C.S., 1927, 1972—1975).—β-Naphthyltrimethylammonium iodide yields a corresponding *picrate*, m. p. 194—195° (decomp.), and *nitrate*, m. p. 190° (decomp.). Nitration of the nitrate with 99% nitric acid gives in almost theoretical yield the single product 5-*nitro*-β-*naphthyltrimethylammonium nitrate*, m. p. 213° (decomp.). The *iodide*, m. p. 194° (decomp.), and *picrate*, m. p. 254° (decomp.), are alternatively obtained by methylation of 5-nitro-β-naphthylamine. This result gives strong support to the theory that the influence of *meta*-directive groups depends on an inhibition of the substitution process, the inhibition applying less to the *meta*- than to the *ortho*- and *para*-positions. M. CLARK.

Amino-oxidation. XI. Oxidation of primary amines; tetrafluorenylhydrazine. S. GOLDSCHMIDT and L. REICHEL (Annalen, 1927, **456**, 152—168).—The yellow product, m. p. 243° (decomp.), obtained together with fluorenone and $\Delta^{9:9'}$-difluorenylene by the atmospheric oxidation of 9-aminofluorene in solar or ultra-violet light (cf. A., 1926, 607), is formed with loss of ammonia when oxygen is passed over the base at 75—80° in the dark. This cannot be fluorenylene-9-aminofluorene, since fluorenone and 9-aminofluorene do not react under these conditions. Further, substances of this type, such as *diphenylmethylenebenzhydrylamine*, $CPh_2{:}N{\cdot}CHPh_2$, m. p. 150° (*picrate*, m. p. 205°), prepared for comparison by passing oxygen into benzhydrylamine at 120°, are colourless and unimolecular in solution. The "anil" is reduced by aluminium amalgam to *s*-tetraphenyldimethylamine. The oxidation product must therefore be *tetrafluorenylhydrazine* and its coloured solutions contain the radical $(C_{13}H_9)_2N{\cdot}$. The solid hydrazine is stable but its solutions decompose rapidly. With bromine it gives reddish-brown 9 : 9′ : N-*tribromo*-9 : 9′-*difluorenylamine*, and with nitrogen dioxide, 9 : 9′ : N-*trinitrodifluorenylamine*, m. p. 205° (decomp.), both of which are readily oxidised to fluorenone. It is decomposed in presence of triphenylmethyl or nitric oxide, with acetic acid it gives fluorenone and acetamidofluorene, and with sulphuric acid, fluorenone and ammonia. Difluorenylnitrogen is unexpectedly stable towards quinol and hydrazobenzene, it is reduced by phenylhydrazine, whilst zinc dust and ammonia give difluorenylamine, m. p. 198° (cf. Curtius and Kof, A., 1912, i, 733). The formation of derivatives of a secondary amine during the oxidation of a compound, $R.CH{\cdot}NH_2$, probably takes place through an intermediate free radical, $R{:}CH{\cdot}NH{\cdot}$. This may be oxidised to an imine, $R{:}C{:}NH$ (A., 1926, 607), or 2 mols. may unite giving ammonia and $(R{:}CH)_2N{\cdot}$, which may either polymerise to the hydrazine $[(R{:}CH)_2N]_2$, or be oxidised to the Schiff's base, $R{:}C{:}N{\cdot}CH{:}R$. A similar mechanism accounts for the formation of secondary amines during the reduction of oximes, nitriles, and acid amides (cf. Rupe and Glenz, A., 1923, i, 100; Kindler, *ibid.*, 568). H. E. F. NOTTON.

***s*-Diarylguanidines.** CHEM. FABR. AUF ACTIEN (VORM. E. SCHERING).—See B., 1927, 669.

Cold oxidation (decolorisation) of colouring matters by sodium hypochlorite in acid solution. II. Oxidation of azo-dyes. A. SEYEWETZ and E. CHAISE.—See B., 1927, 696.

Aromatic sulphonyl fluorides. W. STEINKOPF [with K. BUCHHEIM, K. BEYTHIEN, H. DUDEK, J. EISOLD, J. GALL, P. JAEGER, H. REUMUTH, A. SEMENOFF, and A. WEMME] (J. pr. Chem., 1927, [ii], **117**, 1—82).—Aromatic sulphonyl fluorides have been prepared for the first time, by the action of fluorosulphonic acid on aromatic compounds, sulphones and sulphonic acids being formed as by-products. The best yields are obtained at about 25°; at lower temperatures the yield of sulphone is increased, whilst at 80—120° disulphonyl fluorides are formed, except from benzene itself. The products are, however, more homogeneous than those from sulphonation by sulphuric acid at high temperatures. A second method of preparation consists in the action of fluorosulphonic acid on the sodium salt of a sulphonic acid; a sulphonate with a reactive hydrogen atom may, however, be converted into the monofluoride of a disulphonic acid. Thirdly, sulphonyl chlorides can be converted by fluorosulphonic acid into the sulphonyl fluorides; the reaction is reversible. Aromatic sulphonyl fluorides have no unpleasant odour; many may be distilled unchanged at atmospheric pressure, and they are remarkably stable towards water. They may be boiled with water without reacting, and may be purified by steam distillation; concentrated acids have only a slow action and dilute acids practically none. Nitroarylsulphonyl fluorides may be reduced to the corresponding amino-derivatives, which may then be diazotised etc. without loss of the $-SO_2F$ group. The sulphonyl fluorides react readily with aliphatic primary and secondary but not with aromatic amines. As gaseous ammonia has no action on substances containing the $-SO_2F$ group in ethereal solution, it is possible to prepare water-soluble ammonium salts containing this group. The latter is, however, attacked by aqueous ammonia to give the sulphonamide, which can be better prepared, free from the ammonium sulphonate, by the action of liquid ammonia under pressure; occasionally this yields the disulphonimide.

Anhydrous aluminium chloride (but not ferric chloride) converts sulphonyl fluorides into the corresponding sulphonyl chlorides. Similarly chlorosulphonic acid acts on the fluorides, but the reaction is reversible; also when a reactive hydrogen atom is present, a chlorosulphonylarylsulphonyl fluoride is formed. This enables fluorosulphonylarylsulphonamides to be obtained; a corresponding chlorosulphonylarylsulphonamide has also been prepared. Unlike sulphonyl chlorides, the fluorides do not catalyse the Beckmann inversion.

Some soluble derivatives containing a $-SO_2F$ group stable towards water, *e.g.*, *ammonium* p-*fluorosulphonylbenzoate*, have a fairly high bactericidal action, against even very resistant bacteria (*e.g.*, *B. subtilis*), and especially against lactic acid bacteria. o-*Aminophenol*-4-*sulphonyl fluoride hydrochloride* and *ammonium* m-*fluorosulphonylbenzoate* approach Quinosol in bactericidal action.

Benzenesulphonyl fluoride, b. p. 203—204°, 90—91°/14 mm., n_D^{18} 1·49316, d_4^{20} 1·3286, is obtained by action of fluorosulphonic acid on benzene (62% yield) or on benzenesulphonyl chloride, into which the fluoride is reconverted by the action of aluminium chloride. With alcohol and alkali, the fluoride gives ethyl benzenesulphonate, with ammonia, benzenesulphonamide, with phenylhydrazine, benzenesulphophenylhydrazide, new m. p. 154—155° (cf. Fischer, A., 1878, 309); there is no reaction with an aqueous solution of carbamide, nor with alcoholic benzylamine until heat is applied. The fluoride is hydrolysed slowly by sodium carbonate or hydroxide in the cold, rapidly on heating. It is nitrated by fuming nitric acid and sulphuric acid to m-*nitrobenzenesulphonyl fluoride*, m. p. 48°. Attempts to prepare *o*- and *p*-sulphonyl fluorides of nitrobenzene by the action of fluorosulphonic acid were unsuccessful. *m*-Aminobenzenesulphonyl fluoride has m. p. 29—30°, b. p. 297—299° (decomp.) (*hydrochloride*, m. p. 165—167°). The double *salt* of the hydrochloride with stannic chloride is diazotised to m-*fluorosulphonylbenzenediazonium chlorostannate*, $[C_6H_4(SO_2F)\cdot N_2Cl]_2SnCl_4$, m. p. 155—156° (decomp.). The amine hydrochloride gives, by the usual means, *diazoaminobenzene*-3 : 3′-*disulphonyl fluoride*, m. p. 175—176° (decomp.). The amine sulphate when diazotised yields on treatment with potassium iodide, m-*iodobenzenesulphonyl fluoride*, b. p. 137°/13—14 mm., converted by chlorine into m-*fluorosulphonylphenyl iodide dichloride*, m. p. 98—99°, and on treatment with potassium cyanide and copper sulphate, m-*cyanobenzenesulphonyl fluoride*, m. p. 69—70°, in 30—40% yield. Benzene-*m*-disulphonyl chloride with fluorosulphonic acid yields *benzene*-m-*disulphonyl fluoride*, m. p. 38—39°.

Toluene yields a mixture, b. p. 97—100·8°/11·5 mm., of o- (not isolated) with p-*toluenesulphonyl fluoride*, m. p. 43—44°, b. p. 112·5°/16 mm. to 169·5°/132 mm. The proportion of the *o*-compound is estimated by the method of Hefelmann (Pharm. Zentr., 1894, **35**, 105) at 40% : this proportion is unaffected by change of temperature from 20° to 30°, or by addition of catalysts. *p*-Toluenesulphonyl fluoride may also be prepared from the corresponding chloride (new m. p. 71°), into which it is reconverted by chlorosulphonic acid or aluminium chloride; with dimethylamine it gives p-*toluenesulphondimethylamide*, m. p. 86—87°. It is nitrated to o-*nitrotoluene*-4-*sulphonyl fluoride*, m. p. 48—49°, which is reduced to the 2-*amino*-compound, m. p. 96—97° (*acetyl* derivative, m. p. 188·5—189·5°). The diazotised amine yields 1-p-*fluorosulphonyltoluene*-o-*azo*-β-*naphthol*, m. p. 217°, and by the action of copper regenerates *p*-toluenesulphonyl fluoride. Oxidation of this gives p-*fluorosulphonylbenzoic acid*, m. p. 270°, easily soluble in warm water (*ammonium* salt). Attempts to cause benzoic acid to react with fluorosulphonic acid failed.

p-Fluorosulphonylbenzoic acid is converted by thionyl chloride into p-*fluorosulphonylbenzoyl chloride*, m. p. 53—53·5° (*ethyl* ester, m. p. 49—49·5°; p-*fluorosulphonylbenzamide*, m. p. 187—187·5°). p-*Nitrotoluene*-2-*sulphonyl fluoride*, m. p. 57—58°, from nitration of mixed *o*- and *p*-toluenesulphonyl fluorides, is reduced to p-*toluidine*-2-*sulphonyl fluoride*, m. p. 62° (*acetyl* derivative, m. p. 120—121°), from which pure o-*toluenesulphonyl fluoride*, b. p. 133·9°/56·5 mm., 146·2°/83 mm., was obtained. *p*-Toluenesulphonyl fluoride when heated with fluorosulphonic acid at 130—140° yields *toluene*-2 : 4-*disulphonyl fluoride*, m. p. 87—88°.

m-Chlorosulphonylbenzoic acid (Smiles and Stewart, J.C.S., 1921, **119**, 1792) is converted by fluorosulphonic acid into m-*fluorosulphonylbenzoic acid*, m. p. 154—155° (*ammonium* salt, m. p. 130—132°), of which the acid *chloride*, b. p. 108—110°, and the *anhydride*, m. p. 120—122°, are described. m-*Fluorosulphonylbenzamide*, m. p. 109—110°, is converted by alcoholic methylamine into m-N-*methylamidosulphonylbenzamide*, m. p. 145—147°; *ethyl* m-*fluorosulphonylbenzoate*, m. p. 126·5—128·5°/vac., similarly gives *ethyl* m-N-*methylamidosulphonylbenzoate*, b. p. 192—194°/vac., and the n-*propyl* ester, b. p. 118—120°/vac., with benzylamine gives n-*propyl* m-*benzylamidosulphonylbenzoate*, m. p. 60—61°. m-*Fluorosulphonylbenzanilide*, prepared from *m*-fluorosulphonylbenzoyl chloride, has m. p. 157—158°.

p-Xylene yields p-*xylene*-2-*sulphonyl fluoride*, m. p. 24·5°, b. p. 124—125°/21 mm., converted by chlorosulphonic acid into a mixture of the mono- and disulphonyl chlorides. This fluoride is nitrated to 2-*nitro*-p-*xylene*-6-*sulphonyl fluoride*, m. p. 74—74·5°. *m*-Xylene yields m-*xylene*-4-*sulphonyl fluoride*, b. p. 239—240°, 149—150°/14 mm., which gives 4-*nitro*-m-*xylene*-6-*sulphonyl fluoride*, m. p. 109—110°, and the corresponding 4-*amino*-compound, m. p. 55—56° (*hydrochloride*, m. p. 191—196°), and, with excess of fluorosulphonic acid at 100°, m-*xylene*-2 : 4-*disulphonyl fluoride*, m. p. 116—117°.

Mesitylene yields a *sulphonyl fluoride*, m. p. 73—73·5°, b. p. 125°/12 mm., which gives *nitromesitylenesulphonyl fluoride*, m. p. 58—59°, and, with chlorosulphonic acid, *mesitylenedisulphonyl chloride*, m. p. 121·5—122·5° (*disulphonamide*, m. p. 240—241°). ψ-Cumene yields a *sulphonyl fluoride*, b. p. 123—126°/12 mm., 137—139°/20 mm.; conversion into the sulphonamide shows that this is at least mainly ψ-cumene-5-sulphonyl fluoride. This gives *nitro*-ψ-*cumenesulphonyl fluoride*, b. p. 163—166°/14 mm. It is possible to separate almost quantitatively the sulphonyl fluoride of mesitylene from that of ψ-cumene by freezing out from the fluorosulphonation product of the mixed hydrocarbons.

1 : 3-*Dimethyl*-5-tert.-*butylbenzene*-?-*sulphonyl fluoride*, m. p. 115—116°, which has a slight petroleum-like odour, gives a *dinitro*-derivative, m. p. 127—128°, which has the odour, at great dilution, of "artificial musk" (trinitro-*tert.*-butyltoluene), showing that replacement of one nitro-group by the $-SO_2F$ group does not affect the odour. On the other hand, ?-*dinitro*-1 : 3-*dimethyl*-5-tert.-*butylbenzene*-?-*sulphonyl chloride*, obtained by the action of aluminium chloride, has the characteristic unpleasant sulphonyl chloride odour.

Naphthalene yields an α-*sulphonyl fluoride*, m. p. 56°, also obtained from sodium α-naphthalenesulphonate; the β-sulphonate similarly gives the β-*sulphonyl fluoride*, m. p. 87—88°. Naphthalene at 70—80° gives a mixture of *naphthalene-?-disulphonyl fluoride*, m. p. 125°, which is converted by aluminium chloride into a new *naphthalene-?-disulphonyl chloride*, m. p. 118°, and *naphthalene*-1 : 5-*disulphonyl fluoride*, m. p. 203°, converted by liquid ammonia into *naphthalene*-1 : 5-*disulphonamide*, m. p. above 340°, by aluminium chloride into the chloride, and by chlorosulphonic acid into naphthalene-1 : 3 : 5-trisulphonyl chloride. The α-sulphonyl and 1 : 5-disulphonyl fluorides are extremely stable towards water or 0·5*N*-sulphuric acid. The α-sulphonyl fluoride on treatment with chlorosulphonic acid yields α-*chlorosulphonylnaphthalene*-5-*sulphonyl fluoride*, m. p. 174°, converted by liquid ammonia into the above disulphonamide, and by ammonia in ether into α-*amidosulphonylnaphthalene*-5-*sulphonyl fluoride*, m. p. 252—253°. Similarly β-naphthalenesulphonyl fluoride with chlorosulphonic acid gives 2-*chlorosulphonylnaphthalene*-6-*sulphonyl fluoride*, m. p. 114—116°, whence 2-*amidosulphonylnaphthalene*-6-*sulphonyl fluoride*, m. p. 208°, is obtained, or, by the prolonged action of liquid ammonia, naphthalene-2 : 6-disulphonamide, m. p. 303—305° (cf. Ebert and Merz, A., 1876, ii, 409).

Tetrahydronaphthalene gives mainly, with probably some of the β-compound, *tetrahydronaphthalene*-α-*sulphonyl fluoride*, m. p. 75—77°, which has an odour resembling candied lemon, and which is nitrated to ?-*nitrotetrahydronaphthalene*-α-*sulphonyl fluoride*, m. p. 108—109°, converted by aluminium chloride into a *compound* of one mol. of itself with one of the corresponding chloride, $C_{20}H_{20}O_8N_2FClS_2$, m. p. 87—88°, and by methylamine into ?-*nitrotetrahydronaphthalene*-α-*sulphonmethylamide*, m. p. 169—171°. Nitration of the liquid sulphonyl fluoride gives a small quantity of this substance, with other products. Nitrotetrahydronaphthalene-α-sulphonyl fluoride is reduced to the corresponding *amino*-derivative, m. p. 83—84° (*hydrochloride*, decomp. 226—227°), which by the Sandmeyer reaction yields the ?-*cyano*-derivative, m. p. 113—116° to a cloudy liquid, clearing at 120°.

Phenol gives *phenol*-p-*sulphonyl fluoride*, m. p. 77—78°, also obtainable from sodium phenol-*p*-sulphonate. *Ammonium* p-*fluorosulphonylphenoxide*, m. p. 200—203°, on keeping in aqueous solution deposits p-*phenylenesulphonylide*, m. p. 276—277° (cf. Anschutz, A., 1912, i, 852); the action of liquid ammonia, followed by neutralisation, on the other hand, gives *di*-p-*phenolsulphonimide*, m. p. 154—155°. *Phenol*-p-*sulphon-methylamide*, m. p. 81—82°, and *-dimethylamide*, m. p. 95—96°, are prepared in alcohol; by direct action of aniline, *aniline* p-*anilidosulphonylphenoxide*, m. p. 112—113°, is obtained, showing that the fluorine atom is less strongly bound than in sulphonyl fluorides of hydrocarbons. Phenol-*p*-sulphonyl fluoride and aluminium chloride give with benzene, p-*hydroxydiphenylsulphone*, m. p. 131°, and with phenol in the presence of carbon disulphide, *pp'*-dihydroxydiphenylsulphone. o-*Nitrophenol*-4-*sulphonyl fluoride*, m. p. 66·5—67°, obtained by nitration of phenol-*p*-sulphonyl fluoride, or by fluorosulphonation of o-nitrophenol, is reduced to the corresponding *amino*-compound, m. p. 131·5° (*hydrochloride*, m. p. 203—205°, decomp.), which may also be obtained from *o*-aminophenol and fluorosulphonic acid, and yields an N-*formyl* derivative, m. p. 241—242°. An attempt to eliminate water from this and obtain a benzoxazolesulphonyl fluoride was unsuccessful. Phenol-*p*-sulphonyl fluoride with excess of fluorosulphonic acid at 100° yields *phenol*-2 : 4-*disulphonyl fluoride*, m. p. 120—121° (the *ammonium phenoxide* derivative, m. p. 184—185°, decomp. 188°, is unchanged on recrystallisation from water). Nitration gives o-*nitrophenol*-4 : 6-*disulphonyl fluoride*, m. p. 98·5—99·5°, reduced to the o-*aminophenol* derivative, m. p. 119—120°; the action of aniline in ether yields *phenol*-2 : 4-*disulphanilide*, m. p. 203—204°. Phenol-*p*-sulphonyl fluoride with chlorosulphonic acid gives 2-*chlorosulphonylphenol*-4-*sulphonyl fluoride*, m. p. 75—76°, which with ammonia in ether yields the 2-*amidosulphonyl* derivative, m. p. 175—175·5°, with *p*-toluidine gives p-*fluorosulphonylphenol*-2-*sulphon*-p-*tolylamide*, m. p. 147—148°, and with liquid ammonia, *phenol*-2 : 4-*disulphonamide*, m. p. 239—240°.

p-Cresol gives a 3-*sulphonyl fluoride*, m. p. 58—59°, b. p. 135—136°/20 mm. (*ammonium* salt easily resinifying), giving p-*cresol*-3-*sulphonamide*, m. p. 151—152°. Nitration of the fluoride gives, with warm dilute nitric acid, 3 : 5-dinitro-*p*-cresol, and with cold nitrosulphuric acid, 6-*nitro*-p-*cresol*-3-*sulphonyl fluoride*, m. p. 87—88°, which on heating with dilute nitric acid is converted into the above dinitrocompound, and is reduced to the 6-*amino*-compound (*hydrochloride*). Potassium *p*-cresol-3-sulphonate and fluorosulphonic acid at 80—90° yield a *potassium* salt from which 3-*fluorosulphonyl*-p-*cresol*-5-*sulphonic acid*, m. p. 120—121° (+2·5H_2O), is obtained (*ammonium* salt, decomp. 265°). The potassium salt with excess of chlorosulphonic acid yields *p*-cresol-3 : 5-disulphonyl chloride (Pollak, A., 1926, 514). Potassium 3-bromo-*p*-cresol-5-sulphonate and fluorosulphonic acid at 75—80° give the corresponding *sulphonyl fluoride*, m. p. 75° (*ammonium* salt, m. p. 193—196°, recrystallisable unchanged from water). This gives when dissolved in acetone and heated with potassium acetate, 5-bromo-*o*-toluosulphonoquinone (Zincke and Kempf, A., 1911, i, 287); with diethylamine, 3-*bromo*-p-*cresol*-5-*sulphondiethylamide*, m. p. 162—163°, is obtained.

o-Cresol gives a small yield of a ?-*sulphonyl fluoride*, m. p. 56—57°, b. p. 168—170°/11 mm. (*ammonium* salt behaving in solution as does the *p*-compound), converted by dilute nitric acid into a *nitro*-derivative, m. p. 60—60·5°. m-*Cresol*-?-*sulphonyl fluoride*, m. p. 49—50·5°, b. p. 169—170°/11 mm., gives with liquid ammonia, *di*-m-*cresolsulphonimide*, m. p. 145—146°.

Sodium 2 : 6-di-iodophenoxide gives with fluorosulphonic acid at 70—75°, 2 : 6-*di-iodophenol*-4-*sulphonyl fluoride*, m. p. 132°, of which the *ammonium* salt, m. p. 208—210°, may be recrystallised from water. The stability of this and other ammonium derivatives is attributed to the presence of the halogen atoms.

Anisole-p-*sulphonyl fluoride*, m. p. 13°, b. p. 175°/60 mm., is slowly converted by liquid ammonia into anisole-*p*-sulphonamide, m. p. 116°, and is nitrated by nitrosulphuric acid to a 2-*nitro*-derivative, m. p.

78·5°, also obtained by methylation of *o*-nitrophenol-4-sulphonyl fluoride. The nitro-derivative is reduced to *o-anisidine*-p-*sulphonyl fluoride*, m. p. 66° (*hydrochloride*, m. p. 202°, after sintering and darkening at 180°). *Phenetole*-p-*sulphonyl fluoride*, m. p. 38°, b. p. 170—175°/25 mm., yields on treatment with nitrosulphuric acid an oil from which a *substance*, m. p. 73°, is obtained, not identical with *2-nitrophenetole*-p-*sulphonyl fluoride*, m. p. 73°, obtained by the action of ethyl iodide on *silver 4-fluorosulphonyl-o-nitrophenoxide*.

Sodium β-naphthol-6-sulphonate when treated with chlorosulphonic acid yields β-*naphthol*-3 : 6-*disulphonyl chloride*, m. p. 112—113°, which with aniline in ether gives β-*naphthol*-3-(or 6-)*sulphonyl chloride* 6(or 3)-*sulphanilide*, m. p. 138—139°; and with fluorosulphonic acid yields β-*naphthol*-3 : 6-*disulphonyl fluoride*, m. p. 108—109·5° (*ammonium* salt), also obtainable from β-naphthol (which gives no monosulphonyl fluoride), together with its β-*naphthol*-3(or 6)-*sulphonate*, $C_{10}H_6(OH)\cdot SO_2\cdot O\cdot C_{10}H_5(SO_2F)_2$, m. p. 265° (decomp.). β-*Naphthol*-3 : 6-*di*[*sulphondimethylamide*] has m. p. 159—160·5°.

A salt of β-naphthol-6 : 8-disulphonic acid (G-salt) yields β-*naphthol*-6 : 8-*disulphonyl fluoride*, m. p. 175—176°, slightly soluble in cold water, moderately soluble in hot; the *ammonium* salt is intensely yellow, becoming dark orange-coloured on heating, but colourless at 190—200°, with m. p. above 240°. R-salt similarly gives, in very small yields, β-*naphthol*-3 : 6 : 8-*trisulphonyl fluoride*, m. p., when anhydrous, 152·5—154° (*ammonium* salt described), which is also obtainable in small yield from β-naphthol-3 : 6-disulphonyl fluoride at 115—130°.

The above 6 : 8-di- and 3 : 6 : 8-tri-sulphonyl fluorides differ from the 3 : 6-disulphonyl fluorides in that they contain water of crystallisation. The analytical data from their ammonium salts show, however, that they do not, as might be suspected, contain the sulphonic acid group. In hydrolytic solvents they give intensely yellow solutions, which dye wool; this, with the similar colour of their ammonium salts (that of the 3 : 6-disulphonyl fluoride is quite pale), is attributed to the presence of the $\cdot SO_2F$ group in the 8-position.

Salicylic acid treated at 100° with fluorosulphonic acid gives slowly in 36% yield 5-*fluorosulphonylsalicylic acid*, m. p. 183° (*ammonium* salt, decomp. 190°, easily soluble in water). This with liquid ammonia gives 5-amidosulphonylsalicylic acid, m. p. 228—229°; and with methyl alcohol and hydrogen chloride the *methyl* ester, m. p. 107—108°, which has an unpleasant odour resembling onions; and with acetic anhydride, *fluorosulphonylacetylsalicylic acid*, m. p. 149°.

Attempts to cause sodium ethylsulphonate or ethylsulphonyl chloride to react with fluorosulphonic acid failed, as did attempts to obtain sulphonyl fluorides from the chlorides and arsenic trifluoride.

The action of fluorosulphonic acid on acetophenone is fluorinating, since at 110° there is obtained in small yield a product free from sulphur but containing fluorine, m. p. 115—117°, regarded as a mixture of mono- and di-fluoroacetophenones.

E. W. Wignall.

Bromophenols. XXII. Halogenated phenols from *o*-chlorophenol. XXIII. Diphenyl ether of 2 : 5-dihydroxybenzoquinone and allied compounds. M. Kohn and J. J. Sussmann (Monatsh., 1927, **48**, 193—202, 203—210).—XXII. Reduction of 2-chloro-4 : 6-dibromophenol with zinc dust and acetic acid gives 2-chloro-4-bromophenol, which on nitration furnishes 2-chloro-4-bromo-6-nitrophenol, and is iodinated to 2-*chloro*-4-*bromo*-6-*iodophenol*, m. p. 70° (*methyl ether*, m. p. 39°). Phosphorus pentabromide converts *o*-chloroanisole into 2-*chloro*-4-*bromoanisole*, m. p. 70°, which is demethylated by hydrobromic acid to the corresponding phenol. 2-Chloro-6-bromobenzoquinone, obtained by oxidation of 2-chloro-4 : 6-dibromophenol bromide or 2 : 4-dichloro-6-bromophenol bromide, is reduced by sulphurous acid to the corresponding quinol. Methylation of the quinol, followed by nitration, gives 2-*chloro*-6-*bromo*-3 : 5-*dinitroquinol dimethyl ether*, m. p. 135°. Partial demethylation of this ether furnishes 2-*chloro*-6-*bromo*-3 : 5-*dinitroquinol monomethyl ether*, m. p. 124°. The crystallographic properties of these ethers are described fully.

XXIII. Reduction of tetrabromobenzoquinone (bromanil) or tribromobenzoquinone with zinc dust and acetic anhydride furnishes 2 : 5-dibromoquinol diacetate, m. p. 165° (Schulz, A., 1882, 838, gives m. p. 159·5—161°). Bromanil reacts with potassium phenoxide yielding 3 : 6-dibromo-2 : 5-diphenoxybenzoquinone, which on successive treatment with zinc dust and acetic acid, followed by chromic acid, furnishes 2 : 5-*diphenoxybenzoquinone*, m. p. 236°. This compound is reduced by zinc dust and acetic acid to 2 : 5-*diphenoxyquinol*, m. p. 128° (*diacetate*, m. p. 148°). Methyl sulphate converts the diphenoxyquinol into 2 : 5-*diphenoxy*-1 : 4-*dimethoxybenzene*, m. p. 147°. Reduction of the sodium salt of 2 : 5-dibromo-3 : 6-dihydroxybenzoquinone (bromanilic acid) with zinc dust and acetic anhydride followed by zinc dust and acetic acid furnishes the *tetra-acetate* of 1 : 2 : 4 : 5-*tetrahydroxybenzene*, m. p. 226°. From 2 : 4-dibromotoluquinone there is produced 2 : 6-*dibromo*-3-*methylquinol diacetate*, m. p. 140°.

H. Burton.

Bromophenols. XXIV. Dehalogenation of bromophenols. XXV. Halogenation of chlorophenols. M. Kohn and J. Pfeifer (Monatsh., 1927, **48**, 211—229, 231—241).—XXIV. Reduction of 2 : 4 : 6-tribromophenol with zinc dust and acetic acid affords 2 : 4-dibromophenol (*benzoyl* derivative, m. p. 92°; *methyl ether*, m. p. 62—64°). Nitration of the dibromophenol furnishes 2 : 4-*dibromo*-6-*nitrophenol*, m. p. 118·5° (crystallographic data given). 3 : 4 : 6-*Tribromophenol*, m. p. 79° (*benzoyl* derivative, m. p. 99°), is obtained similarly from pentabromophenol and 2 : 3 : 4 : 6-tetrabromophenol. 3 : 4 : 6-*Tribromoanisole*, b. p. 306—309°/775 mm., m. p. 105°, on nitration furnishes 3 : 4 : 6-*tribromo*-2-*nitroanisole*, m. p. 70°, which is demethylated by hydrobromic acid to 3 : 4 : 6-*tribromo*-2-*nitrophenol*, m. p. 122°. Bromination of the tribromophenol furnishes 2 : 3 : 4 : 6-*tetrabromophenol*, m. p. 114°, oxidised by fuming nitric acid to tribromobenzoquinone. 2-*Chloro*-3 : 4 : 6-*tribromophenol*, m. p. 101° (*benzoyl* derivative, m. p. 142°), yields a *methyl ether*, m. p.

82°, which on nitration gives 2-*chloro*-3 : 4 : 6-*tribromo*-5-*nitroanisole*, m. p. 114°. 2-*Chloro*-3 : 4 : 6-*tribromo*-5-*nitrophenol* has m. p. 156°. Reduction of 2 : 4 : 6-tribromoresorcinol with zinc dust and acetic anhydride furnishes 4 : 6-*dibromoresorcinol diacetate*, m. p. 94°, whilst 4 : 5-*dibromopyrocatechol diacetate*, m. p. 173°, is obtained from tetrabromopyrocatechol.

XXV. 2 : 3 : 4 : 6-Tetrachloroanisole, m. p. 60° (cf. Biltz and Giese, A., 1904, i, 1000), on nitration yields 2 : 3 : 4 : 6-*tetrachloro*-5-*nitroanisole*, m. p. 58°, which is demethylated to 2 : 3 : 4 : 6-*tetrachloro*-5-*nitrophenol*, m. p. 122°. Bromination of 2 : 3 : 4 : 6-tetrachlorophenol in presence of iron powder gives 2 : 3 : 4 : 6-tetrachloro-5-bromophenol (I), m. p. 197° (cf. Kohn and Zandman, this vol., 52).

Bromination of 3 : 5-dichlorophenol in acetic acid solution furnishes 3 : 5-dichloro-2 : 4 : 6-tribromophenol (II), m. p. 189° (Blanksma, Rec. trav. chim., 1908, **27**, 32, gives m. p. 183°) (*methyl ether*, b. p. 349—350°/743 mm., m. p. 149—150°). Oxidation of the dichlorotribromophenol yields 2 : 6-*dichloro*-3 : 5-*dibromo*-p-*benzoquinone*, m. p. above 280°. Iodination of 3 : 5-dichlorophenol gives 3 : 5-*dichloro*-2 : 4 : 6-*tri*-*iodophenol*, m. p. 205° (decomp.) (*methyl ether*, m. p. 197°), which is oxidised to 2 : 6-*dichloro*-3 : 5-*di*-*iodobenzoquinone*, m. p. 240° (decomp.). 3 : 5-*Dichloro*-2 : 4-*dinitroacetanilide*, m. p. 124—125°, reacts with aniline yielding 2 : 4-*dinitro*-3 : 5-*dianilidoacetanilide*, m. p. 235°. Crystallographic data of (I) and (II) are given. H. Burton.

Bromophenols. XXVI. 2 : 4 : 6-Trichloro-3-bromophenol and 2-chloro-4 : 6-dibromophenol. XXVII. Formation of dibromo-o-cresol from tetrabromo-o-cresol by the action of aluminium chloride and benzene. M. Kohn and F. Rabinowitsch (Monatsh., 1927, **48**, 347—360, 361—374; cf. this vol., 51).—XXVI. The ketobromide of 2 : 4 : 6-trichlorophenol when warmed with concentrated sulphuric acid on the water-bath passes into 2 : 4 : 6-*trichloro*-3-*bromophenol*, m. p. 76° (corr.) (*benzoyl* derivative, m. p. 117°), isolated as its *methyl ether*, m. p. 64—65° (corr.). Oxidation of the ketobromide with fuming nitric acid yields 2 : 6-dichloro-*p*-benzoquinone. Nitration of the trichlorobromoanisole furnishes 2 : 4 : 6-*trichloro*-3-*bromo*-5-*nitroanisole*, m. p. 74°, which with hydrobromic acid gives the corresponding *phenol*, m. p. 131°. Nitration of 2-*chloro*-4 : 6-*dibromoanisole*, m. p. 75°, yields a *mononitro*-derivative, m. p. 73°, and 2-*chloro*-4 : 6-*dibromo*-3 : 5-*dinitroanisole*, m. p. 128—129°, the latter on demethylation furnishing the corresponding *phenol*, m. p. 180—181°. Direct iodination of *o*-chlorophenol yields 2-*chloro*-4 : 6-*di*-*iodophenol*, m. p. 96° (*methyl ether*, m. p. 65°). The ketobromide of 2-chloro-4 : 6-dibromophenol when warmed with concentrated sulphuric acid gives a *tribromo*-o-*chlorophenol*, m. p. 96° (*methyl ether*, b. p. 320—325°/757 mm., m. p. 67°). Possibly this substance is a mixture of 2-chloro-4 : 5 : 6-tribromo- and 2-chloro-3 : 4 : 6-tribromophenols. Oxidation of the ketobromide yields 2-chloro-6-bromo-*p*-benzoquinone. Crystallographic data for 2 : 4 : 6-trichloro-, 2-chloro-4 : 6-dibromo-, and 2-chloro-4 : 6-di-iodoanisoles are given.

XXVII. *o*-Cresol is brominated in presence of iron powder yielding the tetrabromo-derivative, which with aluminium chloride in presence of benzene yields 4 : 6-dibromo-*o*-cresol. Chlorination of this last compound furnishes 3 : 5-*dichloro*-4 : 6-*dibromo*-o-*cresol*, m. p. 196—197° (*methyl ether*, m. p. 115—116°), in turn oxidised to 2-*chloro*-3 : 5-*dibromo*-6-*methyl*-p-*benzoquinone*, m. p. 231°. Iodination of the dibromocresol yields 4 : 6-*dibromo*-3 : 5-*di*-*iodo*-o-*cresol*, m. p. 176—177° (*methyl ether*, m. p. 141°), which furnishes on oxidation 3 : 5-*dibromo*-2-*iodo*-6-*methyl*-p-*benzoquinone*, m. p. 216—217°. Nitration of 4 : 6-*dibromo*-o-*tolyl methyl ether*, b. p. 268—272°/743 mm., furnishes 4 : 6-*dibromo*-3 : 5-*dinitro*-o-*tolyl methyl ether*, m. p. 111—112°, which on demethylation gives the corresponding *cresol*, m. p. 165°. 4 : 5 : 6-*Tribromo*-3-*iodo*-o-*cresol*, m. p. 180—182° (*methyl ether*, m. p. 139°), and 3-*chloro*-4 : 5 : 6-*tribromo*-o-*cresol*, m. p. 209—211° (*methyl ether*, m. p. 128°), are obtained by halogenation of the tribromocresol. 5-*Chloro*-4 : 6-*dibromo*-o-*cresol*, m. p. 112—113° (*methyl ether*, m. p. 81°), on further bromination yields 5-*chloro*-3 : 4 : 6-*tribromo*-o-*cresol*, m. p. 197—198° (*methyl ether*, m. p. 132°), which is oxidised to 2 : 3 : 5-*tribromo*-6-*methyl*-p-*benzoquinone*, m. p. 232°. 5-*Chloro*-4 : 6-*dibromo*-3-*iodo*-o-*cresol* (*methyl ether*, m. p. 124°) has m. p. 169—170°. H. Burton.

Condensation of chloral with phenol. F. D. Chattaway and A. A. Morris (J.C.S., 1927, 2013—2017; cf. this vol., 458).—When phenol is dissolved in sulphuric acid with consequent formation of *p*-phenolsulphonic acid, it condenses with chloral giving *anhydro*-2-βββ-*trichloro*-α-*hydroxyethoxy*-1-βββ-*trichloro*-α-*hydroxyethylbenzene*-5-*sulphonic acid* (I), [*trihydrate*; *monohydrate*; *ammonium* salt; *chloride*, m. p. 130·5°; *methyl* ester, m. p. 150°; *ethyl* ester, m. p. 143°; *amide*, m. p. 207°; *dichloroamide*, m. p. 165—174° (decomp.); *anilide*, m. p. 168·5°]. Nitration of (I) yields *anhydro*-3 : 5-*dinitro*-2-βββ-*trichloro*-α-*hydroxyethoxy*-1-βββ-*trichloro*-α-*hydroxyethylbenzene* (II), m. p. 163° (dimorphic), also obtained by nitration of the condensation product from chloral and *p*-nitrophenol (*loc. cit.*). Treatment of (II) with alcoholic potassium hydroxide solution yields ωω-*dichloro*-3 : 5-*dinitro*-2-*ethoxyacetophenone*, m. p. 82—84° (*osazone*, m. p. 224°), which is oxidised by potassium permanganate to 3 : 5-dinitro-2-ethoxybenzoic acid.

Chloral condenses in this way only with phenols in which the hydrogen in the *para*-position to the hydroxyl group has been substituted. The constitution of the resinous product obtained by condensation of phenol itself with chloral suspended in concentrated sulphuric acid is unknown. M. Clark.

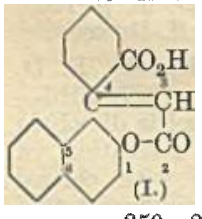
B. p. of *p*-cresol. H. D. Gibbs (J. Amer. Chem. Soc., 1927, **49**, 2118; cf. this vol., 456).—Clemmensen's determination of the b. p. of *p*-cresol as 201°/750 mm. (A., 1914, i, 272) is recorded. F. G. Willson.

Isomeric hydroxybenzyldimethylamines. E. Stedman (J.C.S., 1927, 1902—1906).—*o*-, *m*-, and *p*-Hydroxybenzyldimethylamines are prepared by treatment of the corresponding methoxybenzyl bromides with dimethylamine and subsequent hydrolysis of the methoxyl groupings. The following are described: m-*methoxybenzyldimethylamine*, b. p. 105°/

13 mm. (*hydrochloride*, m. p. 173°); m-*hydroxybenzyldimethylamine*, m. p. 108° (*hydrochloride*, m. p. 173°); *p*-methoxybenzyldimethylamine (*hydrochloride*, m. p. 152°); *p*-hydroxybenzyldimethylamine (*hydrochloride*, m. p. 185°); o-*methoxybenzyldimethylamine*, b. p. 113°/20 mm. (*hydrochloride*, m. p. 149°); o-*hydroxybenzyldimethylamine*, b. p. 99—100°/12 mm. (*methiodide*, m. p. 169°); o-*nitrobenzyldimethylamine* (*hydrochloride*, m. p. 221°); o-*aminobenzyldimethylamine*, m. p. 36—37°, b. p. 107°/14 mm. (*dihydrochloride*, m. p. 205°); m-*nitrobenzyldimethylamine* (*hydrochloride*, m. p. 230°); m-*aminobenzyldimethylamine*, m. p. 46°, b. p. 129°/13 mm. (*dihydrochloride*, m. p. 225°; *chlorostannate*). *p*-Nitrobenzyl chloride treated with dimethylamine yields, in addition to *p*-nitrobenzyldimethylamine (*hydrochloride*, m. p. 188°; *oxalate*, m. p. 155°; *methiodide*, m. p. 198°), *di*-p-*nitrobenzyldimethylammonium chloride*, m. p. 176°.

M. CLARK.

Oxidation of β-naphthol. O. DISCHENDORFER and W. DANZIGER (Monatsh., 1927, **48**, 315—336).—Oxidation of β-naphthol with alkaline potassium permanganate solution (cf. Ehrlich and Benedikt, A., 1888, 1306; Ehrlich, A., 1890, 54) yields the acid, $C_{20}H_{12}O_4$, now shown to be 4-o-*carboxyphenyl*-5 : 6-*benzocoumarin*, (I), m. p. 281° (barium salt; ethyl ester, m. p. 123—124°; *methyl* ester, m. p. 152—153°), formed by the interaction of *o*-carboxycinnamic acid (one of the oxidation products) with β-naphthol. Bromination of (I) yields 3-*bromo*-4-o-*carboxyphenyl*-5:6-*benzocoumarin*, m. p. 250—252° (*ethyl* ester, m. p. 134°). Reduction of (I) with sodium amalgam furnishes 4-o-*carboxyphenyl*-3 : 4-*dihydro*-5 : 6-*benzocoumarin*, m. p. 221° (cf. Ehrlich, *loc. cit.*) (*ethyl* ester, m. p. 147—149°). On distillation at 330—350° (I) yields 4-*phenyl*-5 : 6-*benzocoumarin*, m. p. 161—162°, which is brominated in chloroform solution giving 3-*bromo*-4-*phenyl*-5 : 6-*benzocoumarin*, m. p. 198°. The dihydro-acid on distillation furnishes 4-*phenyl*-3 : 4-*dihydro*-5 : 6-*benzocoumarin*, m. p. 264°. The synthesis of (I) was effected by condensing β-naphthol and phthalylacetic acid in presence of concentrated sulphuric acid. The *acetate*, m. p. 90—91·5°, of phenyl 2-hydroxynaphthyl ketone, and the ketone itself, on long heating with acetic anhydride and sodium acetate, yield 4-phenyl-5 : 6-benzocoumarin.



H. BURTON.

***cyclo*Hexyl-phenols and -phenol ethers.** J. F. BARTLETT and C. E. GARLAND (J. Amer. Chem. Soc., 1927, **49**, 2098—2101).—4-cyclo*Hexylresorcinol*, m. p. 124—125° (phenol coefficient, 24—27), is obtained by condensation of *cyclo*hexyl chloride with resorcinol in nitrobenzene in presence of aluminium chloride. 4-cyclo*Hexylanisole*, b. p. 146—148°/16 mm., d_0^{20} 1·0209, d_0^{25} 1·0004, n^{25} 1·5305, and 4-cyclo*hexylphenetole*, solid, b. p. 155—157°/16 mm., 1·5262, are obtained similarly, but without use of nitrobenzene. 4-*cyclo*Hexylphenol, m. p. 128° (*benzoate*, m. p. 114—114·5°), is obtained by condensation of phenol with *cyclo*hexyl chloride in presence of zinc chloride, and also by hydrolysis of *cyclo*hexylanisole with hydrobromic and acetic acids. F. G. WILLSON.

Alicyclic derivatives of resorcinol. R. H. TALBOT and R. ADAMS (J. Amer. Chem. Soc., 1927, **49**, 2040—2042).—The following compounds, prepared by methods analogous to those of Dohme, Cox, and Miller (A., 1926, 838), have phenol coefficients lower than that of *n*-hexylresorcinol: 4-*hexahydrobenzylresorcinol*, m. p. 116·5—117·5°, 4-β-cyclo*hexylethylresorcinol*, m. p. 109—110°, and 4-cyclo*pentylmethylresorcinol*, m. p. 95—96°. The following compounds, obtained intermediately, are described: *hexahydrobenzoylresorcinol*, m. p. 115·5—116°, b. p. 200—202°/4 mm., 2 : 4-*dihydroxyphenyl* cyclo*hexylmethyl ketone*, m. p. 111—112°, b. p. 202—204°/4 mm., and 2 : 4-*dihydroxyphenyl* cyclo*pentyl ketone*, b. p. 184—190°/4 mm. F. G. WILLSON.

Nitro-derivatives of the homopyrocatechol ethers. A. E. OXFORD (J.C.S., 1927, 1964—1972).—Nitration of *m*-methoxy-*p*-tolyl acetate by acetyl nitrate at −15° gives 2-*nitrocreosol* (I, 5% yield), an uncrystallisable oil (p-*nitrobenzyl* derivative, m. p. 114—114·5°), and 6-*nitrocreosol* (p-*nitrobenzyl* derivative, m. p. 202—203°). When acetyl chloride and silver nitrate are used for generation of the acetyl nitrate, 6(?)-*chlorocreosol*, m. p. 71° (*acetyl* derivative, m. p. 61°; *methyl ether*, m. p. 37—38°; *nitro*-derivative, m. p. 89°), is also obtained. Nitration of (I) with nitric acid in glacial acetic acid solution gives 2 : 5-*dinitrocreosol*, m. p. 86—87° (*acetyl* derivative, m. p. 53—54°), converted by methylation into 2 : 5-*dinitrohomoveratrole*, m. p. 36°. Alkaline hydrolysis of a mixture of 2- and 6-nitrohomoveratroles results in quantitative demethylation of the latter, yielding 6-nitro*iso*creosol (II), m. p. 168—170° (cf. Gulland and Robinson, A., 1926, 1035) (*sodium* salt; *acetyl* derivative, m. p. 98—98·5°), whilst the 2-nitrohomoveratrole, m. p. 6—7·5°, is unattacked. 6-*Bromo*-2-*nitrohomoveratrole* has m. p. 102—103°. Nitration of the acetyl derivative of (II) yields the *acetyl* derivative, m. p. 109—110°, of 5 : 6-*dinitroisocreosol*, m. p. 128—129° (*sodium* salt). Nitration of 3-methoxy-*o*-tolyl acetate in acetic anhydride yields 4-*nitro*-o-*creosol* (?), m. p. 60—61°. M. CLARK.

Displacement of bromine accompanying the nitration of 6-bromohomoveratrole. T. HEAP, T. G. H. JONES, and R. ROBINSON (J.C.S., 1927, 2021—2022).—The statement of Jones and Robinson (J.C.S., 1917, **111**, 919) that a mononitro-derivative is obtained from 6-bromohomoveratrole by treatment with a mixture of nitric acid and acetic anhydride cannot be confirmed, since only 6-nitrohomoveratrole is obtained. It is suggested that the compound isolated was actually 4-bromo-5-nitroveratrole, resulting from contamination with guaiacol of the creosol used in preparation of the 6-bromo-compound. Alkaline hydrolysis of 6-nitrohomoveratrole by the method of Robinson and Pollecoff (J.C.S., 1918, **113**, 641) yields 6-nitro*iso*creosol (*acetyl* derivative, m. p. 100—101°). M. CLARK.

Vinylpyrocatechol monomethyl ether [4-hydroxy-3-methoxystyrene] from beechwood tar. A. FROMM (Annalen, 1927, **456**, 168—177).—Attempts to isolate a compound of the formula $C_{10}H_{14}O_2$ from the fraction, b. p. 235—245°, of beechwood tar were unsuccessful and it is improbable that Pastro-

vich's "cœrulignol" (A., 1883, 1005) was a pure compound. Purification of this fraction through the calcium salt and finally by benzoylation gives *4-hydroxy-3-methoxystyrene*, b. p. 236—238°, d^{15} 1·0635 [*benzoate*, m. p. 67·5°; *glycollate*, m. p. 77°; *carbonate*, m. p. 143°; *phosphate*, $(C_9H_9O_2)_3PO_4$, m. p. 121°; also liquid *monohydrogen* and *dihydrogen phosphates*]. Its constitution is established (*a*) by its oxidation by nitric acid (*d* 1·2) to methoxybenzoquinone, (*b*) by oxidation of its *acetate*, b. p. 265—272°, with permanganate in acetic acid to acetylvanillic acid, (*c*) by oxidation of its *methyl ether* (3 : 4-*dimethoxystyrene*), b. p. 233—237°, d^{15} 1·049, with alkaline permanganate to veratric acid and 3 : 4-dimethoxyphenylglyoxylic acid, and (*d*) by its formation from ferulic acid (4-hydroxy-3-methoxycinnamic acid) with loss of carbon dioxide. H. E. F. Notton.

Sterol from coltsfoot (*Tussilago farfara*). L. Schmid (Monatsh., 1927, 48, 289—291).—Acetylation of the sterol from *Tussilago farfara*, with subsequent bromination in acetic acid solution, yields tetrabromostigmasterol acetate, m. p. 209—210° (decomp.), together with a second acetate which when reduced with sodium amalgam and zinc dust is identical with sitosterol acetate, m. p. 127°. Hydrolysis with alcoholic potassium hydroxide yields sitosterol, m. p. 136—137° (benzoate, m. p. 143—144°). H. Burton.

Cholesterol. III. E. Montignie (Bull. Soc. chim., 1927, [iv], **41**, 947—949; cf. this vol., 556).—Phosphoric oxide converts cholesterol into α-cholesterylene, which with alcoholic sulphuric acid regenerates cholesterol, and a *hydrocarbon*, $C_{26}H_{42}$, m. p. 66—67° (*bromide*, m. p. 61—62°), the latter substance being formed by oxidation of cholesterol. Oxidation of cholesterol with silver dichromate and sulphuric acid yields oxycholestenone as the sole product (cf. Mauthner and Suida, A., 1897, i, 31). The iodine value of cholesterol varies with the time of reaction, a maximum value of 82·55 being obtained after 48 hrs. H. Burton.

Dyes derived from itaconic acid. P. R. Dhar and S. Dutt (J. Indian Chem. Soc., 1927, **4**, 247—252).—Itaconic acid condenses with aromatic hydroxy- and amino-compounds in the presence of sulphuric acid or stannic chloride to yield dyes analogous to the phthaleins. These dyes have deeper colours than the corresponding succineins (A., 1926, 725). The following dyes are prepared: *phenol-itaconein*, m. p. 210° (alkaline solution, pink); *resorcinol-itaconein*, m. p. 195° (decomp.; solution in alkalis, yellow with green fluorescence); *pyrocatechol-itaconein hydrochloride*, m. p. 165° (decomp.); *phloroglucinol-itaconein*, unmelted at 290° (decomp.; solution in alkalis, red); *pyrogallol-itaconein*, m. p. 253° (decomp.); m-*diethylaminophenol-itaconein*, m. p. 80° (decomp.; solution in dilute acids, pink with deep-rown fluorescence). *Tetrabromoresorcinol-itaconein ibromide*, m. p. 187° (decomp.), obtained by the romination of *resorcinol-itaconein* in acetic acid solution with bromine, gives a violet-red, non-fluorescent solution with alkalis. G. A. C. Gough.

Dyes derived from citraconic acid. P. R. Har and S. Dutt (J. Indian Chem. Soc., 1927, **4**, 253—256; cf. preceding abstract).—The following citraconeins have been prepared: phenol-, m. p. 160° (J.C.S., 1921, **119**, 289); *resorcinol-*, m. p. 217° (yellowish-green fluorescence in alkaline solution); *phloroglucinol-*, m. p. above 290°; *pyrocatechol-*, m. p. 260°; *pyrogallol-*, m. p. 230°; *tetrabromoresorcinol-*, m. p. 190° (yellow fluorescence); m-*diethylaminophenol-*, m. p. 95° (yellowish-brown fluorescence). G. A. C. Gough.

Explosions with benzazide. F. Bergel (Z. angew. Chem., 1927, **40**, 974).—The crude benzazide, produced from the unpurified hydrazide made from ethyl benzoate by the method described in Gattermann's "Praxis des organischen Chemikers," explodes when heated at 120—165° but deflagrates only at lower and at higher temperatures, whereas the crude azide prepared from purified hydrazide as well as the purified azide deflagrates between 90° and 230° without exploding, but explodes if it is well packed with a rod before heating. The decomposition of the azide into phenyl cyanate by warming its xylene solution is somewhat accelerated by the passage of a current of carbon dioxide, nitrogen, or hydrogen through the liquid but the method is not suitable for the preparation of large quantities of the cyanate. A. R. Powell.

Addition of ethyl and *tert.*-butyl hypochlorites to cinnamic acid. E. L. Jackson and L. Pasiut (J. Amer. Chem. Soc., 1927, **49**, 2071—2079; cf. A., 1926, 1023).—Treatment of cinnamic acid or ethyl cinnamate in absolute ethyl alcohol with chlorine at below 0° affords *α-chloro-β-ethoxyphenylpropionic acid* (+1H_2O), m. p. 78—79°, together with other products. In presence of calcium carbonate, α-chloro-β-hydroxyphenylpropionic acid is produced. *α-Chloro-β-tert.-butoxyphenylpropionic acid* (+C_6H_6), m. p. 94—94·5° (solvent-free), is obtained similarly using *tert.*-butyl alcohol. Treatment of phenyl styryl ketone with chlorine in *tert.*-butyl alcohol affords phenyl αβ-dichloro-β-phenylethyl ketone, m. p. 113—114°, together with a *stereoisomeride*, m. p. 82—83°, but addition of *tert.*-butyl hypochlorite to the phenyl styryl ketone could not be established. F. G. Willson.

Condensation of *p*-hydroxybenzoic acid with chloral. F. D. Chattaway and C. F. Prats (Anal. Fís. Quím., 1927, **25**, 161—177).—See this vol., 458.

Reactions of displacement in the tropic acid group. II. C. A. Kerr (J.C.S., 1927, 1943—1948).—*r*-Chlorotropic acid, $OH{\cdot}CH_2{\cdot}CPhCl{\cdot}CO_2H$, is obtained in 80% yield by the action of an aqueous solution of monochlorocarbamide on atropic acid, $CH_2{:}CPh{\cdot}CO_2H$. Conversion into tropic acid by means of reducing agents could not be effected. The chlorine atom is replaced by a hydroxyl group with formation of atroglyceric acid on treatment with an aqueous solution of sodium carbonate or of sodium hydroxide or with moist silver oxide. Treatment with concentrated aqueous ammonia gives good yields of *α-amino-β-hydroxy-α-phenylpropionic acid*, m. p. 285—288° (decomp.) [*hydrochloride*, m. p. 225° (decomp.)]. Resolution of *r*-chlorotropic acid can be accomplished by fractional crystallisation of the morphine salt. d-*Chlorotropic acid*, m. p. 123—

124°, has $[\alpha]_D^{18}$ +12·6° in methyl alcohol. In the conversion of *d*-chlorotropic acid into atroglyceric acid by means of moist silver oxide or by aqueous sodium carbonate, complete racemisation occurs. The action of ammonia on the optically-active acid gives a dextrorotatory α-amino-β-hydroxy-α-phenylpropionic acid, $[\alpha]_D^{16}$ +40·6°. M. CLARK.

Interaction of mercaptans with phthalic anhydride and phthalyl chloride. G. C. CHAKRAVARTI and J. M. SAHA (J. Indian Chem. Soc., 1927, 4, 141—147).—Condensation of mercaptans with phthalic anhydride cannot be effected by the use of sulphuric acid, hydrogen chloride, or zinc chloride as condensing agents. By the use of phosphorus pentoxide at 130—140°, *dithio*-esters, and not the thio-analogues of the phthaleins, are produced. The alternative thiophthalide formula for these substances is rejected because they resist the hydrolytic action of boiling aqueous alkalis (cf. Troger and Hornung, A., 1903, i, 95). The same products also arise from the action of phthalyl chloride on the mercaptans in benzene solution or in the homogeneous state. The following compounds are described: *diphenyl dithiophthalate*, m. p. 84—85° (isomeric *compound*, m. p. 101°, with a similar resistance to hydrolysis); *di*-p-*bromophenyl dithiophthalate*, m. p. 186—188°; *di*-p-*iodophenyl dithiophthalate*, m. p. 181—182°; *di*-p-*tolyl dithiophthalate*, m. p. 149°; *di*-β-*naphthyl dithiophthalate*, m. p. 70°; *dibenzyl dithiophthalate* (oily); *diethyl dithiophthalate* (oily); *dipropyl dithiophthalate*, b. p. 229—232°/26 mm.; *dibutyl dithiophthalate*, m. p. 56—57°. αβ-Dithiolethane and phthalic anhydride yield a *compound*, m. p. 169°. G. A. C. GOUGH.

Hydrophthalides. II. S. BERLINGOZZI and L. CIONE. **III.** S. BERLINGOZZI. **IV.** S. BERLINGOZZI and G. LUPO. **V.** S. BERLINGOZZI (Rend. Accad. Sci. Fis. Mat. Napoli, 1926, [iii], **32**, 125—130, 151—157, 174—183, 184—188).—See this vol., 560, 561.

Hydrogenation of salts of aromatic acids under pressure. II. V. IPATIEV and G. RAZUBAIEV (J. Russ. Phys. Chem. Soc., 1926, **58**, 1339—1344).—See A., 1926, 1138.

Condensation of 2-nitrofluorene with aromatic aldehydes. J. LOEVENICH and A. LOESER (J. pr. Chem., 1927, [ii], **116**, 325—330).—2-Nitrofluorene, m. p. 157·5—158° (Diels, A., 1901, i, 521, gives 156°), condenses with aldehydes in the presence of sodium ethoxide and from the appropriate aldehydes are thus obtained: 9-*benzylidene*-, m. p. 148·5—149°; 9-p-*toluylidene*-, m. p. 163·5—164·6°; 9-*anisylidene*-, m. p. 212—213°; 9-p-*anisylidene*-, m. p. 146—147°; 9-o-*ethoxybenzylidene*-, m. p. 162·5—163·5°; 9-p-*ethoxybenzylidene*-, m. p. 156—157°; 9-*piperonylidene*-, m. p. 214—215°; 9-3 : 4-*dimethoxybenzylidene*-, m. p. 179—180°; 9-o-*chlorobenzylidene*-, m. p. 240·5—241·5°; 9-m-*bromobenzylidene*-, m. p. 155·5—156·5°; 9-m-*iodobenzylidene*-, m. p. 168—169°; 9-*cinnamylidene*-, m. p. 230·5—231·5°, and 9-*furfurylidene*-, m. p. 213·5—214·5°, -2-*nitrofluorenes*. All the m. p. are corrected. J. W. BAKER.

Isomerism of the oximes. XXXI. Furfuraldoximes and 2-methoxy- and 4-methoxy-1-naphthaldoximes. O. L. BRADY and R. F. GOLDSTEIN (J.C.S., 1927, 1959—1964).—α-Furfuraldoxime, m. p. 75—76° (lit. 73°), can be regenerated by hydrolysis of *acetyl-α-furfuraldoxime*, m. p. 34—35°, or of benzoyl-α-furfuraldoxime, provided that the solutions of the α-oxime are not warmed. In hot solutions, the α-oxime is partly converted into the β-isomeride. β-Furfuraldoxime, m. p. 91—92° (lit. 89°), is much more stable than β-benzaldoxime. The furfuraldoximes thus occupy an intermediate position between the benzaldoximes and the aliphatic aldoximes. α-2-*Methoxy*-1-*naphthaldoxime*, m. p. 154—155° [*acetyl* derivative, m. p. 79—80°; *hydrochloride*, m. p. 145—147° (decomp.)], yields on methylation a mixture of α-N-*methyl*-2-*methoxy*-1-*naphthaldoxime*, m. p. 118—119° (*monohydrate*, m. p. 88—89°), and α-O-*methyl*-2-*methoxy*-1-*naphthaldoxime*, m. p. 65°, the former preponderating. α-4-*Methoxy*-1-*naphthaldoxime*, m. p. 107—108° [*acetyl* derivative, m. p. 102°; *hydrochloride*, m. p. 144—145° (decomp.)], yields, on methylation, a mixture of α-N-*methyl*-4-*methoxy*-1-*naphthaldoxime*, m. p. 158—159° (dimorphic), and α-O-*methyl*-4-*methoxy*-1-*naphthaldoxime*, m. p. 38—39°, in approximately equal amount. The β-isomeride could not be obtained in either case. M. CLARK.

Synthesis of a new resorcylaldehyde. F. MAUTHNER (J. pr. Chem., 1927, [ii], **116**, 314—320).—Alkylation of methyl 3 : 5-dihydroxybenzoate (obtained by esterification of the free acid with methyl alcohol and hydrogen chloride under specified conditions) with 1 mol. of sodium hydroxide and methyl sulphate yields 3-*hydroxy*-5-*methoxybenzoic acid*, m. p. 202—203°, which on treatment with methyl chlorocarbonate yields 3-*carbomethoxy*-5-*methoxybenzoic acid*, m. p. 145—146°. The *acid chloride*, m. p. 57—58°, of the latter on catalytic reduction with a palladium–barium sulphate catalyst yields 3-*carbomethoxy*-5-*methoxybenzaldehyde*, which is hydrolysed by dilute alkali in an atmosphere of hydrogen to 3-*hydroxy*-5-*methoxybenzaldehyde*, m. p. 130—131° (p-*nitrophenylhydrazone*, m. p. 221—222°; *semicarbazone*, m. p. 197—198°). This aldehyde condenses with malonic acid in the presence of piperidine to yield 3-*hydroxy*-5-*methoxycinnamic acid*, m. p. 198—199°. J. W. BAKER.

Preparation of α-hydrindone and α-ketotetrahydronaphthalene. (MLLE.) P. AMAGAT (Bull. Soc. chim., 1927, [iv], **41**, 940—943; cf. Kipping, J.C.S., 1894, **65**, 480; Kipping and Hall, *ibid.*, 1899, 75, 147).—β-Phenylpropionyl chloride (1 mol.), when treated with aluminium chloride (1 mol.) in cold benzene (5 mols.), gives a good yield of α-hydrindone. α-Ketotetrahydronaphthalene is obtained similarly from γ-phenylbutyryl chloride. H. BURTON.

Derivatives of 1 : 3-diphenylhydrindene. R. WEISS and S. LUFT (Monatsh., 1927, **48**, 337—345).—Bromination of 1 : 3-diphenylindene in ether solution yields 2 : 3-*dibromo*-1 : 3-*diphenylhydrindene*, decomp. 92—96°, which with boiling methyl alcohol gives 2-*bromo*-1-*methoxy*-1 : 3-*diphenylhydrindene*, m. p. 150—151°. Bromination of 3-phenyl-1-hydrindone in chloroform solution furnishes 2 : 3-*dibromo*-3-*phenyl*-1-*hydrindone*, m. p. 123—124°, which on heat-

ing with methyl alcohol at 150° loses 1 mol. of hydrogen bromide, producing 2-*bromo*-3-*phenyl*-1-*indone*, m. p. 112—113°. Magnesium phenyl bromide converts the dibromophenylhydrindone into 2-*bromo*-3-*phenyl*-1-*hydrindone*, m. p. 78—80°, whilst monobromination of phenylhydrindone in chloroform solution yields a monobromo-derivative, m. p. 88—90° (cf. Kohler, A., 1910, i, 563). Magnesium phenyl bromide reacts with the bromophenylindone forming 2-bromo-1-hydroxy-1 : 3-diphenylindene, isolated as its *acetyl* derivative, m. p. 115—117°. Similarly 2 : 2-dimethyl-1 : 3-diketohydrindene is converted into 3-*hydroxy*-3-*phenyl*-2 : 2-*dimethyl*-1-*hydrindone*, m. p. 139—141° (*methyl ether*, m. p. 160—162°; *chloride*, m. p. 107—108°), together with what is probably crude dihydroxydiphenyldimethylhydrindene, m. p. 115—125°. Magnesium phenyl bromide converts 3-methoxy-3-phenyl-2 : 2-dimethyl-1-hydrindone into 1-*hydroxy*-3-*methoxy*-1 : 3-*diphenyl*-2 : 2-*dimethylhydrindene*, m. p. 172—174°. H. Burton.

Co-ordination compounds of beryllium and *m*- and *p*-nitrobenzoylacetone. H. Burgess (J.C.S., 1927, 2017—2019).—Condensation of ethyl *p*-nitrobenzoate and acetone under the influence of sodamide yields p-*nitrobenzoylacetone*, m. p. 112—113·5° (*beryllium* derivative, m. p. 243—244°). Benzoylacetone is stable towards concentrated sulphuric acid at the ordinary temperature, and nitration in sulphuric acid by treatment with nitric acid (*d* 1·42) at low temperatures gives m-*nitrobenzoylacetone*, m. p. 114—115° (*beryllium* derivative, m. p. 207—208°). Ethyl sodioacetoacetate condenses with *p*-nitrobenzyl bromide with simultaneous formation of *ethyl* p-*nitrobenzylacetoacetate*, m. p. 43—45°, and *ethyl bis*-p-*nitrobenzylacetoacetate*, m. p. 137—139°. M. Clark.

Salt formation by αγ-diketones. II. Alkali and alkaline-earth salts of benzoylacetone. C. Weygand [with H. Forkel] (J. pr. Chem., 1927, [ii], **116**, 293—306).—The sodium compound of benzoylacetone has been obtained in a colourless and a yellow form which are interconvertible under certain conditions. The two forms may be true isomerides or merely chromoisomerides. The action of sodium on a solution of benzoylacetone in dry ether, contrary to the observations of Claisen and Lowmann (A., 1888, 692), yields a yellow, crystalline powder, COPh·CH:CMe·ONa(?), soluble in water and insoluble in benzene, having, in a high vacuum, m. p. 225—228°. The melted substance on slow cooling yields a crystalline form which is soluble in benzene. By the action of sodium on benzoylacetone in moist ether is obtained, according to the quantity of water present, either the dihydrate (cf. Sidgwick and Brewer, A., 1926, 71); the *trihydrate*, which melts to a colourless liquid when placed in a bath at 100°, loses water, again solidifies, again melts at ---°, and finally becomes yellow and anhydrous at 1.0°, or the *tetrahydrate*, which passes into the trihydrate on exposure to the air. Conversion of the colourless into the yellow form is effected either through the hydrate or by heating at 130—140°, the reverse change being brought about by treatment with cold benzene or toluene, or by prolonged heating in chloroform solution. The *potassium* derivative, obtained similarly by the action of potassium on a solution of benzoylacetone in dry ether, is yellow, soluble in warm benzene, has m. p. 193—195° in a high vacuum, and after fusion is insoluble in benzene. In moist ether a colourless *monohydrate*, m. p. (indef.) 150°, insoluble in benzene is obtained, whilst crystallisation of the anhydrous salt from a mixture of benzene and alcohol yields a *monoalcoholate*, m. p. (indef.) 150°, both of which compounds have been assumed by Sidgwick and Brewer (*loc. cit.*) to be the anhydrous salt. The corresponding *lithium*, m. p. 235°, *magnesium*, m. p. 267° (*trihydrate*), *barium*, m. p. 170° (*trihydrate*; *alcoholate*), *strontium*, m. p. 237—238°, and *calcium*, m. p. about 200°, compounds were obtained only in colourless forms which are insoluble in benzene, but, with the exception of the lithium compound, all pass into benzene-soluble forms on melting. All these compounds yield colourless hydrates which, with the exception of the potassium compound, are soluble in benzene. By boiling this benzene solution the pure anhydrous compound is obtained in its benzene-insoluble form, whilst dehydration of the hydrates with phosphoric oxide in a vacuum yields the pure, anhydrous benzene-soluble forms. J. W. Baker.

Synthesis of αβ-diacylstyrenes and their reaction with hydrogen bromide. C. F. H. Allen and H. B. Rosener (J. Amer. Chem. Soc., 1927, 49, 2110—2113).—Benzil condenses in presence of sodium methoxide with acetophenones substituted in the *m*- or *p*- but not the *o*-position (cf. Japp, J.C.S., 1897, **71**, 1138), with formation of αβ-diacylstyrenes, of which the following were prepared: α-*benzoyl*-β-p-*toluoyl*-, m. p. 158°; -β-3 : 4-*dimethylbenzoyl*-, m. p. 190°; -β-p-*anisoyl*-, m. p. 177°; -β-3 : 4-*dimethoxybenzoyl*-, m. p. 177°; -β-p-*chlorobenzoyl*-, m. p. 183°; -β-p-*chloro*-m-*toluoyl*-, m. p. 189°, and α-*benzoyl*-β-p-*bromobenzoyl-styrene*, m. p. 208°. When treated with hydrogen bromide in glacial acetic acid, the above ketones afford the corresponding 5-substituted derivatives of 4-bromo-2 : 3-diphenylfuran, of which the following are described: 4-*bromo*-2 : 3-*diphenyl*-5-p-*tolyl*-, m. p. 134°; -5-*phenyl*-, m. p. 129°; -5-(3′ : 4′-*dimethylphenyl*)-, m. p. 137°; -5-p-*anisyl*-, m. p. 151°; -5-p-*chlorophenyl*-, m. p. 127°; -5-p-*chloro*-m-*tolyl*-, m. p. 135°, and -5-p-*bromophenyl-furan*, m. p. 157°. The bromine in these derivatives is unaffected by heating for 24 hrs. with alcoholic potassium hydroxide, and the compounds do not form Grignard reagents. F. G. Willson.

Intermolecular condensation of styryl methyl ketones. I. R. Dickinson, I. M. Heilbron, and F. Irving (J.C.S., 1927, 1888—1897).—3 : 4-Dimethoxystyryl methyl ketone (*semicarbazone*, m. p. 205°, phototropic) obtained by alkaline condensation of acetone and veratraldehyde has m. p. 86° (cf. Ryan and Plunkett, A., 1916, i, 656). The compound of m. p. 168° similarly obtained by Franscesconi and Cusmano (A., 1908, i, 801) is 3-mp-*dimethoxyphenyl*-5-mp-*dimethoxystyryl*-Δ^5-cyclo*hexen*-1-*one* (*semicarbazone*, m. p. 226—227°). Proof of this is obtained by condensation of 3 : 3′ : 4 : 4′-tetramethoxydistyryl ketone (*tetrabromide*, m. p. 152° decomp.) with ethyl

acetoacetate to give *ethyl* 3-mp-*dimethoxyphenyl*-5-mp-*dimethoxystyryl*-Δ^5-cyclo*hexen*-1-*one*-2-*carboxylate*, m. p. 160—161°, which yields the above ketone when boiled with 20% sulphuric acid. The *cyclo*hexenone is also obtained by the action of sodium hydroxide on 3 : 4-dimethoxystyryl methyl ketone in acetone solution. The following are described: 3-*methoxy*-4-*ethoxystyryl methyl ketone*, m. p. 106° (yellow and colourless modifications; *semicarbazone*, m. p. 208—209°); 3 : 3′-*dimethoxy*-4 : 4′-*diethoxydistyryl ketone*, m. p. 123—124°; *propylvanillin*, m. p. 59—60° (*semicarbazone*, m. p. 156°); 3-*methoxy*-4-*propoxystyryl methyl ketone*, m. p. 92—93°; 3-m-*methoxy*-p-*propoxyphenyl*-5-m-*methoxy*-p-*propoxystyryl*-Δ^5-cyclo*hexen*-1-*one*, m. p. 152—153°; iso*propylvanillin*, b. p. 150—152°/13 mm. (*semicarbazone*, m. p. 151—152°); 3-*methoxy*-4-iso*propoxystyryl methyl ketone*, m. p. 51—53° (*semicarbazone*, m. p. 203—204°); 3-*methoxy*-4-*benzyloxystyryl methyl ketone*, m. p. 93° (*semicarbazone*, m. p. 200—201°); 3 : 3′-*dimethoxy*-4 : 4′-*dibenzyloxydistyryl ketone*, m. p. 155° [*tetrabromide*, m. p. 141° (decomp.)], *isomeride* (?), m. p. 174—175°; *phenyl* 3 : 4-*dimethoxystyryl ketone*, m. p. 88°. Treatment with piperidine of 3 : 4-dimethoxy- and of 3-methoxy-4-ethoxy-styryl methyl ketones yields in each case a *dimeride*. These have m. p. 209—210° and 187° respectively, and are presumed to be *cyclo*butane derivatives. M. Clark.

Condensation products of vanillin and salicylaldehyde with acetone, and the mechanism of the condensation. E. Glaser and E. Tramer (J. pr. Chem., 1927, [ii], **116**, 331—346).—By the condensation of acetone with various aromatic aldehydes in the presence either of alkali or hydrochloric acid a series of diarylideneacetones has been prepared, and it is supposed that the mechanism of the condensation involves the formation of unstable intermediate additive products of the type $R\cdot CH(OH)_2$ or $R\cdot CHCl\cdot OH$. Thus vanillylideneacetone condenses with salicylaldehyde to yield 2 : 4′-*dihydroxy*-3′-*methoxydistyryl ketone*, m. p. 155° (decomp.) (*diacetate*, m. p. 149°; *dibenzoate*, m. p. 175—176°), together with a small quantity of 2 : 2′-*dihydroxydistyryl ketone*, m. p. 152° (decomp.). By similar methods from the appropriate aldehyde are obtained, 4 : 4′-*dihydroxy*-3 : 3′-*dimethoxydistyryl ketone*, m. p. 155—156° (also $+H_2O$) [*diacetate*, m. p. 182°; *dibenzoate*, m. p. 192°; *tetrabromide* of the diacetate, m. p. 159—161° (decomp.)]; and 5-*bromo*-4-*hydroxy*-3-*methoxystyryl methyl ketone*, m. p. 147—148° (*acetate*, m. p. 135—136°; *sodium* salt). J. W. Baker.

Synthesis of acetopiperone. F. Mauthner (J. pr. Chem., 1927, [ii], **116**, 321—324).—Methyl piperonylate condenses with ethyl acetate in the presence of sodium wire to yield *ethyl* 3 : 4-*methylenedioxybenzoylacetate*, m. p. 70—71° (*pyrazalone* derivderivative, m. p. 145—146°), which when heated with 10% sulphuric acid under reflux for 8 hrs. yields acetopiperone (Ciamician and Silber, A., 1892, 62) (p-*nitrophenylhydrazone*, m. p. 205—206°; *semicarbazone*, m. p. 241—242°). The latter condenses with trimethylgallaldehyde to yield 4 : 5-*methylenedioxyphenyl* 3 : 4 : 5-*trimethoxystyryl ketone*, m. p. 147—148°. J. W. Baker.

Action of nitromethane and its homologues on benzil. I. Kasiwagi (Bull. Chem. Soc. Japan, 1927, **2**, 202—207).—See this vol., 246.

Pungent principles of ginger. III and IV. Constitution and synthesis of shogaol. H. Nomura and S. Tsurumi (Sci. Rep. Tohoku Imp. Univ., 1927, **16**, 581—588, 589—592).—See A., 1926, 1145; this vol., 770.

Synthesis of purpurin by condensation of phthalic anhydride with 2 : 4-dibromophenol. M. Tanaka (Proc. Imp. Acad. Tokyo, 1927, **3**, 345—347).—Phthalic anhydride (30 g.) and 2 : 4-dibromophenol (20 g.) are heated with boric acid (15 g.) and sulphuric acid monohydrate (160 g.) at 210—230° for 3 hrs. and the resulting bromoquinizarin is converted into purpurin by hydrolysis with aqueous potassium hydroxide. B. W. Anderson.

Polyhydroxymethylanthraquinones. IX. Structure of rubiadin. F. D. Stouder and R. Adams (J. Amer. Chem. Soc., 1927, **49**, 2043—2045).—Condensation of 2 : 4-dichlorotoluene with phthalic anhydride in presence of aluminium chloride affords 2 : 4-*dichloro*-5-*methylbenzophenone*-2′-*carboxylic acid*, m. p. 140°. On treatment with concentrated sulphuric acid and boric acid for 4 hrs. at 100°, the latter yields 2 : 4-*dichloro*-1-*methylanthraquinone*, yellow, m. p. 155°, which, when boiled with methylalcoholic sodium methoxide, is converted into 2 : 4-*dimethoxy*-1-*methylanthraquinone*, yellow, m. p. 162°. This is hydrolysed to 2 : 4-*dihydroxy*-1-*methylanthraquinone*, yellow, m. p. 251° (*diacetate*, yellow, m. p. 176·5°), when boiled with hydrobromic and glacial acetic acids. This dihydroxymethylanthraquinone is not identical with rubiadin, which is therefore probably 1 : 3-dihydroxy-2-methylanthraquinone (cf. Schunck and Marchlewski, J.C.S., 1894, 65, 182). F. G. Willson.

Elimination of sulphonic acid groups in anthraquinone derivatives. C. Marschalk (Bull. Soc. chim., 1927, [iv], **41**, 943—947).—Sodium 4 : 8-diaminoanthrarufin-2 : 6-disulphonate when treated with sodium hyposulphite yields 4 : 8-diaminoanthrarufin, both sulphonic acid groups being eliminated. Priority is claimed against I. G. Farbenind. A.-G., F.P. 618308. H. Burton.

Vat dyes of the perylene series. [**Dihalogenated diacylperylenes.**] F. Bensa.—See B., 1927, 698.

Halogenated dibenzpyrenequinones. I. G. Farbenind. A.-G.—See B., 1927, 647.

Colour reactions of santonin. L. Ekkert (Pharm. Zentr., 1927, **68**, 545—546).—The colour changes produced when 1 and 2 c.c. of a 1% alcoholic santonin solution are mixed with 4 drops of 1% furfuraldehyde solution and 0·5—3 and 1—6 c.c. o concentrated sulphuric acid, are tabulated. There is no necessity to heat the mixture on the water-bath (cf. Thater, A., 1898, ii, 59). If a 1% dextrose or lævulose solution is used instead of furfuraldehyde the coloration is garnet-brown to garnet-red. H. Burton.

Selective reduction of furfuracrolein [furfuracraldehyde] by means of platinum oxide-

platinum-black and hydrogen. XVI. R. H. Bray and R. Adams (J. Amer. Chem. Soc., 1927, 49, 2101—2106; cf. this vol., 552).—Furfuracraldehyde is not reduced by hydrogen in presence of platinum oxide–platinum-black unless a promoter, such as a ferrous salt, is present, when 4·3—4·4 mols. of hydrogen are absorbed, and the chief product is *tetrahydrofurylpropyl alcohol*, b. p. 106—107°/2 mm., 221°/747 mm., n_D^{25} 1·4540, d_{20}^{20} 1·0032 (3 : 5-*dinitrobenzoate*, m. p. 65·5—66°; *acetate*, b. p. 99°/2 mm., 228·5—229°/750 mm., n_D^{25} 1·4380, d_{20}^{20} 1·0207), together with αδ-*dihydroxy*-n-*heptane*, b. p. 126·5—128·5°/4 mm., 240—245°/750 mm., n_D^{25} 1·4510, d_{20}^{20} 0·9559 (α-*naphthylurethane*, m. p. 81—82°; *diacetate*, b. p. 113—113·5°/1 mm., 249—252°/748 mm., n^{23} 1·4268, 0·9934). If the reduction is interrupted when about 3 mols. of hydrogen have been absorbed, the reaction mixture contains *furylpropyl alcohol*, b. p. 90—91°/4 mm., 201—208°/747 mm., n^{25} 1·4760, d_{20}^{20} 1·0613, becoming yellow when kept (α-*naphthylurethane*, m. p. 49°; *acetate*, b. p. 92°/2 mm., 217—218°/747 mm., n_D^{25} 1·4553, 1·0601, becoming yellow when kept), and *tetrahydrofurylallyl alcohol*, b. p. 100—101°/4 mm., n_D^{25} 1·4675, d_{20}^{20} 1·0317, becoming red when kept (*acetate*, b. p. 90—91°/2 mm., n^{25} 1·4468, d_{20}^{22} 1·0374, becoming yellow-orange when kept). In presence of zinc acetate the reduction ceases when 1 mol. of hydrogen has been absorbed, and the product is *furylallyl alcohol*, b. p. 108—110°/4 mm., n_D^{27} 1·5520, d^{20} 1·1439, resinifying when kept (α-*naphthylurethane*, m. p. 93—93·5°). F. G. Willson.

Halogeno- and hydroxy-derivatives of 2-keto-dihydro- and 2-ketohexahydro-indole-3-propionic acid, and of 2-ketohexahydrobenzfuran-3-propionic acid. E. C. Kendall and A. E. Osterberg (J. Amer. Chem. Soc., 1927, 49, 2047—2060; cf. A., 1926, 734).—Treatment of 2-keto-2 : 3 : 4 : 5 : 6 : 7-hexahydrobenzfuran-3-propionic acid with hydrobromic acid and bromine affords 3-*bromo*-4-*hydroxy*-2-*keto*-*octahydrobenzfuran*-3-*propionic acid* (I), m. p. 147°, together with a little of the corresponding δ-*lactone*, m. p. 144°, the latter being obtained when a solution of (I) in xylene is boiled, or when the sodium salt of the above (hexahydro-) acid is brominated in aqueous sodium carbonate. When the sodium salt of (I) is boiled with 2 mols. of aqueous sodium hydroxide, it is converted into the γ-*lactone*, m. p. 146°, of 3 : 4-*dihydroxy*-2-*keto*-*octahydrobenzfuran*-3-*propionic acid* (II), m. p. 164°. When the latter is warmed with aqueous sodium hydroxide, it forms a disodium salt, owing to fission of the furan ring. This ring is again closed when the disodium salt is treated with 1 mol. of acid, and the solution on boiling reverts to the lactone form. When) is heated with aqueous sodium hydroxide at 200° in hydrogen, it yields *trans*-*cyclo*hexane glycol, together with succinic and valeric acids. Treatment of -ketohexahydroindole-3-propionic acid with hydrobromic acid and bromine affords, analogously, -*bromo*-4-*hydroxy*-2-*keto*-*octahydroindole*-3-*propionic acid* (III), m. p. 156°, whilst bromination of the ium salt in aqueous solution yields the δ-*lactone*, p. 53°, of (III). Treatment of (III) with aqueous ium hydroxide yields 3 : 4-*dihydroxy*-2-*keto*-*octahydroindole*-3-*propionic acid*, (IV), m. p. 180°, converted by boiling dilute mineral acid into the γ-*lactone*, m. p. 206°. The latter is also obtained from the above bromo-acid by treatment with dilute aqueous sodium hydroxide. Treatment of 2-ketohexahydrobenzfuran-3-propionic acid with sodium hydroxide at 200° in hydrogen affords *cyclohexadieneglutaric acid*, m. p. 219°. At 170°, (IV) yields similarly an *indole* derivative, m. p. 132°, together with succinic and acetic acids and, probably, 2-amino*cyclo*hexanol. 2-Ketodihydroindole-3-propionic acid is not attacked by sodium hydroxide at 200°, but the 3-hydroxy- and 5 : 7-di-iodo-3-hydroxy-derivatives of this substance yield, on similar treatment, aniline and 2 : 4-di-iodoaniline, respectively. A *dimethyl* derivative, m. p. 140°, of 5 : 7-dibromo-3-hydroxy-2-ketodihydroindole is described. The three bromine derivatives of 2-ketohexahydroindole-3-propionic acid previously described (*loc. cit.*) are now regarded as the 5-bromo-, 5 : 7-dibromo-, and 3 : 5 : 7-tribromo-derivatives. F. G. Willson.

Catalytic oxidations in aqueous solution. I. Oxidation of furfuraldehyde. N. A. Milas (J. Amer. Chem. Soc., 1927, 49, 2005—2011).—Fumaric acid is obtained in 77·8% yield by adding furfuraldehyde (20 g.) gradually to a solution of sodium chlorate (46 g.) in water (100 c.c.) containing vanadium pentoxide (0·2 g.) at 70—75°, and maintaining the mixture at this temperature for 12·5 hrs. after the vigorous reaction has subsided. Maleic semialdehyde is also formed together with an *acid*, $C_5H_4O_5$ (*barium* salt $+1H_2O$). Pyromucic acid similarly affords fumaric and oxalic acids. In presence of osmium tetroxide, furfuraldehyde and pyromucic acid are oxidised by aqueous sodium chlorate, with formation of *i*-tartaric acid and some oxalic acid. F. G. Willson.

Isomerism of the oximes. XXXI. Furfuraldoximes and 2-methoxy- and 4-methoxy-1-naphthaldoximes. O. L. Brady and R. F. Goldstein (J.C.S., 1927, 1959—1964).—The furfuraldoximes are intermediate in stability between benzaldoximes and aliphatic aldoximes; the α-oxime is partly converted by hot solvents into the β-oxime, which is much more stable than β-benzaldoxime. 2- and 4-Methoxy-1-naphthaldehydes form only α-oximes, which on methylation give a mixture of *N*- and *O*-ethers, the 4-methoxy-compound yielding equal proportions, the 2-isomeride larger amounts of *N*-ether.

α-Furfuraldoxime, m. p. 75—76° (*acetate*, m. p. 34—35°; benzoate, m. p. 138—139°), is obtained from furfuraldehyde, hydroxylamine hydrochloride, and aqueous sodium hydroxide under specified conditions. When boiled for 4 hrs. in benzene it gives a mixture of α- and β-oximes, m. p. 47—48°. The β-oxime, m. p. 91—92°, obtained by the action of hydroxylamine hydrochloride and sodium acetate in aqueous alcohol on furfuraldehyde, is converted by acetic anhydride into a nitrile, which is hydrolysed to pyromucic acid.

α-2-*Methoxy*-1-*naphthaldoxime*, m. p. 154—155° [*acetate*, m. p. 79—80°; *hydrochloride*, m. p. 145—147° (decomp.)], is converted by sodium ethoxide and methyl iodide into a separable mixture of 2-*methoxy*-N-*methyl*-1-*naphth*-α-*aldoxime*, m. p. 118—119° or 88—89° ($+H_2O$), and the O-*ether*, m. p. 65°, which

is also obtained from *O*-methylhydroxylamine and the aldehyde. 4-*Methoxy*-1-*naphthaldehyde*, obtained from 4-hydroxy-1-naphthaldehyde and methyl sulphate, gives an α-*oxime*, m. p. 107—108° [*acetate*, m. p. 102°; *hydrochloride*, m. p. 144—145° (decomp.); N-*methyl ether*, dimorphic, m. p. 158—159°; O-*ether*, m. p. 38—39°]. C. HOLLINS.

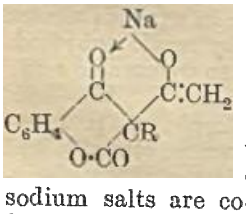
Action of diazonium salts on pyrones and their parent substances. I. R. T. MULLEN and W. H. CROWE (J.C.S., 1927, 1751—1753).—Ethyl acetonedioxalate couples with benzenediazonium chloride to give *ethyl dibenzeneazoacetonedioxalate*, m. p. 130°, and *ethyl dibenzeneazochelidonate*, m. p. 117°, which is also obtained by boiling the former product with alcohol. There is formed during the coupling 2 : 6-*dibenzeneazopyrone*, m. p. 131°, which also results when benzenediazonium chloride reacts with chelidonic acid. From 2 : 6-dimethylpyrone and diacetylacetone, respectively, are obtained 3-*benzeneazo*-2 : 6-*dimethylpyrone*, m. p. 92°, and the 3 : 5-*dibenzeneazo*-derivative, m. p. 150°. C. HOLLINS.

Microchemistry of coumarin. C. VAN ZIJP (Pharm. Weekblad, 1927, 64, 841—844).—On adding a few particles of mercuric chloride to a drop of a solution containing coumarin, needles begin to form in and spread through the liquid. Addition of a trace of Congo-red before that of the mercuric chloride prevents the separation of coumarin, which might be mistaken for the reaction product. S. I. LEVY.

Nitration of coumarin. B. B. DEY and P. KRISHNAMURTHI (J. Indian Chem. Soc., 1927, 4, 197—199).—Coumarin is nitrated (cf. Morgan and Micklethwait, J.C.S., 1904, **85**, 1233) 93% in position 6 and 7% in position 8. Whilst 5-nitrocoumaric acid readily reverts to 6-nitrocoumarin, 3-nitrocoumaric acid is comparatively stable. 3-*Nitrocoumaric acid*, m. p. 149° (decomp.), gives 8-nitrocoumarin, m. p. 187°, when boiled with dilute hydrochloric acid, and 3-nitrosalicylic acid when oxidised with alkaline potassium permanganate (cf. Miller and Kinkelin, A., 1889, 989). M. p. of different mixtures of 6- and 8-nitrocoumarin are given; an equimolecular mixture melts sharply at 140—141°. G. A. C. GOUGH.

Synthesis of coumaryl-4-acetic acid. B. D. LIMAYE (J. Indian Chem. Soc., 1927, 4, 159).—*Coumaryl*-4-*acetic acid*, m. p. 170° (decomp.), prepared from phenol and acetonedicarboxylic acid in sulphuric acid solution (Dey and Row, A., 1925, i, 149), when heated above its m. p. gives carbon dioxide and 4-methylcoumarin. G. A. C. GOUGH.

Preparation of 4-hydroxycoumarin derivatives. I. M. HEILBRON and D. W. HILL (J.C.S., 1927, 1705—1708).—When *o*-acetoxybenzoyl chloride is condensed with α-substituted ethyl sodioacetoacetates in ether, the products are sodium salts convertible on acidification into 4-hydroxycoumarins with elimination of the acetyl group. This distinction from 4-hydroxy-3-acetylcoumarin itself suggests that the sodium salts are co-ordinated compounds (annexed formula) stable only in non-aqueous media.



4-*Hydroxy*-3-*methylcoumarin*, m. p. 230° (*methyl ether*, m. p. 89·5°), 4-*hydroxy*-3-*benzylcoumarin*, m. p. 205°, and 4-*hydroxy*-3-*benzoylcoumarin*, m. p. 144°, are described. 4-Methoxycoumarin, m. p. 124°, is prepared by methylation of 4-hydroxycoumarin with methyl sulphate or, better, with diazomethane. 4 : 7-Dimethoxycoumarin, m. p. 155—156°, is similarly obtained (Sonn, A., 1918, i, 31). C. HOLLINS.

Pyrylium salts and *spiro*dipyrans. II. Condensation products from methyl ethyl ketone and *o*-hydroxyaldehydes. S. C. DE (J. Indian Chem. Soc., 1927, 4, 137—140; cf. A., 1926, 1254—1255).—Salicylaldehyde and methyl ethyl ketone condense in ethereal solution in the presence of hydrogen chloride, giving 2-*o*-*hydroxystyryl*-3-*methylbenzopyrylium chloride*, m. p. 198° (red *ferric* salt and *perchlorate* described), which is converted by aqueous ammonia into the ψ-base, 3-*methyl*spiro*dibenzopyran*, m. p. 80°. Resorcylaldehyde and methyl ethyl ketone similarly yield 7-*hydroxy*-2-2′ : 4′-*dihydroxystyryl*-3-*methylbenzopyrylium chloride*, m. p. 290°, which in turn gives 7 : 7′-*dihydroxy*-3-*methyl*spiro*dibenzopyran*. β-Naphthol-1-aldehyde and methyl ethyl ketone yield 2-*o*-hydroxy-α-benzostyryl-3-methyl-β-naphthapyrylium chloride, unmelted at 290°, and 3-*methyl*spiro*dinaphthapyran*, m. p. 201°. All three ψ-bases are converted into the corresponding pyrylium chloride by hydrochloric acid. G. A. C. GOUGH.

Synthesis of anthocyanins. III. A. ROBERTSON and R. ROBINSON (J.C.S., 1927, 1710—1717).—The possibility of nuclear alkylation, induced by inorganic catalysts, during anthocyanidin syntheses renders desirable alternative routes not involving demethylation. Attempts to prepare monoacetyl or monocarbomethoxy-derivatives of phloroglucinaldehyde were unsuccessful, but addition of acetic anhydride to a mixture of the aldehyde in *N*-sodium hydroxide and ether at −5° yields O-*diacetylphloroglucinaldehyde*, m. p. 102—103°, which is probably 4 : 6-diacetoxysalicylaldehyde. Cautious benzoylation of phloroglucinaldehyde at −5° in presence of potassium hydroxide gave O-*benzoylphloroglucinaldehyde*, m. p. 198—200° (becoming pink at 155°, dark at 185°, and brick-red at 195°), which is either the 2- or the 4-benzoyloxy-compound. This is condensed with *p*-*O*-tetra-acetyl-β-glucosidoxy-ω-methoxyacetophenone in ethereal hydrogen chloride after hydrolysis with methyl-alcoholic ammonia and treatment with hydrochloric acid to form 4′-β-*glucosidoxy*-5 : 7-*dihydroxy*-3-*methoxyflavylium chloride*, $C_{22}H_{23}O_{10}Cl,H_2O$, m. p. 130—131° [*picrate*, m. p. 186—188° (decomp.)], which closely resembles a natural monoglucosidic anthocyanin. The corresponding sugar-free 5 : 7 : 4′-*trihydroxy*-3-*methoxyflavylium chloride* is obtained by hydrolysis of the glucosido-compound and by synthesis from *p*-hydroxy-ω-methoxyacetophenone and *O*-triacetylphloroglucinaldehyde. The 3 : 5 : 7-*trihydroxy*-4′-*methoxyflavylium chloride* is prepared by hydrolysis of the condensation product from anisoylcarbinol and *O*-triacetylphloroglucinaldehyde.

The sodium carbonate colour reactions indicate that callistephin and other pelargonidin anthocyanins are not 4′-glucosides, callistephin being probably a

3-glucoside, and that partial demethylation of pelargonidin chloride 3 : 4′-dimethyl ether with hydriodic acid yields the 4′-monomethyl ether (above).

C. HOLLINS.

Dissociation into free radicals of substituted dixanthyls. IV. Dixanthyl and dixanthyl-9 : 9′-dicarboxylic acid. J. B. CONANT and B. S. GARVEY (J. Amer. Chem. Soc., 1927, 49, 2080—2088; cf. A., 1926, 842).—Dixanthyl reacts with bromine in carbon disulphide, with formation of xanthyl bromide perbromide (cf. Gomberg and Cone, A., 1910, i, 869). It is converted into sodium xanthyl when treated with sodium–potassium alloy or 40% sodium amalgam in ether, the sodium xanthyl being also obtained from sodium–potassium alloy and xanthan. Dixanthyl absorbs oxygen at 150° in *p*-dibromobenzene solution, or without solvent, with formation of xanthone, whilst it is hydrolysed to xanthanol by treatment with concentrated sulphuric acid. Analogy is drawn between these reactions and those of addition to an ethylenic linking. Sodium xanthyl and carbon dioxide afford *xanthanoic acid*, m. p. 222—223°, the *methyl* ester of which, m. p. 85—86°, is converted by bromine in carbon disulphide into a *perbromide*, $C_{15}H_{11}O_3Br_3$, red, m. p. 158—159° (decomp.), and this, on reduction with vanadous chloride, yields *dixanthyl-9 : 9′-dicarboxylic acid*, decomp. 155° after darkening from 125° [*methyl* ester, m. p. 85—110° (indefinite)]. The latter is obtained by treating dixanthylene first with sodium–potassium alloy, and then with carbon dioxide. It absorbs oxygen slowly in aqueous alkaline solution, and in *p*-dibromobenzene, with production of xanthone, the methyl ester being similarly oxidised in *p*-dibromobenzene. Both the acid and the methyl ester exhibit reversible colour changes when heated in solvents above 100°, the temperatures at which the colours appear indicating that the carboxyl and carbomethoxyl groups have slightly greater power of promoting dissociation than primary alkyl groups. F. G. WILLSON.

Greenish-blue to green vat dyes of the thioindigo series. R. HERZ and others.—See B., 1927, 697.

Stereochemistry of tervalent nitrogen and heterocyclic nitrogen compounds. L. ORTHNER (Annalen, 1927, 456, 225—252).—4-Aminopiperidine, b. p. 65°/18 mm. [*dipicrate*, m. p. 252—253° (decomp.)], and carbon disulphide in cold ether yield *α-piperidyldithiocarbamate*, $C_5H_{10}N{\cdot}NH{\cdot}CS{\cdot}SH$, m. p. 88—89°, which in aqueous solution passes into the β-*dithiocarbamate*, m. p. 250°. Both dithiocarbamates give piperidine when treated with iodine or mercuric chloride. The two dithiocarbamates obtained from α-4-amino-2 : 2 : 6-trimethylpiperidine (Harries, A., 1897, i, 293), when treated with iodine, yield the same thiocarbamide, m. p. 205—206° (cf. Harries, A., 1919, i, 131). 4-amino-2 : 2 : 6-trimethylpiperidine (*dipicrate*, m. p. —°) is converted by carbon disulphide in cold ether into β-a-2 : 2 : 6-*trimethylpiperidyldithiocarb-* , m. p. 183—184°, which in alcoholic solution hen heated with water gives the β-*b*-dithio- m. p. 197°, of Harries. Iodine converts these compounds into the same thiocarbamide, m. p. 166—167°, whilst treatment with mercuric chloride regenerates the original amine.

N-Methyltriacetonalkamine, m. p. 60°, b. p. 125°/12 mm., obtained from triacetonalkamine and formaldehyde, is oxidised by chromic–acetic acid to *N-methyltriacetonamine* (1 : 2 : 2 : 6 : 6-*pentamethyl*-4-*piperidone*), b. p. 122°/23 mm., also synthesised from methylamine and phorone. Reduction of *N-methyltriacetonamineoxime*, m. p. 143°, with sodium and amyl alcohol gives 4-*amino*-1 : 2 : 2 : 6 : 6-*pentamethylpiperidine*, b. p. 99—100°/14 mm. (*dipicrate*, m. p. 248°), converted by carbon disulphide in ether into α-1 : 2 : 2 : 6 : 6-*pentamethylpiperidyldithiocarbamate*, m. p. 125°. This, in aqueous solution, passes into the β-*dithiocarbamate*, m. p. 173—174°.

The relationships of the above isomeric dithiocarbamates, and those obtained by Pauly (A., 1902, i, 560) from aminopyrrolidines, are discussed, as is also the stereochemistry of substituted *cyclo*pentanes.

H. BURTON.

Manufacture of *O*-acyl derivatives of 4-hydroxy-2 : 6-dimethylpiperidine-3-carboxylic acid esters. I. G. FARBENIND. A.-G.—See B., 1927, 669.

Halogeno- and hydroxy-derivatives of 2-keto-dihydro- and 2-ketohexahydro-indole-3-propionic acid etc. E. C. KENDALL and A. E. OSTERBERG.—See this vol., 973.

Production of an iodopyridine. A. BINZ and others.—See B., 1927, 669.

Factors controlling the formation of some derivatives of quinoline. Substitution in the quinoline series. E. ROBERTS and E. E. TURNER (J.C.S., 1927, 1832—1857).—Combes' synthesis of 2 : 4-dimethylquinolines from the condensation products, $NAr{:}CMe{\cdot}CH_2{\cdot}COMe$ or $NHAr{\cdot}CMe{:}CH{\cdot}COMe$, of arylamines and acetylacetone is affected greatly by substituents in the aryl group, this being due in part to directive influence and in part to diminution of basicity of the nitrogen atom. Cyclisation readily occurs if a strongly *o-p*-directing substituent is present *meta* to the nitrogen atom, whilst of the three chloro-compounds only the *meta* gives a quinoline, and the 3 : 4-dichloro-compound may be cyclised, but not the 2 : 4-, 2 : 5-, and 3 : 5-derivatives. In the Skraup and Doebner–Miller syntheses *m*-substituted anilines give 5-substituted quinolines if the substituent is *m*-directing, 7- or a mixture of 5- and 7-substituted quinolines if the substituent is *o-p*-directing. The Beyer synthesis, from arylamine, paraldehyde, and acetone, like the Combes synthesis, is influenced by steric factors not affecting the Skraup and Doebner–Miller reactions, the difference being apparently due to the absence of a γ-substituent in the last two cases.

The nitration of 2 : 4-dimethylquinoline and its chloro-derivatives indicates that the quinoline molecule exhibits 5 : 8-reactivity, independent of the orienting effect of chlorine, methyl, or nitro-substituents, similar to the α-reactivity of naphthalene. The ring-nitrogen atom appears to have no power as a directive influence. Chlorine atoms show the usual *o-p*-directing influence. The above facts and others related to them are discussed and new formulæ suggested for quinoline, *iso*quinoline, pyridine, and thiazoles, on the basis of Thiele's conception.

When dibenzoylmethane is boiled with freshly distilled aniline for 9 hrs. the products are benzanilide, m. p. 161°, and phenyl α-anilinostyryl ketone, NHPh·CPh:CH·COPh, m. p. 102—103°, identical with Watson's product (J.C.S., 1903, 83, 1326) from aniline and benzoylphenylacctylene. The formation of acetanilide from acetylacetone and aniline (Turner, *ibid.*, 1917, 111, 1) thus indicates that the anils of acetylacetone are to be formulated as β-arylaminopropenyl methyl ketones. The *p*-toluidine compound, m. p. 68—69°, not 39—40° (Combes), is cyclised quantitatively by concentrated sulphuric acid at 100°, giving 2 : 4 : 6-trimethylquinoline, m. p. 43—45° (Pfitzinger's compound, A., 1888, 1207, of m. p. 63—64°, is the hydrate). The following substituted β-anilinopropenyl methyl ketones are described: o-*chloro*-, m. p. 66—67°; p-*chloro*-, m. p. 60—61°; m-*chloro*-, m. p. 42°, b. p. 187°/13 mm.; 2 : 4-*dichloro*-, m. p. 100·5°; 2 : 5-*dichloro*-, m. p. 46°, b. p. 190—200°/15 mm.; 3 : 5-*dichloro*-, oily; 3 : 4-*dichloro*-, m. p. 73°; o-*methoxy*-, m. p. 51—52·5°; 3-*chloro*-6-*acetamido*-. 3 : 4-Dichloro-6-nitroaniline does not condense with acetylacetone even at 200°. Salicylidene derivatives of the substituted anilines melt as follows: m-*chloro*-, 99°; 2 : 4-*dichloro*-, 90·5°; 2 : 5-*dichloro*-, 107°; 3 : 4-*dichloro*-, 113°. 3 : 5-Dichloroaniline, m. p. 65°, is obtained by reduction of 3 : 5-dichloronitroaniline prepared from 2 : 6-dichloro-4-nitroaniline. Attempts to prepare 2 : 3-dichloroaniline were unsuccessful. 7-*Chloro*-2 : 4-*dimethylquinoline*, m. p. 46·5—48·5° [*hydrate*, m. p. 61°; *hydrochloride*, m. p. 277° (decomp.); *sulphate*; *dichromate*; silver nitrate additive *compound*, m. p. 197° (decomp.)], and 6 : 7-*dichloro*-2 : 4-*dimethylquinoline*, m. p. 119—120° (*hydrochloride*, m. p. 235°; *chloroaurate*; *sulphate*; *dichromate*; silver nitrate *compound*, m. p. 218—219°), are obtained from the corresponding anils by Combes' method.

Beyer's method is applied to the synthesis of the following 2 : 4-dimethylquinolines: 8-*chloro*-, m. p. 74°, b. p. 185°/15 mm.; 6-*chloro*-, m. p. 98—99° (*hydrate*, m. p. 84—85·5°; *dichromate*); 7-chloro- (see above); 6 : 8-*dichloro*-, m. p. 148—148·5°; 5 : 8-*dichloro*-, m. p. 117—118·5°; 5 : 6- and 6 : 7-dichloro- (6 : 7-isomeride isolated); 5 : 7-*dichloro*-, m. p. 84—86° (together with a *substance*, m. p. 168—169°, convertible by ammonia into a second *substance*, m. p. 69—70°); and 5 : 6 : 8-*trichloro*-, m. p. 113—114°. *o*- and *p*-Nitroanilines give by the Beyer method *substances*, m. p. 145—147° and 159—162°, respectively; *m*-nitroaniline is unchanged, whilst 3-chloro- and 3 : 4-dichloro-6-nitroanilines give tars.

2 : 4-*Dichloroacetophenone*, m. p. 33—34°, b. p. 140—150°/15 mm., fails to react with alcoholic ammonia at 180°, and other attempts to synthesise 4-chloro-2-aminoacetophenone were unsuccessful. 3 : 4-*Dichloroacetophenone*, m. p. 76°, b. p. 135°/12 mm., prepared from *o*-dichlorobenzene, yields on nitration with nitric acid (*d* 1·5) at 30—40° the 2-*nitro*-derivative, m. p. 100—102°, reduced by iron, water, and a little ferric chloride to 3 : 4-*dichloro*-2-*aminoacetophenone*, m. p. 154—156°. This amine condenses with acetone to give 6 : 7-dichloro-2 : 4-dimethylquinoline identical with the product obtained by the Combes and Beyer reactions.

Nitration of 2 : 4-dimethylquinoline with mixed acid gives only 8-*nitro*-2 : 4-*dimethylquinoline* (this fact showing the steric effect of the 4-methyl group), m. p. 118—119°, the constitution of which is proved by reduction to 8-*amino*-2 : 4-*dimethylquinoline*, m. p. 89—92° (*sulphate* and *picrate* described), and conversion into 8-chloro-2 : 4-dimethylquinoline previously synthesised. 8-*Chloro*-5-*nitro*-2 : 4-*dimethylquinoline*, m. p. 107—108° (*sulphate* described), obtained by nitration, is reduced to the *amine*, m. p. 170—172°, and converted into 5 : 8-dichloro-2 : 4-dimethylquinoline, m. p. 117—118°. Nitration of 6-chloro-2 : 4-dimethylquinoline yields the 5-*nitro*-compound, m. p. 132—133° (*sulphate* described), which is reduced to the *amine*, m. p. 131—133°, and converted into 5 : 6-*dichloro*-2 : 4-*dimethylquinoline*, m. p. 119—120° (*hydrochloride* described). From 7-*chloro*-8-*nitro*-2 : 4-*dimethylquinoline*, m. p. 189—189·5°, obtained by nitration of the 7-chloro-compound, there are prepared the 8-*nitro*-7-*piperidino*-compound, m. p. 168—170°, the 7-*chloro*-8-*amino*-compound, m. p. 51—53°, and 7 : 8-*dichloro*-2 : 4-*dimethylquinoline*, m. p. 104—104·5°. 6 : 8-Dichloro-2 : 4-dimethylquinoline gives on nitration the 5(?)-*nitro*-derivative, m. p. 122—123°, reducible to the *amine*, m. p. 194—195°. From 5 : 8-dichloro-2 : 4-dimethylquinoline are obtained the 6-*nitro*-compound, m. p. 155—157°, and the corresponding *amine*, m. p. 192—193°, which is converted into 5 : 6 : 8-trichloro-2 : 4-dimethylquinoline, m. p. 111—112·5°. Nitration of 6 : 7-dichloro-2 : 4-dimethylquinoline gives the 8(?)-*nitro*-compound, m. p. 197°. Whilst 7-chloro-8-nitro-2 : 4-dimethylquinoline reacts with piperidine, the 6-chloro-5-nitro-isomeride does not. This appears to throw doubt on the conclusions of Borsche (cf., *e.g.*, A., 1914, i, 28).

Chlorination of 8-chloro-2 : 4-dimethylquinoline in presence of glacial acetic acid and sodium acetate yields a *tetrachloro*-2 : 4-*dimethylquinoline*, m. p. 150—152°, different from the *isomerides*, m. p. 75·5—81° and 157—158°, respectively, obtained by chlorination of 6-chloro- and 5 : 6-dichloro-2 : 4-dimethylquinolines. A *trichloro*-compound, m. p. 195°, is obtained by chlorination of 7-chloro-2 : 4-dimethylquinoline, the 5 : 8- and 6 : 8-dichloro-compounds give the same *pentachloro*-2 : 4-*dimethylquinoline*, m. p. 127—128°. All these derivatives contain mobile (negative) chlorine, indicating chlorination in the methyl groups.

C. Hollins.

6-Hydroxy-o-β-acrylic acids (*cis*- and *trans*-) and their derivatives. B. B. Dey and T. Seshadri (J. Indian Chem. Soc., 1927, 4, 189—196; cf. J.C.S., 1919, **115**, 531).—The substituted *cis*-6-hydroxyquinolyl-5-β-acrylic acids, produced by the action of alkalis on quinolino-6 : 5-α-pyrones, rapidly revert to the original pyrone on keeping. Whilst the corresponding *trans*-acids cannot be produced by the action of aqueous alkali, alkali ethoxide, or molten potassium hydroxide on the pyrones, they may be obtained from the pyrones by successive treatment with sodium sulphite and sodium hydroxide (Dey and Row, A., 1924, i, 538). The acids are stable substances, soluble in acids and alkalis without fundamental change. When warmed with concentrated sulphuric acid they afford the origin-

pyrones, and above their m. p. lose carbon dioxide, giving the corresponding hydroxyquinolylcthylenes. Heat converts their ethyl esters into the original pyrone and ethyl alcohol (*trans*-elimination). The esters undergo hydrolysis to the parent acids. The following are described: cis-6-*hydroxy*-2-*methylquinolyl*-5-β-*acrylic acid*, decomposing at about 175° to give quinolino-6 : 5-pyrone (*silver* salt); trans-6-*hydroxyquinolyl*-5-β-*acrylic acid*, m. p. 220° (decomp.) [*hydrochloride*; *silver*, *copper*, *ferric*, *lead* salts; *methyl* and *ethyl* esters, m. p. 202° (decomp.) and 198—199° (decomp.) respectively]; 6-*hydroxyquinolyl*-5-*ethylene*, m. p. 256—257°; trans-6-*hydroxy*-2-*methylquinolyl*-5-β-*acrylic acid*, m. p. 193° (decomp.) [*hydrochloride*; *silver* salt; *ethyl* ester, m. p. 146° (decomp.)]; 6-*hydroxy*-2-*methylquinolyl*-5-*ethylene*, m. p. 241—242°; trans-6-*hydroxy*-8-*methylquinolyl*-5-β-*acrylic acid*, m. p. 195° (decomp.), (*silver* salt; *ethyl* ester, m. p. 165—166°); 6-*hydroxy*-8-*methylquinolyl*-5-*ethylene*, m. p. 244—245° (*hydrochloride*). G. A. C. GOUGH.

***Bz*-Tetrahydroquinazolines.** P. C. MITTER and A. BHATTACHARYA (J. Indian Chem. Soc., 1927, **4**, 149—157; cf. Pinner, "Die Iminoaether," p. 292).—Condensation of substituted acetyl*cyclo*hexanones with benzamidine hydrochloride in the presence of piperidine yields substituted tetrahydroquinazolines (33—47% yield). Quantitative condensations occur between benzamidine and substituted *cyclo*hexanonecarboxylic esters in the presence of sodium ethoxide. The following are described: from acetyl*cyclo*hexanone and benzamidine, 2-*phenyl*-4-*methyl*-Bz-*tetrahydroquinazoline*, m. p. 103° (*picrate*, m. p. 144—145°); from *p*-toluamidine and acetyl*cyclo*hexanone, 2-p-*tolyl*-4-*methyl*-Bz-*tetrahydroquinazoline*, m. p. 129—130°; from acetyl*cyclo*hexanone and guanidine nitrate, 2-*amino*-4-*methyl*-Bz-*tetrahydroquinazoline*, m. p. 177—178°; from 6-acetyl-2-methyl*cyclo*hexanone and benzamidine, 2-*phenyl*-4 : 8-*dimethyl*-Bz-*tetrahydroquinazoline*, m. p. 84—85°; from 6-acetyl-2-methyl*cyclo*hexanone and *p*-toluamidine, 2-p-*tolyl*-4 : 8-*dimethyl*-Bz-*tetrahydroquinazoline*, m. p. 95°; from 6-acetyl-2-methyl*cyclo*hexanone and guanidine nitrate, 2-*amino*-4 : 8-*dimethyl*-Bz-*tetrahydroquinazoline*, m. p. 103—104°; from 6-acetyl-3-methyl*cyclo*hexanone and benzamidine, 2-*phenyl*-4 : 7-*dimethyl*-Bz-*tetrahydroquinazoline*, m. p. 111—112°; from 6-acetyl-3-methyl*cyclo*hexanone and *p*-toluamidine, 2-p-*tolyl*-4 : 7-*dimethyl*-Bz-*tetrahydroquinazoline*, m. p. 135°; from ethyl *cyclo*hexanone-2-carboxylate and benzamidine, 4-*hydroxy*-2-*phenyl*-Bz-*tetrahydroquinazoline*, m. p. 238°; from ethyl *cyclo*hexanone-2-carboxylate and *p*-toluamidine, 4-*hydroxy*-2-p-*tolyl*-Bz-*tetrahydroquinazoline*, m. p. 255—257°; from ethyl *cyclo*hexanone-2-carboxylate and guanidine nitrate, 2-*amino*-4-*hydroxy*-Bz-*tetrahydroquinazoline*, unmelted at 300°; from ethyl -methyl*cyclo*hexanone-6-carboxylate and benzamidine, 4-*hydroxy*-2-*phenyl*-8-*methyl*-Bz-*tetrahydroquinazoline*, m. p. 200°; from the last-named ester and *p*-toluamidine, 4-*hydroxy*-2-p-*tolyl*-8-*methyl*-Bz-*tetrahydroquinazoline*, m. p. 231—133° (? 233°); from the ester and guanidine nitrate, 2-*amino*-4-*hydroxy*-8-*methyl*-Bz-*tetrahydroquinazoline*, unmelted at 300°; from ethyl 3-methyl*cyclo*hexanone-6-carboxylate and benzamidine, 4-*hydroxy*-2-*phenyl*-7-*methyl*-Bz-*tetrahydroquinazoline*, m. p. 214—216°; from the last-named ester and *p*-toluamidine, 4-*hydroxy*-2-p-*tolyl*-7-*methyl*-Bz-*tetrahydroquinazoline*, m. p. 254—256°; from the ester and guanidine nitrate, 2-*amino*-4-*hydroxy*-7-*methyl*-Bz-*tetrahydroquinazoline*, unmelted at 300°; from hydroxymethylene*cyclo*hexanone and benzamidine, 2-*phenyl*-Bz-*tetrahydroquinazoline*, m. p. 52—53°. Reduction of 2-phenyl-4-methyl-*Bz*-tetrahydroquinazoline, with sodium and alcohol, yields a small amount of a *substance* giving a *picrate*, m. p. 240°. G. A. C. GOUGH.

ψ-Thiohydantoins and α-mercapto-acids from higher fatty acids. B. H. NICOLET and L. F. BATE (J. Amer. Chem. Soc., 1927, **49**, 2064—2066).—Treatment of the α-bromo-derivatives of hexoic, lauric, myristic, palmitic, and stearic acids with alcoholic thiocarbamide affords the following corresponding ψ-thiohydantoins: 5-*butyl*-, m. p. 183°; 5-*decyl*-, m. p. 182·5°; 5-*dodecyl*-, m. p. 180·5°; 5-*tetradecyl*-, m. p. 176·5°, and 5-*hexadecyl*-ψ-*thiohydantoin*, m. p. 175°. Mixtures of these show little depression of m. p. On hydrolysis with sodium hydroxide in 85% alcohol, they yield the corresponding α-thiol acids: α-*thiolhexoic*, b. p. 234°; -*lauric*, m. p. 59°; -*myristic*, m. p. 66°; -*palmitic*, m. p. 72—73°, and -*stearic acid*, m. p. 80°. Treatment of α-thiol-lauric acid with iodine in acetic acid in presence of sodium acetate affords the corresponding *disulphide*, m. p. 48°, whilst oxidation of α-thiolhexoic acid with potassium chlorate and hydrochloric acid yields α-*carboxy*-n-*amylsulphonic acid*, m. p. 196°. F. G. WILLSON.

Dyes derived from glyoxalinedicarboxylic acid. J. D. TEWARI and S. DUTT (J. Indian Chem. Soc., 1927, **4**, 201—204; cf. A., 1926, 1153).—Glyoxalinedicarboxylic acid condenses with aromatic amino- and hydroxy-compounds in presence of sulphuric acid or stannic chloride giving dyes analogous to phthaleins: *phenol-iminazophthalein*, m. p. 282° (colourless; dissolving in alkalis to pink); *resorcinol-iminazophthalein*, m. p. 267° (decomp.; yellow, dissolving in alkalis to an orange-red solution with green fluorescence); *phloroglucinol-iminazophthalein*, unmelted at 290° (non-fluorescent, red solution with alkalis); *hydroxyquinol-iminazophthalein*, m. p. 258—260° (decomp.); *pyrocatechol-iminazophthalein*; m-*phenylenediamine-iminazophthalein*, unmelted at 290° (yellow solution with green fluorescence in alkalis). G. A. C. GOUGH.

Gold and mercury derivatives of 2-thiolglyoxalines. Mechanism of the oxidation of 2-thiolglyoxalines to glyoxalines. I. E. BALABAN and H. KING (J.C.S., 1927, 1858—1874).—Ethyl 2-thiol-4(5)-methylglyoxaline-5(4)-carboxylate, m. p. 236—239°, is hydrolysed by boiling sodium carbonate solution to the free *acid*, m. p. 240—241° (decomp.), which with alcoholic hydrogen chloride yields *ethyl* 2-*ethylthiol*-4(5)-*methylglyoxaline*-5(4)-*carboxylate*, m. p. 144—145° (+1·5H_2O; *hydrochloride*, oily *chloroaurate*, and *picrate*, m. p. 135—136°), also formed directly from the first-mentioned ester. Hydrolysis of the ethylthiol ester with sodium carbonate gives 2-*ethylthiol*-4(5)-*methylglyoxaline*, m. p. 69—71° (*picrate*, m. p. 136—137°; *chloroaurate*, m. p. 130—131°), and its 5(4)-*carboxylic acid*, m. p. 179—180° [decomp.;

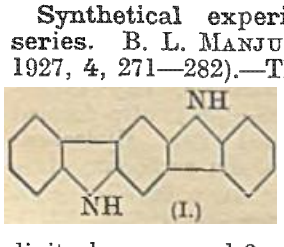
semihydrochloride, m. p. 122—125° (decomp.); *hydrochloride*, m. p. 189—190° (+H_2O, decomp.)]. Ethyl 2-thiol-4(5)-methylglyoxaline-5(4)-carboxylate is oxidised by iodine solution, ferricyanide, or nitrous acid to the *disulphide*, m. p. 222—223°, which is readily reduced again by sulphur dioxide. Alkaline hydrolysis converts the disulphide into 2-thiol-4(5)-methylglyoxaline and its 5(4)-carboxylic acid and ethyl ester; acid hydrolysis gives 2-thiol-4(5)-methylglyoxaline and other products. In each case sulphur dioxide is evolved, the amount being 73% of that required by the equation: $2(RS)_2+2H_2O=SO_2+3R{\cdot}SH+RH$. Oxidation of 2-thiol-4(5)-methylglyoxaline with hydrogen peroxide at 0° to −5° gives the 2-*sulphinic acid*, m. p. 73°, decomposing at 92°. When kept for a few hours the sulphinic acid loses sulphur dioxide, giving 4-methylglyoxaline sulphite. The stable 2-*sulphonic acid*, m. p. about 280° (*ammonium*, *calcium*, and *barium* salts described), is obtained by further oxidation. It is suggested that the desulphurisation of 2-thiolglyoxalines by nitric acid (Wohl and Marckwald, A., 1889, 866) and the hydrolysis of the disulphides proceed by way of the sulphinic acid.

By the action of methyl-alcoholic auric chloride on ethyl 2-thiol-4(5)-methylglyoxaline-5(4)-carboxylate there is obtained the 2-*aurothiol* ester, $(CO_2Et{\cdot}C<^{NH}_{CMe{\cdot}N}>C{\cdot}SAu)_n$, m. p. 252° (decomp.), together with other *substances*, m. p. 254° (decomp.) and 170°. The corresponding 2-*aurothiol acid* could not be obtained by hydrolysis, but was prepared directly from auric chloride and 2-thiol-4(5)-methylglyoxaline-5(4)-carboxylic acid in methyl alcohol. Alcoholic mercuric acetate converts ethyl glyoxaline-4(5)-carboxylate into the 1-*acetoxymercuri*-derivative (shrinks at 222° and is not melted at 300°). Alcoholic mercuric chloride with ethyl 2-thiol-4(5)-methylglyoxaline-5(4)-carboxylate gives the 2-*chloromercurithiol* ester, R·S·HgCl, m. p. 167—168°; with 2-thiol-4(5)-methylglyoxaline-5(4)-carboxylic acid the corresponding 2-*chloromercurithiol acid*, m. p. 257° (decomp.).

The colour reactions of thiolglyoxalines, thiocarbamide, allylthiocarbamide, and ergothioneine from blood are discussed and compared. Thiocarbamides and 2-thioglyoxalines give an intense blue colour with phosphomolybdic acid.

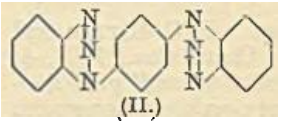
Sodium 2-aurothiol-4(5)-methylglyoxaline-5(4)-carboxylate inhibits growth of tubercle bacilli *in vitro* but does not sterilise, although the virulence is diminished. The toxicity of this compound (0·05 mg. per g. in mice) and of the sodium 2-chloromercurithiol compound (0·005 mg. per g.) is determined; neither has any trypanocidal action. C. Hollins.

Synthetical experiments in the carbazole series. B. L. Manjunath (J. Indian Chem. Soc., 1927, 4, 271—282).—The following compounds were prepared in an attempt to synthesise a molecule (I) composed of 3 benzene and 2 pyrrole rings. 3-op-*Dinitroanilinocarbazole*, m. p. 258°, prepared from chloro-2:4-dinitrobenzene and 3-aminocarbazole, affords 3-*nitro*-o-*aminoanilinocarbazole*, m. p. 256—258° (darkening at 220—250°), when reduced with sodium hydrogen sulphide. The nitroamine is converted by nitrous acid into 1:3-*carbazyl*-5-*nitrobenztriazole*, m. p. 283° (decomp.), which in turn gives 1-(3′-*carbazyl*)-5-*aminobenztriazole*, m. p. 187—190° (*acetyl* derivative, m. p. 292°), on reduction with stannous chloride. Attempts to prepare the amino-derivative of the desired compound by elimination of nitrogen were unsuccessful (cf. A., 1924, i, 1349). Azophenine, prepared by the action of amyl nitrite and hydrochloric acid on an acetic acid solution of 4:6-diamino-1:3-dianilinobenzene, followed by crystallisation of the *product* from xylene, could not be condensed with methylamine or with dimethylamine.



(I.)

1:4-*Di*-o-*nitroanilinobenzene*, m. p. 233°, prepared from *p*-dibromobenzene and *o*-nitroaniline in the presence of nitrobenzene, potassium carbonate, and copper powder at 200°, is reduced by sodium hydrogen sulphide to 1:4-*di*-o-*aminoanilinobenzene*, m. p. 159°, which in turn yields 1:4-*di*-1′-*benztriazolobenzene* (II), m. p. 279°, on treatment with nitrous acid. No individual decomposition product formed in ring closure experiments was identified.


(II.)

3-op-*Diaminoanilinocarbazole*, m. p. 256°, was prepared by reducing the corresponding nitro-compound with sodium hydrogen sulphide. Reduction with stannous chloride causes the elimination of one nitro-group with formation of 3-p-*aminoanilinocarbazole*, m. p. 256°. 1-p-2′:4′-*Dinitroanilinophenylbenztriazole*, m. p. 228°, produced by condensing chloro-2:4-dinitrobenzene with 1-*p*-aminophenylbenztriazole, yields 1-p-2′:4′-*diaminoanilinophenylbenztriazole*, m. p. 155—157°, on reduction with stannous chloride. 2:7-Diaminocarbazole forms a *diacetyl* derivative, m. p. 320° (decomp.), a *dibenzylidene* derivative, m. p. 290°, and a *di-dimethylaminobenzylidene* derivative, m. p. 284°. Attempts to nitrate this diamine or its diacetyl derivative or to replace the amino- by hydroxyl groups, were unsuccessful. 3-p-*Toluenesulphamidocarbazole*, m. p. 227°, gives the *methyl sulphonamide*, m. p. 168°, on treatment with methyl sulphate and sodium hydroxide. It was not found possible to remove the sulphonyl group from this compound. 9-Aminocarbazole condenses with *cyclo*hexanone to give the *hydrazone*, m. p. 96°, from which it was not found possible to remove ammonia to produce an indole ring closure. Attempts to prepare 9-aminohexahydrocarbazole from 9-*nitrosohexahydrocarbazole*, m. p. 61—62°, resulted mainly in the elimination of the nitroso-group. 9-Nitrosohexahydrocarbazole, when reduced with zinc dust and acetic acid in the presence of *cyclo*hexanone, gives 8:9-(1′:2′-cyclo*hexyl*)*tetrahydrocarbazole*, b. p. 230—240°/13 mm., m. p. 83° [*picrate*, m. p. 138° (decomp.)]. The last-named compound could not be dehydrogenated by heating with lead monoxide, but was further reduced electrolytically to 8:9-(1′:2′-cyclo*hexyl*)*hexahydrocarbazole*, b. p. 235—245°/15 mm., m. p. 144° [*hydrochloride*, m. p. 225° (decomp.); *picrate*, m. p. 160°; *methiodide*, m. p. 187° (decomp.)]. Similarly 6-*methylhexahydrocarbazole*, b. p. 230—240°/14 mm., m. p. 43—44° [*picrate*, m. p. 174° (decomp.);

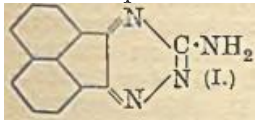
nitroso-derivative, m. p. 71°], gives 6-*methyl*-8 : 9-(1′ : 2′-cyclo*hexyl*)-*tetrahydrocarbazole*, b. p. 240—250°/13 mm. [*picrate*, m. p. 118° (decomp.)].

G. A. C. Gough.

Metallic salts of lophine, 1 : 2 : 4-triazole, and tetrazole. H. H. Strain (J. Amer. Chem. Soc., 1927, **49**, 1995—2000).—Glyoxaline and lophine dissolve in liquid ammonia, but do not form ammonium salts. A *magnesium* salt of glyoxaline is obtained by dissolving magnesium in the liquid ammonia solution of glyoxaline. The following salts of lophine were obtained by treating a solution of lophine in liquid ammonia with the appropriate metal or metallic amide, or by double decomposition in the same solvent: *magnesium*; *calcium* ($+6NH_3$), *calcium*; *potassium* ($+3NH_3$), *potassium*; *silver* ($+2NH_3$), colourless; *silver*, grey; *cupric* ($+xNH_3$), greenish-blue; *cupric*; *cuprous*, light orange; *lithium* ($+xNH_3$), *lithium*; and *sodium*. None of these salts is stable in presence of water. 1 : 2 : 4-Triazole is soluble in liquid ammonia, but does not form an ammonium salt. The following metallic salts were prepared by treating the liquid ammonia solution with the appropriate metal or amide: *sodium*; *silver* ($+NH_3$), *silver*, grey; *magnesium* ($+4NH_3$), *magnesium*; *calcium* ($+xNH_3$), *calcium*; *cuprous* ($+xNH_3$), colourless, and *cuprous*. All are hydrolysed by water. Tetrazole combines with gaseous ammonia, with formation of *ammonium tetrazole*, $CHN_4{\cdot}NH_4$, a solution of which in liquid ammonia reacts with metallic calcium giving hydrogen and *calcium tetrazole*. The salts of tetrazole are not hydrolysed by water. The conductivities of pyrrole, glyoxaline, triazole, and tetrazole in liquid ammonia solution indicate that their strengths as acids are in the order given. The strengths of acids of the ammonia system are therefore, like those of their oxygen analogues, increased by negative substituents.

F. G. Willson.

Action of hydrazides. I. Synthesis of triazines from aminoguanidine and diketones. S. C. De (J. Indian Chem. Soc., 1927, 4, 183—188; cf. Thiele and Bihan, A., 1899, i, 46).—Acenaphthaquinone condenses with aminoguanidine hydrochloride in boiling acetic acid solution to give deep yellow 5 : 6-*acenaphtho*-3-*amino*-1 : 2 : 4-*triazine* (I), unmelted at 305° (*acetyl* derivative, m. p. 268°). β-Naphthaquinone similarly gives red 5 : 6-*naphtha*-3-*amino*-1 : 2 : 4-*triazine*, m. p. 240° (*acetyl* derivative, m. p. 208°), converted by concentrated potassium hydroxide solution into 5 : 6-*naphtho*-3-*hydroxy*-1 : 2 : 4-*triazine* (yellow; the red alcoholic solution has green fluorescence). From substituted quinones the following are prepared: 5 : 6-*isato*-3-*amino*-1 : 2 : 4-*triazine* (yellow, changing to brown at 200° and unmelted at 296°; *acetyl* derivative, m. p. 200°); 5 : 6-2′-*bromophenanthro*-3-*amino*-1 · 2 . 4-*triazine*, m. p. 235° (*acetyl* derivative, m. p. 278°); 5 : 6-4′ : 5′-*dibromophenanthro*-3-*amino*-1 : 2 : 4-*triazine*, unmelted at 305° (*acetyl* derivative, unmelted 5 : 6-2′ : 7′-*dibromophenanthro*-3-*amino*-1 : 2 : 4-*triazine*, m. p. 288°; 5 : 6-2′-*nitrophenanthro*-3-*amino*-1 : 2 : 4-*triazine*, m. p. 280° [*acetyl* derivative, m. p. 298° (changing to brown at 280°)]; 5 : 6-4′-*nitrophenanthro*-3-*amino*-1 : 2 : 4-*triazine*, m. p. 215° (*acetyl* derivative, m. p. 270°); 5 : 6-2′ : 7′-*dinitrophenanthro*-3-*amino*-1 : 2 : 4-*triazine*, unmelted at 310° (*acetyl* derivative, unmelted at 310°); 5 : 6-4′ : 5′-*dinitrophenanthro*-3-*amino*-1 : 2 : 4-*triazine*, m. p. 265° (*acetyl* derivative, m. p. 275°).


(I.)

G. A. C. Gough.

Synthesis of purines. F. Montequi (Anal. Fís. Quím., 1927, **25**, 182—185).—4-Nitro-5-cyano-2-methyl-1-ethylglyoxaline gives 5-*cyano*-4-*amino*-2-*methyl*-1-*ethylglyoxaline hydrochloride*, m. p. 214°, when reduced with tin and hydrochloric acid. The free *base*, m. p. 162°, when heated for 8 hrs. at 180° with urethane yields 8-*methyl*-7-*ethylxanthine*. 5-*Cyano*-4-*amino*-1-*methylxanthine hydrochloride*, m. p. 256—257°, is prepared by the reduction of the corresponding nitro-compound. The free *base* has m. p. 178°. It yields by reaction with urethane a small quantity of heteroxanthine.

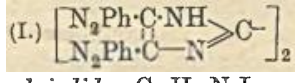
G. W. Robinson.

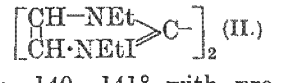
Detection of purines with *p*-aminophenols. E. Pittarelli (Arch. Farm. sperim., 1927, **43**, 142—144).—A colorimetric method for the detection of uric acid in urine is described based on the yellow colour given by an alkaline solution of uric acid in the presence of an oxidising agent such as sodium persulphate, and either *p*-aminophenol or "metol." It is claimed that the reaction is sensitive to 1 part of uric acid in 100,000 parts, and is not affected by the presence either of dextrose or of protein in the urine. Suggestions are made for the use of this reaction in volumetric and colorimetric analysis. The yellow colour is given by other purines.

E. A. Lunt.

Glycosine, $C_6H_6N_4$, of Debus. I. K. Lehmstedt (Annalen, 1927, **456**, 253—275).—Glycosine (see Debus, *ibid.*, 1859, **107**, 199; Japp and Cleminshaw, J.C.S., 1887, **51**, 552) (*picrate*, m. p. above 270°; *silver* salt, $C_6H_4N_4Ag_2$) when treated in hydrochloric acid solution with two equivalents of iodine yields a *compound*, $C_6H_6N_4,HI_3$, m. p. 194—195° (corr.). When a large excess of iodine is used, a *substance*, $C_6H_6N_4,2HI_3$, m. p. 204—206° (corr.), is obtained, and in addition a *compound*, $C_6H_8N_4I_8$, m. p. 185—186°, which loses iodine when heated, giving the former.

[With A. Bahn.]—Oxidation of glycosine in sulphuric acid solution with 3 mols. of hydrogen peroxide yields a dye (cf. Radziszewski, A., 1884, 986), whilst with 10 mols. of hydrogen peroxide, oxamide is produced. Glycosine couples with benzenediazonium chloride only in concentrated alkaline solution and then gives a *dye*, $C_{30}H_{22}N_{12},8H_2O$, probably (I) $+8H_2O$, m. p. 230—232°. Glycosine and ethyl iodide give a diquaternary *tetraethyl di-iodide*, probably (II), m. p. 244—245° (corr.), together with a

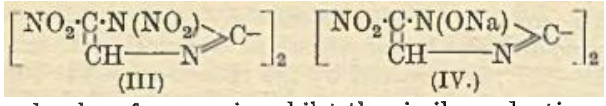

(I.)


(II.)

polyiodide, $C_{14}H_{24}N_4I_6$, m. p. 140—141° with previous sintering. Fission of the diquaternary ammonium hydroxide yields methyl alcohol, ethylamine, formic acid, a *substance*, $C_7H_{14}O_2N_2$, b. p. 55·5—57·5°/0·5 mm., which is probably 2-hydroxy-1 : 3-diethylglyoxalinium hydroxide, and an *isomeride*, $C_7H_{14}O_2N_2$, which is obtained by heating the former

substance, and when distilled at 15 mm. loses water, yielding 1 : 3-*diethyl*-2-*glyoxalone*, b. p. 118—119°/15 mm.

[With O. ZUMSTEIN.]—Glycosine is difficult to nitrate but can be made to yield a *dinitro*-derivative, $C_6H_4O_4N_6,H_2O$, m. p. 283° (decomp.), together with *trinitro*-, $2C_6H_3O_6N_7,3H_2O$, chars above 300°, and (mainly) *tetranitro*-, $C_6H_2O_8N_8,2H_2O$, probably (III) $+2H_2O$, m. p. 276° (decomp.) [*dipotassium* $+2H_2O$ · *disilver* $+2H_2O$; and *disodium* $+2H_2O$, salts], derivatives. Reduction of the tetranitro-compound in sodium hydroxide solution with sodium hydrosulphide gives the *sodium* derivative (IV, $+4H_2O$) and two



(III) (IV.)

molecules of ammonia, whilst the similar reduction of the dinitro-compound yields the *sodium* derivative of the nitro-amine, $(C_6H_4O_2N_6Na_2,2H_2O),3H_2O$. The elimination of ammonia during the reduction of the tetranitro-derivative indicates that two of the nitro-groups are attached to nitrogen. The nitration of glycosine (2 : 2′-diglyoxalinyl) proceeds without formation of isomerides, viz., glycosine ⟶ mono- ⟶ di- ⟶ tri- ⟶ tetra-nitroglycosine.

H. BURTON.

Porphyrins. XIII. Porphyrin formation and the structure of hæmin. W. KUSTER and K. SCHLAYER (Z. physiol. Chem., 1927, **168**, 294—314).—Acetic–hydrobromic acid converts dichlorodimethylchlorohæmin into *chlorobromohæmatoporphyrindimethyl ether*, $C_{36}H_{40}O_6N_4ClBr$, prisms having no definite m. p. (*zinc* and *copper* salts). When treated with excess of diazomethane in ethereal solution, or boiled with methyl-alcoholic hydrogen chloride, the ether yields the *dimethyl* ester, sintering at 78°, m. p. 126° (decomp.). This forms a complex *iron* salt, the solution of which in glacial acetic acid or chloroform gives, on addition of hydrazine hydrate, a hæmochromogen spectrum. On oxidation with sulphuric–chromic acid a mixture of 2 mols. of hæmatic acid with a molecule each of methylbromomethoxyethylmaleinimide, m. p. 75°, and *methylchloromethoxyethylmaleinimide*, m. p. 65°, is obtained.

H. D. KAY.

Formation and constitution of benz*iso*oxazoles [indoxazens]. H. LINDEMANN and W. PICKERT (Annalen, 1927, **456**, 275—283; cf. A., 1926, 1047).—2-Hydroxyacetophenoneoxime monoacetate is converted by means of warm aqueous sodium hydroxide into 2-methylbenz*iso*oxazole. Similarly, the *monoacetate*, m. p. 109°, of 2-*hydroxy*-4 : 6-*dimethylbenzaldoxime*, m. p. 130°, yields 3 : 5-*dimethylbenziso-oxazole*, b. p. 117°/14 mm., d_4^{20} 1·1061, n_D^{20} 1·55362. This compound, on nitration, furnishes 4-*nitro*-3 : 5-*dimethylbenz*isooxazole, m. p. 112°, is converted by hot 20% sodium hydroxide solution into 2-*hydroxy*-4 : 6-*dimethylbenzonitrile*, m. p. 180° (*acetate*, m. p. 54°), and when hydrogenated in acetic acid solution in presence of palladium yields 2-hydroxy-5-methylacetophenone. When hydrogenation is carried out in absolute ether there is formed the *ketimine*, m. p. 167° (decomp.). 5-*Nitro*-2-*hydroxy*-4 : 6-*dimethylbenzonitrile*, m. p. 193°, is obtained from the above nitro*iso*oxazole by treatment with hot sodium hydroxide solution. A table giving the densities, refractive indices, and spectrochemical data of benz-*iso*oxazole, 2-methyl-, 2 : 4- and 3 : 5-dimethylbenz*iso*oxazoles, is appended.

H. BURTON.

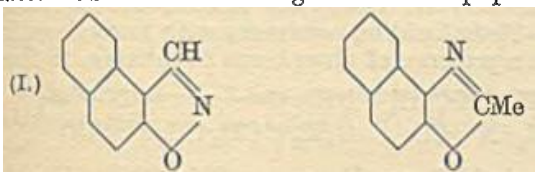
Benz*iso*oxazoles [indoxazens]. H. LINDEMANN, H. KÖNITZER, and S. ROMANOFF (Annalen, 1927, **456**, 284—311; cf. preceding abstract).—2 : 4-*Dihydroxybenzaldoxime monoacetate*, m. p. 139°, is converted by warm sodium hydroxide solution into 5-*hydroxybenz*iso*oxazole*, m. p. 157° (*acetate*, m. p. 59°), which on nitration furnishes 4-*nitro*-5-*hydroxybenz*iso*oxazole*, m. p. 188° (*acetate*, m. p. 157°). The above *iso*oxazoles are transformed by hot sodium hydroxide solution into 2 : 4-*dihydroxybenzonitrile*, m. p. 179° (*diacetyl* derivative, m. p. 75°), and 5-*nitro*-2 : 4-*dihydroxybenzonitrile*, m. p. 220° (*diacetyl* derivative, m. p. 119°), respectively. 4 : 6-*Dinitro*-5-*hydroxybenz*iso*oxazole*, m. p. 114°, yields similarly 3 : 5-*dinitro*-2 : 4-*dihydroxybenzonitrile*, m. p. 175° (*disodium* salt, explodes at 230°). From the *monoacetate*, m. p. 157°, of 2 : 5-dihydroxyacetophenoneoxime, m. p. 156° (Perkin, J.C.S., 1895, **67**, 998, gives m. p. 149—150°), there is obtained 4-*hydroxy*-2-*methylbenz*iso*oxazole*, m. p. 146° (*acetate*, m. p. 76°), which is also obtained by the action of nitrous acid on 4-amino-2-methylbenz*iso*oxazole. 4-*Methoxy*-2-*methylbenz*iso*oxazole*, m. p. 47°, is prepared by methylation of the 4-hydroxy-derivative, and also by heating the *monoacetate*, m. p. 125°, of 2-*hydroxy*-5-*methoxyacetophenoneoxime*, m. p. 121°. 2-*Methylbenziso-oxazole*-4-*azo*-2′-*aminonaphthalene* has m. p. 186°.

4-*Aminobenz*iso*oxazole*, m. p. 74—75° (*acetyl* derivative, m. p. 136°), is converted by sodium hydroxide solution into 5-*amino*-2-*hydroxybenzonitrile*, m. p. 162°; when diazotised and coupled with β-naphthol yields *benz*iso*oxazole*-4-*azo*-β-*naphthol*, m. p. 182°, which can be converted into 4-*hydroxy*-3-*cyanobenzeneazo*-β-*naphthol*, m. p. 269°; when diazotised and coupled with β-naphthylamine yields *benz*iso*oxazole*-4-*azo*-2′-*aminonaphthalene*, m. p. 112°, which is converted into 4-*hydroxy*-3-*cyanobenzeneazo*-2′-*aminonaphthalene*, m. p. 210°. 3-*Chloro*-6-*amino*-2 : 4-*dimethylbenz*iso*oxazole* has m. p. 147°.

Instead of the *iso*oxazole, 5-*hydroxy*-1-*methylbenzoxazole*, m. p. 196° (*benzoyl* derivative, m. p. 116°), is obtained from *resacetophenoneoxime monoacetate*, m. p. 127°. The benzoyl derivative on treatment with warm 2*N*-hydrochloric acid yields 4-*acetamido*-3-*hydroxyphenyl benzoate*, m. p. 184°, which regenerates the oxazole on dissolving in alkali. Similarly, 5-*methoxy*-1-*methylbenzoxazole*, m. p. 57°, is obtained from the *monoacetate*, m. p. 123°, of 2-hydroxy-4-methoxyacetophenone (pæonol) oxime. The methoxy-compound is hydrolysed by concentrated hydrochloric acid forming 2-*hydroxy*-4-*methoxyacetanilide*, m. p. 166°. 4-*Bromo*-5-*methoxy*-1-*methylbenzoxazole*, m. p. 150°, is prepared from the *monoacetate*, m. p. 187°, of 5-*bromopæonoloxime*, m. p. 160°, and also by bromination of the above methoxy-compound. The bromo–oxazole yields on acid hydrolysis, 5-*bromo*-2-*hydroxy*-4-*methoxyacetanilide*, m. p. 168°. 4-*Nitro*-5-*methoxy*-1-*methylbenzoxazole*, m. p. 182°, is similarly produced from the *monoacetate*, m. p. 178°, of 5-*nitro*-

pæonoloxime, m. p. 238° (decomp.), and by direct nitration of the methoxyoxazole. Hydrolysis yields *5-nitro-2-hydroxy-4-methoxyacetanilide*, m. p. 207°.

2-Hydroxy-α-naphthaldoxime monoacetate, m. p. 124°, when heated in a vacuum at 120—135°, gives a mixture of *2-hydroxy-1-cyanonaphthalene* (*2-hydroxy-α-naphthonitrile*), m. p. 157° (*acetyl* derivative, m. p. 56°), and the *naphthisooxazole* (I), m. p. 83°. The latter substance on heating above its m. p. passes into

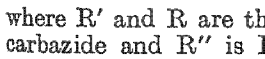


the former, and furnishes, on nitration, a *nitro*-derivative, m. p. 165—167°, which is converted by sodium hydroxide into a *nitro-2-hydroxy-1-cyanonaphthalene*, m. p. 213—214° (decomp.).

Unlike the aldoxime, the *monoacetate*, m. p. 94° (*diacetate*, m. p. 226°), of *methyl 2-hydroxynaphthyl ketoxime*, m. p. 134°, yields *1-methylnaphthoxazole* (II), b. p. 158°/14 mm. (*hydrochloride*, m. p. 177°), which is hydrolysed by hydrochloric acid to *1-acetamido-β-naphthol*, m. p. 235°. H. BURTON.

Violet vat dye of the 1-thionaphthen-2-indole-indigo series. R. HERZ and others.—See B., 1927, 674.

Thiodiazines. V. P. K. BOSE and D. C. RAY-CHAUDHURY (J. Indian Chem. Soc., 1927, **4**, 257—264; cf. A., 1925, i, 1465).—Phenacyl bromides or chloroacetone condense with βδ-disubstituted thiosemicarbazides in alcoholic or acetic acid solution to give dihydrothiodiazines of the type,



where R′ and R are the βδ-substituents of the semicarbazide and R″ is Ph or Me. The products are weak bases which resist acetylation and do not react with phenylthiocarbimide in boiling acetone solution. In this way phenacyl bromide converts βδ-diphenylthiosemicarbazide into *2-phenylimino-3 : 5-diphenyl-2 : 3-dihydro-1 : 3 : 4-thiodiazine*, m. p. 184°; β-phenyl-δ-*p*-tolylthiosemicarbazide into 2-p-*tolylimino-3 : 5-diphenyl-2 : 3-dihydro-1 : 3 : 4-thiodiazine*, m. p. 166°; β-phenyl-δ-*o*-tolylsemicarbazide into 2-o-*tolylimino-3 : 5-diphenyl-2 : 3-dihydro-1 : 3 : 4-thiodiazine*, m. p. 131—132°; *β-phenyl-δ-m-tolylthiosemicarbazide*, m. p. 123°, into 2-m-*tolylimino-3 : 5-diphenyl-2 : 3-dihydro-1 : 3 : 4-thiodiazine*, m. p. 119—120°; δ-phenyl-β-*p*-tolylthiosemicarbazide into *2-phenylimino-5-phenyl-3-p-tolyl-2 : 3-dihydro-1 : 3 : 4-thiodiazine*, m. p. 122—123°; δ-o-tolyl-β-*p*-tolylthiosemicarbazide into 2-m(?o-)-*tolylimino-5-phenyl-3-p-tolyl-2 : 3-dihydro-1 : 3 : 4-thiodiazine*, m. p. 112°; βδ-di-*p*-tolylthiosemicarbazide into 2-p-*tolylimino-5-phenyl-3-p-tolyl-2 : 3-dihydro-1 : 3 : 4-thiodiazine*, m. p. 145—146°; β-p-*tolyl-δ-o-anisylthiosemicarbazide* into 2-o-*anisylimino-5-phenyl-3-p-tolyl-2 : 3-dihydro-1 : 3 : 4-thiodiazine*, m. p. 109°; δ-m-*tolyl-β-p-tolylthiosemicarbazide*, m. p. [illegible], 2-m-*tolylimino-5-phenyl-3-p-tolyl-2 : 3-dihydro-1 : 3 : 4-thiodiazine*, m. p. 106—107°; and δ-phenyl-β-*m*-tolylthiosemicarbazide into *2-phenylimino-5-phenyl-3-m-tolyl-2 : 3-dihydro-1 : 3 : 4-thiodiazine*, m. p. 153°. Similarly, *p*-methylphenacyl bromide converts βδ-diphenylthiosemicarbazide into *2-phenylimino-3-phenyl-5-p-tolyl-2 : 3-dihydro-1 : 3 : 4-thiodiazine*, m. p. 165°; δ-phenyl-β-*m*-tolylthiosemicarbazide into *2-phenylimino-3-m-tolyl-5-p-tolyl-2 : 3-dihydro-1 : 3 : 4-thiodiazine*, m. p. 130°; and β-phenyl-δ-*p*-tolylthiosemicarbazide into 2-p-*tolylimino-3-phenyl-5-p-tolyl-2 : 3-dihydro-1 : 3 : 4-thiodiazine*, m. p. 180°. βδ-Diphenylthiosemicarbazide and chloroacetone afford *2-phenylimino-3-phenyl-5-methyl-2 : 3-dihydro-1 : 3 : 4-thiodiazine*, m. p. 153—154°.

β-Phenyl-δ-*o*-tolyl- and β-phenyl-δ-*m*-tolyl-thiosemicarbazides are converted into the αδ-substituted compounds on warming with pyridine.

G. A. C. GOUGH.

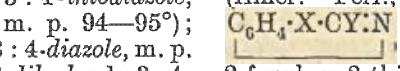
Action of ring-closing agents on δ-substituted thiosemicarbazide methyl dithiocarboxylates and δ-substituted semicarbazide methyl dithiocarboxylates. Formation of different types of thiodiazoles and oxdiazoles. P. C. GUHA and S. C. GUHA (J. Indian Chem. Soc., 1927, **4**, 161—172; cf. A., 1922, i, 876).—The δ-substituted thiosemicarbazide-α-methyl dithiocarboxylates and the δ-substituted semicarbazide-α-methyldithiocarboxylates, obtained by the interaction of methyl dithiocarbazinate with thiocarbimides or carbimides respectively, undergo ring-closure in the presence of acetic anhydride with the loss of hydrogen sulphide to give dihydrothiodiazoles and dihydro-oxdiazoles of the types (I) and (II). Ring-closure of the former type of substance in the presence of hydrogen chloride yields substituted amine (1 mol.) and (III) (1 mol.), whilst in the presence of sodium hydroxide equal mols. of methyl mercaptan and (IV) are formed. *δ-Phenyl-thiosemicarbazide-α-methyl dithiocarboxylate*, m. p. 143—144°, prepared by the interaction of methyl dithiocarbazinate and phenylthiocarbimide in warm alcohol, yields *2-phenylimino-5-methylthiol-2 : 3-dihydro-1 : 3 : 4-thiodiazole*, m. p. 132—133° (*acetyl* derivative, m. p. 153—154°), when boiled in alcohol. The same product also results by the interaction of methyldithiocarbazinate and phenyl thiocarbimide in hydrochloric acid solution. The *acetyl* derivative may also be obtained by boiling δ-phenyl thiosemicarbazide-α-methyl dithiocarboxylate with acetic anhydride and may be hydrolysed to the base with concentrated hydrochloric acid. *2-Thion-5-methylthiol-2 : 3-dihydro-1 : 3 : 4-thiodiazole* (III), m. p. 143—144°, obtained by heating δ-phenylthiosemicarbazide-α-methyl dithiocarboxylate with concentrated hydrochloric acid, gives *2 : 5-dimethylthiol-1 : 3 : 4-thiodiazole*, m. p. 136° (cf. Busch and Ziegele, A., 1899, i, 825), on methylation. On boiling with 2*N*-sodium hydroxide, δ-phenylthiosemicarbazide-α-methyl dithiocarboxylate yields *2-phenylimino-5-thiol-2 : 3-dihydro-1 : 3 : 4-thiodiazole* (IV, R = Ph), m. p. 215—216° (*methyl* derivative, m. p. 132—133°; *benzyl* derivative, m. p. 140—141°). Similarly, *p*-tolylthiocarbimide and methyl dithiocarbazinate yield suc-

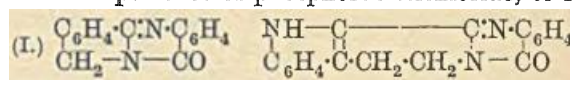




cessively δ-p-*tolylthiosemicarbazide-α-methyl dithiocarboxylate*, m. p. 135—136° (decomp.); 2-p-*tolylimino-5-methylthiol-2 : 3-dihydro-1 : 3 : 4-thiodiazole*, m. p. 137—138° (*acetyl* derivative, m. p. 94—95°); 2-*thion-5-methylthiol-2 : 3-dihydro-1 : 3 : 4-diazole*, m. p. 143—144°; 2-p-*tolylimino-5-thiol-2 : 3-dihydro-1 : 3 : 4-thiodiazole*, m. p. 215—216° (oxidation with iodine gives the *disulphide*, m. p. 210—212°). δ-*Xylylthiosemicarbazide-α-methyl dithiocarboxylate* could not be obtained pure, but from the crude product the following were prepared: 2-*xylylimino-5-methylthiol-2 : 3-dihydro-1 : 3 : 4-thiodiazole*, m. p. 135—136° (*acetyl* derivative, m. p. 128—129°); 2-*thion-5-methylthiol-2 : 3-dihydro-1 : 3 : 4-thiodiazole*, m. p. 143—144°. Allylthiocarbimide and methyldithiocarbazinate yield successively, δ-*allylthiosemicarbazide-α-methyl dithiocarboxylate*, m. p. 139—140°; 2-*allylimino-5-methylthiol-2 : 3-dihydro-1 : 3 : 4-thiodiazole*, m. p. 77—78° (*acetyl* derivative, m. p. 93—94°); 2-*thion-5-methylthiol-2 : 3-dihydro-1 : 3 : 4-thiodiazole*, m. p. 143—144°. Phenylcarbimide and methyl dithiocarbazinate give δ-*phenylsemicarbazide-α-methyl dithiocarboxylate*, m. p. 197—198° (decomp.), and 2-*phenylimino-3-acetyl-5-methylthiol-2 : 3-dihydro-1 : 3 : 4-oxdiazole*, m. p. 139—140°. δ-*Naphthylsemicarbazide-α-methyl dithiocarboxylate*, m. p. 202—203° (decomp.), and 2-*naphthylimino-3-acetyl-5-methylthiol-2 : 3-dihydro-1 : 3 : 4-oxdiazole*, m. p. 149—150°, are also described. G. A. C. GOUGH.

Formation of heterocyclic compounds. I. Action of methyl dithiocarbazinate on *o*-diketones and their monoximes, and on chlorides and esters of dibasic acids. P. C. GUHA and S. C. GUHA (J. Indian Chem. Soc., 1927, 4, 239—246).—Methyl dithiocarbazinate condenses with *o*-diketones to give the following compounds together with methyl hydrogen sulphide: with phenanthraquinone, 2-*thion-5 : 6-phenanthro-1 : 3 : 4-oxdiazine*, m. p. 205—206° (red); with acenaphthaquinone, 2-*thion-5 : 6-acenaphtho-1 : 3 : 4-oxdiazine*, m. p. 208—209° (decomp.); with isatin, 2-*thiol-5 : 6-isato-1 : 3 : 4-oxdiazine*, m. p. 227° (decomp.; *benzoyl* derivative, m. p. 228—229°; *acetyl* derivative, m. p. 161—162°). Methyl dithiocarbazinate condenses with phenanthraquinonemonoxime to give water (2 mols.) and 7-*methylthiol-3 : 4-phenanthro-1 : 2 : 5 : 6-heptathiotriazine* (1 mol.), m. p. 209—210° (decomp.). By the interaction of methyl dithiocarbazinate with dibasic acid chlorides in benzene solution, the following are produced: with thionyl chloride, *methyl dithiocarbazinate sulphite* (5-*methylthiol-2-keto-1 : 2-dithion-3 : 4-diazine*), m. p. 122—123°; with oxalyl chloride (or alcoholic ethyl oxalate), 5-*hydroxy-6-keto-2-methylthiol-1 : 3 : 4-thiodiazine*, m. p. 127° (decomp.; *acetyl* derivative, m. p. 174—175°); with phthalyl chloride, 5-*hydroxy-8-keto-6 : 7-benzo-2-methylthiol-1 : 3 : 4-octathiodiazine*, m. p. 161—162° (shrinking at 155°); with fumaryl chloride, 5-*hydroxy-8-keto-2-methylthiol-1 : 3 : 4-octathiodiazine*, m. p. 171° (decomp.); with succinyl chloride, 5-*hydroxy-8-keto-2-methylthiol-6 : 7-dihydro-1 : 3 : 4-octathiodiazine*, m. p. 137° (decomp.); with carbonyl chloride, 2-*hydroxy-5-methylthiol-1 : 3 : 4-thiodiazole*, m. p. 96—97° (shrinking at 91°). G. A. C. GOUGH.

Odour and chemical constitution in the benzselenazole group. M. T. BOGERT and A. STULL (Amer. Perf., 1927, 22, 63).—The compounds,  where X = S or Se, Y = phenyl, 2-furyl, or 2-thienyl, all possess an agreeable geranium or tea-rose type of odour. CHEMICAL ABSTRACTS.

Synthesis of rutæcarpine. Y. ASAHINA, R. H. F. MANSKE, and R. ROBINSON (J.C.S., 1927, 1708—1710).—Phthalimidine condenses with methyl anthranilate in presence of phosphorus trichloride, to form  (I.) (II.) isoquinazindol-2-one (I), m. p. 205—206°. By the use of 3-keto-3 : 4 : 5 : 6-tetrahydro-4-carboline for phthalimidine, rutæcarpine (II), m. p. 257—258°, is obtained, identical with the natural alkaloid. C. HOLLINS.

Alkaloids of *Picralima Klaineana*. T. A. HENRY and T. M. SHARP (J.C.S., 1927, 1950—1959; cf. Clinquart, Bull. Acad. roy. med. Belge, 1926, 492; J. Pharm. Belge, 1927, **9**, 187).—The seeds of *P. Klaineana* contain at least four alkaloids, two of which are obtained crystalline. *Akuammine*, $C_{\infty}H_{28}O_4N_2$, m. p. 255° (decomp.; cf. Clinquart's alkaloid, m. p. 242—243°), $[\alpha]^{20}$ −66·7° in alcohol, −73·4° in chloroform, is obtained by fractionation from alcohol of the ether-soluble bases. It forms a *hydrobromide*, m. p. 228° (+H_2O, decomp.), $[\alpha]_D^{20}$ −26·05° in water, *hydrochloride*, m. p. 227° (+H_2O, decomp.), $[\alpha]_D^{\infty}$ −26·6° in water or −32·8° in alcohol, *sulphate*, m. p. 221° (+10H_2O, decomp.), $[\alpha]_D^{19}$ −40·3° in water, *hydriodide*, m. p. 226° (decomp.), *nitrate*, m. p. 224° (decomp.), *thiocyanate*, m. p. 218° (decomp.), *perchlorate*, m. p. 215° (decomp.), *picrate*, m. p. 199° (decomp.), and *picrolonate*, m. p. 194° (decomp.). The alkaloid contains one methoxyl and one methylimino-group, and reduces auric chloride, platinic chloride, and silver nitrate in the cold. It gives slowly a *monomethiodide*, m. p. 274° (decomp.), and by the action of sodium methoxide and methyl iodide a new oily *base*, $C_{22}H_{29}O_5N_2Me$ [*picrate*, m. p. 205° (decomp.)], containing two methoxyl groups. *Acetylakuammine*, m. p. 226° (decomp.), forms a *hydrobromide*, m. p. 236° (decomp.), and *picrate*, m. p. 168° (decomp.). Akuammine dissolves in alcoholic *N*-sodium ethoxide, and from the sodium compound is obtained *akuammine hydrate*, which does not sinter or melt up to 310°. The crude akuammine sulphate from one sample of the seeds contained a second crystalline *alkaloid-D*, m. p. 177·5° (decomp.), $[\alpha]_D^{19}$ −737·5° in alcohol or chloroform [*sulphate*, m. p. 161° (decomp.), $[\alpha]_D^{15}$ −594° in water; *nitrate*, m. p. 180—181° (decomp.); *picrate*, m. p. 169° (decomp.)]. C. HOLLINS.

Error due to hydrolysis in the determination of atropine by the ether extraction method. C. SCHOUSEN (Dansk Tidssk. Farm., 1927, **1**, 443—445).—Ethereal solutions of atropine obtained by extraction should be titrated immediately after evaporation of the solvent. Any further heating of the residue leads to results which may be as much as 8% low owing to hydrolysis. The presence of small amounts

of alcohol in the ether depresses the hydrolysis, and the use is recommended of a mixture of 4·5 c.c. of absolute alcohol and 295·5 c.c. of dried ether for the extraction of 0·05 g. of atropine. H. F. HARWOOD.

Vanillin and piperonal as reagents for alkaloids. L. VAN ITALLIE and A. J. STEENHAUER (Pharm. Weekblad, 1927, **64**, 925—928).—A table is given of the colour reactions with the commoner alkaloids. The most distinctive colours are given by morphine, codeine, *apo*morphine, aspidospermine, and veratrine. S. I. LEVY.

Production of 3-bromo-2-hydroxypyridine-5-arsinic acid. A. BINZ and C. RÄTH.—See B., 1927, 734.

Production of heterocyclic arsenic compounds [arseno- and other derivatives of pyridine and quinoline]. DEUTSCHE GOLD- U. SILBER-SCHEIDEANSTALT VORM. ROESSLER.—See B., 1927, 670.

Manufacture of benziminazolone-5-arsinic acids. I. G. FARBENIND. etc.—See B., 1927, 670.

Sodium 3-chloro-4-acetamidophenylstibinate. S. C. NIYOGY (J. Indian Chem. Soc., 1927, **4**, 96—97).—Sodium 3-chloro-4-acetamidophenylstibinate is prepared by the action of sodium hydroxide on the additive compound of antimony trichloride with diazotised 3-chloro-4-acetamidoaniline (cf. Brahmachari and Das, A., 1926, 541).

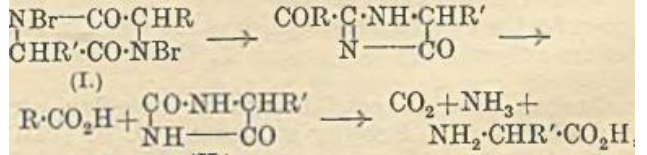
G. A. C. GOUGH.

Selenium organic compounds. VII. Synthesis of 2-phenyl-, 2-furyl-, and 2-thienyl-benzoselenazoles, of 2-phenylbenzoselenazole-4′-arsinic acid, and of other benzoselenazoles. M. T. BOGERT and A. STULL (J. Amer. Chem. Soc., 1927, **49**, 2011—2016; cf. A., 1926, 311).—2-m-*Nitrophenylbenzoselenazole*, m. p. 148°, and 2-p-*nitrophenylbenzoselenazole*, m. p. 211°, are obtained by heating the zinc salt of *o*-aminoselenophenol (cf. Bogert and Andersen, Proc. Nat. Acad. Sci., 1925, **11**, 217) with *m*- and *p*-nitrobenzoyl chlorides, respectively, at 100°. Under similar conditions, *o*-nitrobenzoyl chloride reacts explosively (cf. Schmidth, Diss., Columbia, 1925) and pure 2-*o*-nitrophenylbenzoselenazole could not be obtained from the reaction product, although 2-o-*aminophenylbenzoselenazole*, greenish-yellow, m. p. 142·5°, was obtained by reducing the crude nitro-derivative with tin and hydrochloric acid. 2-m-*Amino*-, pale yellow, m. p. 159·5°, and 2-p-*amino-phenylbenzoselenazole*, similar, m. p. 156°, are obtained analogously. When boiled with the above zinc salt in glacial acetic acid, salicylaldehyde and *p*-hydroxybenzaldehyde yield, respectively, 2-o-*hydroxy*-, pale yellow, m. p. 131°, and 2-p-*hydroxy-phenylbenzoselenazole*, colourless, m. p. 223°. When boiled with 1 mol. of oxalyl chloride, the above zinc salt affords 2 : 2′-*dibenzoselenazolyl*, m. p. 314°, becoming brown on exposure to light and air. Diazotisation of 2-*p*-aminophenylbenzoselenazole, with subsequent treatment with potassium arsenite, sodium carbonate, and copper powder, affords *-pnenylbenzoselenazole-4′-arsinic acid*, pale yellow, m. p. above 360° (decomp.) (*monosodium* salt). When heated at 100° with the zinc salt of *o*-aminoe enophenol, furfuroyl chloride and 2-thienoyl chloride afford, respectively, 2-α-*furyl*-, m. p. 133°, and 2-α-*thienyl-benzoselenazole*, m. p. 114·5°. Selenium is satisfactorily determined by heating the sample (0·2—0·3 g.) with 8—10 c.c. of sulphuric acid until a clear solution is obtained, with subsequent dilution to 200 c.c., neutralisation with ammonia solution, addition of concentrated hydrochloric acid (50—60 c.c.), and precipitation of metallic selenium at the b. p. with hydrogen sulphide. F. G. WILLSON.

Proteins. IV. S. GOLDSCHMIDT, E. WIBERG, F. NAGEL, and K. MARTIN (Annalen, 1927, **456**, 1—38; cf. Goldschmidt and Steigerwald, A., 1925, i, 1109).—Further study of the action of neutral and alkaline hypobromite on proteins, amino-acids, polypeptides, and diketopiperazines indicates that other cyclic structures besides the diketopiperazine ring are present in proteins. Provided that no hydrolysis occurs, even long acylated polypeptide chains are not attacked by hypobromite. Neutral hypobromite converts polypeptides into α-ketoacylamino-acids: $NH_2{\cdot}CHR{\cdot}CO{\cdot}NH{\cdot}CHR'{\cdot}CO_2H \longrightarrow NBr{:}CR{\cdot}CO{\cdot}NH{\cdot}CHR'{\cdot}CO_2H \longrightarrow COR{\cdot}CO{\cdot}NH{\cdot}CHR'{\cdot}CO_2H$. In presence of alkali the intermediate bromoimine is hydrolysed and the products are a nitrile, R·CN, and the next lower peptide or amino-acid, $NH_2{\cdot}CHR'{\cdot}CO_2H$. The action of hypobromite on amino-acids is independent of the presence or absence of alkali, the product being, with excess of hypobromite, the nitrile or, with only 2 mols. of hypobromite, the aldehyde, of the next lower acid (cf. Langheld, A., 1909, i, 138, 557).

Leucylglycine is converted by neutral potassium hypobromite at 0° into (*α-ketoisohexoyl*)*glycine*, $CH_2Pr^{\beta}{\cdot}CO{\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}CO_2H$ (*phenylhydrazone*, m. p. 200°); by alkaline hypobromite at 0° into a mixture, b. p. 129—131°, of *iso*valeronitrile, and its *bromo*-derivative. Valylglycine similarly yields (*α-ketoisovaleryl*)*glycine* (*phenylhydrazone*, m. p. 152°), and *iso*butyronitrile, b. p. 109°. Leucine, with excess of neutral hypobromite, gives *iso*valeronitrile, b. p. 129°; with 2 mols. of hypobromite, an oil (bromoimine), and finally *iso*valeraldehyde (phenylhydrazone, m. p. 110°). From glycine and alkaline hypobromite carbamide is obtained.

Amino-acid anhydrides (diketopiperazines) yield with neutral hypobromite only the *NN*-dibromo-compounds, or, if the nitrogen atoms carry substituents, are not attacked. In presence of alkali the *NN*-dibromo-compounds undergo profound changes, giving first a *C*-acylhydantoin, which is oxidised and hydrolysed to an aliphatic acid, ammonia, carbon dioxide, and the amino-acid; these products are formed in pairs from unsymmetrical anhydrides, according to the scheme:



R and R′ being interchangeable. Alanine anhydride (R=R′=Me) gives an NN′-*dibromo*-compound, decomposing at 110°, whilst the NN′-*dibromo*-derivative of leucine anhydride (R = R′=Bu$^{\beta}$) decomposes at

134°. From leucylglycine anhydride (R=H; R′=Bu$^{\beta}$) by the action of alkali and hypobromite 4-*iso*butylhydantoin, m. p. 211°, and *iso*valeric acid are obtained, whilst leucine anhydride gives leucine, *iso*valeric acid, and *iso*valeronitrile. These reactions are specific for the diketopiperazine system, hydantoins and pyrrolidonecarboxylic acid or ester being unattacked by hypobromite.

By the action of alkaline hypobromite on a solution of egg-albumin at −2° a crystalline *compound*, $C_2O_2Br_6S$, m. p. 134° (4 g. from 200 g. of albumin), is obtained, which loses Br_2 when treated with cold hydriodic acid, giving a *compound*, m. p. 161—162°. The mother-liquors contain acetic, succinic, and benzoic acids, together with valero- and other nitriles formed during the later stages of the reaction, and finally glyoxal (isolated as osazone, m. p. 169°). About 20% of the total nitrogen appears as ammonia, of which 50—70% is liberated only after heating with sodium hydroxide. It is suggested that less than 25% of the total nitrogen is present in the form of diketopiperazine rings, and a smaller proportion as other cyclic structures attacked by hypobromite.

C. Hollins.

Structure of proteins. E. Abderhalden and W. Kroner (Z. physiol. Chem., 1927, **168**, 201—215).—The evidence put forward by Brigl and Held (A., 1926, 630) with regard to their suggestion that proteins may be composed of polypeptide chains united through a carbonyl group to form complex ureides has been investigated. The findings of these authors as to the effect of phthalic anhydride, of hypobromite, and of trypsin on their model ureide, carbonylbis-(glycylglycine) or its ester, have been confirmed. In addition, *carbonylbis(glycyl-*l*-leucine)* has been prepared. Like Brigl and Held's ureide, it is resistant to trypsin, but attacked by hypobromite solutions. Carbonylbis(glycylglycine) is a fairly strong acid and its aqueous solution has a much higher hydrogen-ion concentration than any protein hydrolysis product. Hypobromite also reacts with dipeptides, *e.g.*, *dl*-leucylglycine, glycyl-*l*-leucine, and *dl*-leucyl-*dl*-leucine.

H. D. Kay.

Titration of protein hydrolysates. W. L. Davies (Biochem. J., 1927, **21**, 815—822).—When protein hydrolysates (caseinogen and gelatin) are titrated to phenolphthalein in neutralised formaldehyde-alcohol solution there is no change in the total values of the various fractions separated by Van Slyke's method, as compared with the value of the complete hydrolysate. The titration value for the diamino-acid fractions is uniformly greater than the expected values as calculated from the figures by the Van Slyke method by 22% of the latter. This is balanced by a lower titration value than that calculable in the monoamino-acid fraction.

S. S. Zilva.

Detection and determination of methyl chloride. K. Roka and O. Fuchs (Z. anal. Chem., 1927, **71**, 381—386).—About 10—15 c.c. of the solution of methyl chloride in absolute alcohol containing 0·05—0·1 g. of the chloride are heated with 2·5—4 g. of sodium iodide in a pressure flask or sealed tube at 60° for 3—4 hrs., whereby the methyl chloride is converted into iodide. The latter is then separated by fractional distillation and the distillate treated with alcoholic silver nitrate. The presence of methyl chloride in the original alcoholic solution is indicated if an opalescence (due to the separation of the compound MeI,$AgNO_3$) appears. The latter is hydrolysed with water and the silver iodide collected and weighed; the amount obtained is always 94% of the theoretical. Di- and tri-chloromethane and carbon tetrachloride do not interfere. The use of potassium iodide in place of the sodium salt results in low and erratic figures being obtained.

A. R. Powell.

Colour reactions of phenols and aldehydes. L. Ekkert (Pharm. Zentr., 1927, **68**, 563—565).—Tables are given showing the colour reactions of each of fifteen common phenols with each of thirteen common aldehydes. The reaction is carried out in each case by mixing 4 drops of each of the 1% alcoholic reagent solutions with 0·5 c.c. of alcohol and 0·5 c.c. of concentrated sulphuric acid.

S. I. Levy.

Biochemistry.

Oxygen consumption of human blood. G. Endres (Z. Biol., 1927, **86**, 260—268).—A method is described for measuring in a known volume of blood the total volume of white blood-corpuscles and blood-platelets, the cells which are responsible for the oxygen consumption of the blood. Figures are given for the oxygen consumption of the blood in the human subject.

W. O. Kermack.

Carbon dioxide equilibrium in alveolar air and blood. II. Resting subjects. D. B. Dill, L. M. Hurxthal, C. van Caulaert, A. Folling, and A. V. Bock. **III. Exercising subjects.** D. B. Dill, J. S. Lawrence, L. M. Hurxthal, and A. V. Bock (J. Biol. Chem., 1927, **74**, 303—311, 313—320).—II. The method employed by Henderson and Haggard (Amer. J. Physiol., 1925, **77**, 193) yields, in resting subjects, much lower results for the carbon dioxide tension of arterial blood than the method of Haldane and Priestley. The discrepancy can be reduced, but not abolished, by diminishing the dead space of the automatic valve employed by the former workers.

III. During exercise the method of Henderson and Haggard gives accurate results for the carbon dioxide tension of arterial blood, whilst those obtained by the method of Haldane and Priestley are variable.

C. R. Harington.

Spectrophotometric determination of hæmoglobin. G. E. Davis and C. Sheard (Arch. Int. Med., 1927, **40**, 226—236).—The determination of hæmoglobin by means of the spectrophotometer

gives results in good agreement with those obtained by the Van Slyke oxygen absorption method.

W. O. KERMACK.

Physical chemistry of fibrinogen. II. Solubility minimum and acid-binding power in salt solution. E. WOHLISCH and J. SCHLOSS (Z. Biol., 1927, 85, 542—550).—The optimum of coagulation for horse-fibrinogen in 0·85% sodium chloride solution has been determined at p_H 4·46. The coagulation was brought about by the addition of acetic acid and p_H was determined electrometrically. This value is constant with variation of the concentration of protein in solution. Data are given to show that throughout the range investigated, p_H 4·0—5·0, solutions of fibrinogen bind hydrogen ions.

E. A. LUNT.

Alkali reserve of the blood. A. Y. KHARIT (Arkh. Biol. Nauk, 1926, 26, 133—140).—During the digestion of protein by dogs the alkali reserve is greater in the blood of the portal and renal veins than in peripheral blood, whilst it is less in the blood of the hepatic vein. The increase in the alkalinity in the portal vein is due to an increase in the ammonia content, and in the renal vein it is due to the excretion of acids by the kidney, whilst the decrease in alkalinity in the hepatic vein is attributed to the formation of ammonium salts other than carbonates. The liver as well as the kidneys and lungs should be considered of importance in the regulation of the alkali reserve and of the reaction of the blood.

CHEMICAL ABSTRACTS.

Importance of buffering capacity in biochemistry. H. MOSER.—See this vol., 937.

Electrolyte equilibrium in blood. Modification in the electrolyte content of the blood after the intravenous injection of potassium salts. L. CONDORELLI (Arch. Farm. sperim., 1927, 43, 44—50).—The intravenous injection of solutions of potassium chloride produces a diminution in the amount of sodium and an increase in the amount of chlorine present in the blood, but no characteristic variation in the amounts of other anions or cations. The amount of salt necessary to produce death depends on the concentration and rate of injection and not on the actual amount injected.

E. A. LUNT.

Chloride determinations [in blood] by modified Volhard titration. J. C. WHITEHORN (J. Biol. Chem., 1927, 74, 299—301).—A reply to Short and Gellis (this vol., 689).

C. R. HARINGTON.

Determination of calcium in oxalated whole blood. C. S. ROTHWELL (J. Biol. Chem., 1927, 74, 263).—Oxalated whole blood is diluted and treated with trichloroacetic acid; the protein-free ultrate is neutralised and treated with excess of ammonium oxalate, and the precipitated calcium oxalate is determined by the method of Clark and 1925, i, 713). The error of the method is ± 2%.

C. R. HARINGTON.

Partition of serum-calcium into diffusible and non-diffusible portions. S. H. LIU (Chinese J. , 1927, 1, 331—344).—Using a method of mbined ultrafiltration and dialysis for the partition of calcium, the decrease of serum-calcium in tetany is found chiefly in the diffusible form, whilst that in nephrosis and kala-azar with no evidence of tetany is entirely in the non-diffusible form. Under the influence of both parathyroid hormone and cod-liver oil, the rise of serum-calcium is mainly in the diffusible portion. These findings suggest that the diffusible calcium controls neuro-muscular irritability. Evidence is advanced that the non-diffusible calcium is bound to serum-proteins, especially to the albumin.

W. ROBSON.

Determination of copper and iron and the copper content of blood-serum. O. WARBURG (Biochem. Z., 1927, 187, 255—271).—A method is described for the determination of minute amounts of copper, iron, and manganese in organic substances. Copper and iron can be determined in 0·1 c.c. of serum, the copper content of serum being found to be constant. In 1 g. of the dry substance of a pure culture of a *Torula* yeast 0 1 mg. of iron and 0·07 mg. of copper, and in 1 g. of bottom yeast 0·09 mg. of iron and 0·035 mg. of copper are present. Future examination of such enzyme preparations as peroxydase and catalase must, therefore, take account of both the copper and iron contents.

P. W. CLUTTERBUCK.

Colorimetric determination of lactic acid in blood. Z. DISCHE and D. LASZLO (Biochem. Z., 1927, 187, 344—362).—Previously described colorimetric methods for determination of lactic acid are critically examined, the specificity of the Fletcher–Hopkins reaction is ascertained, and a modification elaborated which enables quantitative determination. A method using quinol is recommended for the determination of lactic acid in blood and organs. The solution obtained from 0·5 c.c. of blood after removal of proteins and carbohydrates is heated for 15 min. on a boiling water-bath with quinol–sulphuric acid, when an orange-brown colour is obtained, the depth of which is proportional to the amount of lactic acid. The reaction readily determines lactic acid at a dilution of 0·001%. It is not specific, however, and is also given by acetaldehyde, paraldehyde, methylglyoxal, and dihydroxyacetone, whilst 1% dextrose gives the same colour as 0·014%, 1% glycerol as 0·016%, and 1% β-hydroxybutyric acid as 0·003% lactic acid. On the other hand, acetone, acetoacetic acid, amino-acids, carbamide, uric acid, creatine, creatinine, 5% caseinogen solutions, and caseinogen hydrolysates give no colour reaction.

P. W. CLUTTERBUCK.

Determination of lactic acid in blood. E. RONZONI and Z. WALLEN-LAWRENCE (J. Biol. Chem., 1927, 74, 363—377).—Whilst lactic acid in pure aqueous solution can be determined with equal accuracy by the method of Clausen (A., 1922, ii, 593) and by that of Friedemann and others (this vol., 800), the latter method yields lower, and probably more accurate, results when applied to protein-free filtrates of blood. In preparing such filtrates by the use of mercuric nitrate it is important to maintain a reaction of p_H 7·0 in order to avoid loss of lactic acid by retention in the protein precipitate.

C. R. HARINGTON.

Muscle-glycogen as a source of blood-sugar. S. Soskin (Amer. J. Physiol., 1927, **81**, 382—391).—The effects of adrenaline, ether anæsthesia, and asphyxia on the blood-sugar of dogs after abdominal evisceration led to the conclusion that muscle glycogen is not an available source of blood-sugar in the absence of the liver. R. K. Cannan.

Effect of alkali on blood-sugar. M. A. Battie and R. J. S. McDowall (J. Physiol., Proc. Physiol. Soc., 1927, **62**, xxxiii).—Sodium hydrogen carbonate when injected intravenously (cat) or taken by the mouth (man) causes a temporary fall in the blood-sugar. A. A. Eldridge.

Comparison of blood-sugar curves following ingestion and intravenous injection of dextrose. W. G. Lennox and M. Bellinger (Arch. Int. Med., 1927, **40**, 182—194).—Blood-sugar curves obtained after intravenous injection into non-diabetic subjects of dextrose (0·33 g. per kg.) agree generally with those after oral administration of dextrose (1·5 g. per kg.). Glycosuria is more frequent after intravenous injection. W. O. Kermack.

Fluctuations in the blood-sugar content of cattle. M. S. Awdejewa, E. L. Prowatorowa, N. G. Sawitsch, and E. L. Thal (Biochem. Z., 1927, **187**, 369—376).—The blood-sugar content of fasting cows is maintained at a very low level, and fodder containing carbohydrate does not produce any increase. The variations in one and the same cow on different days are greater than the differences between different cows on the same day. It was not possible to correlate the variations in blood-sugar with the secretion of milk. P. W. Clutterbuck.

Modification of the Folin and Wu method for the determination of dextrose in blood. F. M. Eliçabe (Anal. Oficina Quím. Prov. Buenos Aires, 1927, **1**, 67—70).—The protein-free filtrate is treated with Fehling's solution and the cuprous oxide formed is determined colorimetrically with Folin and Wu's phosphomolybdic reagent, G. W. Robinson.

Determination of blood-amylase with the viscosimeter. R. Elman and J. M. McCaughan (Arch. Int. Med., 1927, **40**, 58—64).—The determination of amylase, based on the time required to effect an arbitrary reduction in the outflow-time of a buffered starch solution in an Ostwald viscosimeter, is described. The time values obtained vary inversely with the concentration of the amylase. The amylase unit selected is that concentration which is capable of lowering the viscosity of a 7% starch solution by 20% in 1 hr. The plasma of normal dogs contains 1·5—2·5 such units. Feeding, fasting, and external draining of the total pancreatic juice did not affect the amylase content. W. Robson.

Saproporphyrins. [*a*] Copratoporphyrin as product of the putrefaction of flesh and blood-rich organs. [*b*] A new saproporphyrin. O. Schumm (Z. physiol. Chem., 1927, **169**, 3—9; 52—58; cf. A., 1925, i, 1347).—[*a*] The observations of Fischer and Schneller (A., 1924, i, 894) that coproporphyrin is present in the products of putrefaction of animal tissues and that this pigment is derived from "hæmoglobin-*B*" cannot be confirmed. Only a minute trace of coproporphyrin could be detected, whereas much greater amounts of copratoporphyrin were present, together with a new porphyrin ("saproporphyrin-*D*") which is similar in spectrochemical properties to Nencki's hæmatoporphyrin, but is readily soluble in chloroform (cf. this vol., 685). The presence of copratoporphyrin and saproporphyrin-*D* would account for the spectrometric results of Fischer and Schneller.

[*b*] Some properties of the new porphyrin, *saproporphyrin*-D, which is formed by the long putrefaction of blood-rich organs and flesh, are given and methods are described by which this pigment may be distinguished from other porphyrins. The pronounced solubility in chloroform and also in 0·1*N*-potassium hydroxide, and the irregular behaviour in the bromine spectrum test, serve to differentiate saproporphyrin-*D* from coproporphyrin. In general chemical properties it resembles copratoporphyrin but gives different spectra in concentrated sulphuric acid. Unlike mesoporphyrin, coproporphyrin, and copratoporphyrin, saproporphyrin-*D* when dissolved in 25% hydrochloric acid and exposed to sunlight undergoes a moderately rapid alteration in spectrochemical properties. Attempts to obtain the new porphyrin in the crystalline state have been unsuccessful, but although no definite proof of purity can be given, it is concluded that a new natural porphyrin is concerned. Mixtures of the two known saproporphyrins (hæmateric acid and copratoporphyrin), with or without coproporphyrin, do not yield on fractionation by Willstätter's or Schumm's methods any fraction having properties similar to those of the porphyrin described. A. Wormall.

Denaturation of proteins. IV. Effect of denaturation on antigenic properties of egg-albumin. S. Wu, C. Tenbroeck, and C. P. Li (Chinese J. Physiol., 1927, **1**, 277—296).—The antigenic power of egg-albumin is much decreased by denaturation by acid, alkali, alcohol, or heat. The original specificity is destroyed and a new specificity is created when albumin is denatured, whilst some denatured albumins retain a trace of the original specificity. Egg-albumin denatured by any of the above methods yields substances which are closely related immunologically. W. Robson.

Biological importance of potassium in the human and animal organism. O. Hagemann and E. Ohl (Landw. Versuchs-Stat., 1927, **106**, 125—284).—A critical review of the literature of the subject, under the headings: localisation and amount of potassium salts in the organism; physiological action on the blood-vessels, nervous system, etc.; importance in metabolism; the rôle of potassium compounds in medicine; and the radioactivity of potassium. C. T. Gimingham.

Microchemistry of the nervous system. Sulphur and phosphorus content of the cerebral hemispheres of the guinea-pig. R. M. May (Compt. rend., 1927, **185**, 368—370).—In the two hemispheres of a given guinea-pig, the sulphur and phosphorus contents vary within very small limits only. The sulphur content has a mean value of 5·15 mg. per g. dry weight, with a mean variation

between the two hemispheres of 3%; the phosphorus content has a mean value of 14·85 mg. per g. dry weight, with a mean variation between the two hemispheres of 2%. Experiments to determine the change in these values due to nervous degeneration are projected. E. A. LUNT.

Lactic acid maximum of cardiac muscle. D. Y. ARNING (J. Physiol., 1927, **63**, 107—112).—Comparative determinations of the maximum production of lactic acid *in vitro* by skeletal and by cardiac muscle showed that the former consistently gave the lower values. For the frog the ratio was 0·5 and for the tortoise it was 0·7. R. K. CANNAN.

Adipocere. S. GOY (Biochem. Z., 1927, **187**, 470—471).—Further analytical figures are similar to those already reported (A., 1922, i, 969). P. W. CLUTTERBUCK.

Determination of iron in tissues. R. P. KENNEDY (J. Biol. Chem., 1927, **74**, 385—391).—The tissue is incinerated with a mixture of sulphuric and perchloric acids. The incineration mixture is treated with nitric acid and diluted, and an aliquot portion is treated with sodium thiocyanate and amyl alcohol; the amyl alcohol layer, containing all the ferric thiocyanate, is compared colorimetrically with a similar extract prepared from a standard solution of ferric sulphate which has been treated throughout in the same manner. C. R. HARINGTON.

Boa constrictor fat. R. H. KERR (J. Amer. Chem. Soc., 1927, **49**, 2046—2047).—Boa constrictor fat, after rendering with a small proportion of sodium hydrogen carbonate at 125°, has m. p. 28·5°, iodine value (Hanus) 79·43, iodine value of liquid fatty acids, 113·17, n^{40} 1·4619, d_1^{100}, 0·8629, saponification value 196·83, and free fatty acids, 0·17%. The acids consist of palmitic, stearic, oleic, and linoleic acids, together with a highly unsaturated *acid*, the bromide of which appears to be an octabromostearic acid. F. G. WILLSON.

Dihydroxyphenylalanine in the cocoons of *Samia cecropia*, L. (Saturnidæ). H. PRZIBRAM and H. SCHMALFUSS (Biochem. Z., 1927, **187**, 467—469).—3 : 4-Dihydroxyphenylalanine is isolated from the cocoons of the moth by the methods of Schmalfuss and Müller (this vol., 586). P. W. CLUTTERBUCK.

Extractives of reptilian muscle (python). W. KEIL, W. LINNEWEH, and K. POLLER (Z. Biol., 1927, 86, 187—198).—Creatine, methylguanidine, adenine, carnosine, and γ-butyrobetaine have been identified in the extract of the muscle of *Python molurus* and *reticulatus*. A picrolonate has been isolated, possibly that of histidine, as well as a picrate of the formula $C_5H_{14}N_2,2(C_6H_3O_7N_3)$. W. O. KERMACK.

Identity of actinine with γ-butyrobetaine. D. ACKERMANN (Z. Biol., 1927, **86**, 199—202).—Actinine isolated from *Actinia equina* (cf. A., 1924, i, 243, 978) is identical with γ-butyrobetaine, $\begin{matrix}CH_2\cdot CH_2\cdot CH_2\\ | \quad\quad | \quad\quad |\\ NMe_3\text{–}O\text{—}CO\end{matrix}$. W. O. KERMACK.

Diffusion of carbamide in different fluids of the [illegible] C. T. RIETTI (Rev. Soc. [illegible]ana 3 , 1927, **3**, 399—408).—Carbamide in physiological solution was injected intravenously into dogs with ligatured kidneys. In the case of the blood, a large initial increase in the carbamide content was followed by a slow decrease. The figures for serum-carbamide followed those for blood. The carbamide in the bile increased and eventually reached a higher figure than that for the blood. Similar results were obtained for the pancreatic juice. The carbamide in the cerebrospinal fluid increased slowly and only in a single case, after 4 hrs., exceeded that in the blood. The smallest increases were obtained for carbamide in the saliva. G. W. ROBINSON.

Inorganic constituents of human saliva. G. W. CLARK and L. LEVINE (Amer. J. Physiol., 1927, **81**, 264—275).—Resting saliva is compared with that obtained by paraffin stimulus. Short fasting does not appreciably change the inorganic composition of the saliva. Ingestion of chloride does not increase the concentration in the saliva but excess phosphate is excreted by this route. Notable uncontrolled and individual variations in the composition of human saliva are reported. R. K. CANNAN.

Acidity of urine. G. TELLERA (Boll. Chim. farm., 1927, **66**, 449—456).—Instructions are given for the colorimetric determination of the p_H of urine based on the methods of Sørensen, Clark and Lubs, and Michaelis. The use of Bruere's modification of this method is also described; this consists in the use of solutions of inorganic salts as colour standards: mixtures of cobalt nitrate and copper sulphate for the range p_H 6·0—7·6 (bromothymol-blue); of potassium dichromate and cobalt chloride in acetic acid for the ranges p_H 4·4—6·0 (methyl-red) and p_H 6·8—8·4 (phenyl-red). E. A. LUNT.

Urine analysis. C. OTTO (Pharm. Ztg., 1927, **72**, 996—997).—A discussion of modern methods of testing urine for acetone and for acetoacetic acid, either alone or together, for dextrose, and for melanin. W. ROBSON.

Detection and identification of reducing sugars in urine by Castellani's mycological method. P. PIETRA (Rev. sud-amer. endocrinol. immunol. quinioterap., 1927, **10**, 21—28).—The sugars occurring in normal and pathological urines and the monilias and bacteria fermenting each are tabulated. Identification is nearly always possible. CHEMICAL ABSTRACTS.

Blood bilirubin. Determination and clinical significance. F. S. PERKIN (Arch. Int. Med., 1927, **40**, 195—202).—A modification of the Thannhauser–Andersen method for the determination of bilirubin in the blood (cf. Deut. Arch. klin. Med., 1921, **137**, 179) is described, and the clinical significance of the figures obtained is discussed. W. O. KERMACK.

Animal calorimetry. XXXV. Mechanism of phloridzin diabetes. H. J. DEUEL, jun., H. E. C. WILSON, and A. T. MILHORAT (J. Biol. Chem., 1927, **74**, 265—297).—Injection of phloridzin into well-nourished dogs after a starvation period of 18 hrs. had no immediate effect on the respiratory quotient. Administration of dextrose to fasting phloridzinised dogs caused a slight rise in the respiratory quotient; when 16 g. of dextrose were so administered 19% was oxidised, but after 5 g. of dextrose none was

oxidised. In fasting and nephrectomised dogs phloridzin failed to reduce the respiratory quotient to the diabetic level; it had no effect on the blood-sugar; it increased the glycogen content, but not sufficiently to indicate absence of oxidation; it had no effect on the course followed by the non-protein nitrogen of the blood, nor did it cause a heavy excretion of ketones; the results therefore indicate that the action of phloridzin is exclusively renal and that it does not interfere with the oxidation of carbohydrate. C. R. HARINGTON.

Peptide nitrogen of blood in arterial hypertension. H. JACKSON, jun., D. W. SHERWOOD, and O. J. MOORE (J. Biol. Chem., 1927, 74, 231—233).—No significant increase in the peptide nitrogen of the blood was observed in cases of arterial hypertension. C. R. HARINGTON.

Relationship of blood-sugar, cholesterol, and hypertonia. M. DORLE and W. LIEHR (Biochem. Z., 1927, 187, 385—387).—There does not appear to exist any relationship between blood-sugar, blood-cholesterol, and blood-pressure in cases of arteriosclerosis and hypertonia. P. W. CLUTTERBUCK.

Inorganic constituents of the blood-plasma of dogs after removal of the hypophysis. P. MAZZOCCO (Rev. Soc. Argentina Biol., 1927, 3, 213—216).—The content of sodium chloride, inorganic phosphorus, calcium, magnesium, potassium, and sodium in the plasma of dogs from which the hypophysis has been removed is normal. G. W. ROBINSON.

Calcium in jaundice with special reference to the effect of parathyroid extract on the distribution of calcium. A. CANTAROW, S. M. DODEK, and B. GORDON (Arch. Int. Med., 1927, 40, 129—139).—In cases of jaundice the calcium content of the whole blood shows marked variation and is sometimes abnormally low. The calcium content of the serum, however, does not differ markedly from that of normal serum, so it appears that sometimes very little calcium separates in the clot. By the administration of parathyroid extract the calcium content of the blood in cases of jaundice may be brought to a normal level. As the deficiency of calcium appears to be related to a tendency towards bleeding, the administration of parathyroid hormone has a beneficial effect. W. O. KERMACK.

Rickets in rats. III. Calcium and phosphorus metabolism of rats on restricted diets. A. T. SHOHL and H. B. BENNETT (J. Biol. Chem., 1927, 74, 247—256).—Rats on a rickets-producing diet were restricted to one third of the maximum amount of this diet which they would voluntarily consume; under these conditions no healing of the rickets took place. It is concluded that the increased deposition of calcium recently observed (this vol., 790) to follow addition of phosphates to such a diet was due to the phosphates as such and not to a reduction in the total food intake. C. R. HARINGTON.

Determination of guanidine and its alleged occurrence in urine during tetany. F. M. KUEN (Biochem. Z., 1927, 187, 283—306).—The older methods for the determination of guanidine and methylguanidine, depending on precipitation with silver–barium hydroxide solutions or mercuric sa solutions are discarded since methylguanidine ma arise by oxidation of creatine. The method Findlay and Sharpe (precipitation of guanidine wit picric acid) is not satisfactory since it is impossibl to obtain a sharp separation of guanidine and creati ine picrates. Removal of creatinine with zinc chlorid also is never complete. A better method is th precipitation of guanidine as picrolonate, creatinin picrolonate being readily soluble. Addition of guan idine to normal urine gave 50—90% yields of th picrolonate. The presence of methylguanidine ma be detected after decomposing the picrolonate wit sulphuric acid and extracting the picrolonic aci with ether, by means of a modification of the colou reaction of Sakaguchi (J. Biochem. Japan, 1925, 5 25, 133; cf. Poller, A., 1926, 1284). This reactio is used as a colorimetric method for determinatio of quantities above 50 mg. per litre, and as a qualitative test for smaller amounts. Guanidin and methylguanidine are further identified by boilin the solution with sodium hydroxide and determining the ammonia and methylamine resulting. Urines, both normal and from cases of tetany (idiopathic, post-operative, and in children), when tested b means of the nitroprusside reaction, by Sakaguchi' reaction, and by the gravimetric picrolonic acid method give completely negative results. The results do not support the guanidine theory of tetany. P. W. CLUTTERBUCK.

Prevention of tetany by magnesium lactate. W. F. WENNER (Amer. J. Physiol., 1927, 81, 392—404).—Continuous administration of magnesium lactate to parathyroidectomised animals prevented tetany and mitigated the fall in the concentration of calcium in the blood. It is suggested that the magnesium keeps the calcium in solution in the blood by unitin with the excess phosphate. The lactates of potassium, sodium, and cadmium were without effect. R. K. CANNAN.

Biological decomposition and respirator processes. H. VON EULER, R. NILSSON, and D. RUNEHJELM (Z. physiol. Chem., 1927, 169, 123—163).—Biological respiration consists of two "mai phases," one anaerobic and the other aerobic. Th change in the first phase is effected by the reductase (redoxase) type of enzyme and results in the formation of substances which are more easily oxidisec In this way, carbohydrates undergo a dismutatio process as a result of the action of mutase and its co-enzyme (co-zymase). Oxidation catalysts, som of peroxydase nature and others such as hæmoglobi and cytochrome, are responsible for the aerobi phase. The methods involving the reduction o methylene-blue and the measurement of the absorp tion of molecular oxygen do not, therefore, giv parallel results. The former is not a measure of t total respiratory power but is a true record of t anaerobic phase of carbohydrate decomposition an similar processes. The activating influence of co zymase on respiration is due to its effect on anaerobic phase, the dismutation of dextrose. dialysed succino-dehydrogenase solution may av lost its respiratory power, as measured by the oxyge usage in the presence of succinic acid, but yet re a

the power to reduce methylene-blue, a process activated by succinic acid. The respiratory power and cytochrome content of many yeast preparations show a striking parallelism, and treatment which inactivates the cytochrome, such as drying the yeast or poisoning with potassium cyanide, leads to inhibition of respiration, although the reductase power (methylene-blue experiments) may still be retained in full. Hæmoglobin has an activating influence on the respiration of muscle and liver extracts but little or none on yeast respiration. Methylene-blue can be used as an artificial oxidation catalyst since it accelerates the respiration of liver extracts, which are almost free from oxidation catalysts, in the presence of succinic acid, and the respiration of washed dried bottom yeast with hexosediphosphate. In the presence of the natural oxidation catalysts (dried top yeast), methylene-blue does not activate the respiration of the yeast–hexosediphosphate–co-zymase system. The functions of co-zymase are considered; yeast reductase can utilise lactic acid in the absence of co-zymase and the addition of co-zymase has no effect on this process. The theory of specific oxidation catalysts is discussed and the conclusion is reached that from the oxidation potential alone no deductions as to the velocity of the oxidation are justifiable. A. WORMALL.

Trimethylamine oxide as hydrogen acceptor in intermediary metabolism with particular reference to the sulphydryl group. D. ACKERMANN, K. POLLER, and W. LINNEWEH (Z. Biol., 1927, 85, 435—452).—Fresh or boiled ox-liver in a slightly alkaline medium converts trimethylamine oxide into trimethylamine; the reduction is not due to any of the following substances: dextrose, lævulose, adrenaline, phenylglycine, α-alanine, muscle stroma, albumin, globulin, hæmoglobin, ovalbumin, succino-dehydrogenase, Schardinger's enzyme, catalase, or purine-dehydrogenase. Trimethylamine oxide converts cysteine into cystine and the reduced form of glutathione into the oxidised form at 40° in a medium of p_H 9·3 and is itself reduced to trimethylamine. This reduction is effected only by means of a sulphydryl group linked to a carbon atom. Dimethylaniline oxide behaves similarly.

The addition of cystine or oxidised glutathione to a system of washed muscle-tissue and trimethylamine oxide results in the production of trimethylamine, trimethylamine oxide acting as a hydrogen acceptor. This result is discussed with reference to the theories of Hopkins and of Wieland on the mechanism of biological oxidations. Data are given for the relative activity of methylene-blue, thionine, and trimethylamine oxide as hydrogen acceptors.

Trimethylamine oxide is reduced to trimethylamine by hydrogen in the presence of palladised animal charcoal. E. A. LUNT.

Increase in the calcium of hen's blood accompanying egg production. J. S. HUGHES, R. W. ITTUS, and B. L. SMITS (Science, 1927, 65, 264).—e calcium content of the blood of hens during the period of egg production is about double that during e s non-production. Average values (mg. c.c. of plasma) are: immature pullets and capons 13, mature cockerels and moulting hens not in production 14, mature pullets not in production 20, in production 27, mature hens after moulting in production 31. A. A. ELDRIDGE.

Biochemistry of iodine. S. WEISER and A. ZAITSCHEK (Biochem. Z., 1927, 187, 377—384).—Administration of potassium iodide to pigs has no effect on the period of gestation nor on the number in or weight of the litter, but the mean weight at weaning of the pigs receiving no iodide was 13·17 kg., and with those receiving iodide 18·54 kg. Administration of iodide to cows had a delayed action, the amount of milk being increased by 7·1% after the iodide administration had ceased. P. W. CLUTTERBUCK.

Chemical exchange as a basis for the uptake of basic and acidic foreign substances by the cell. I. II. K. ZIPF (Arch. exp. Path. Pharm., 1927, 124, 259—285, 286—325).—Perfusion of the livers of cold-blooded animals with fluids of various compositions shows that at normal reaction basic substances are retained more readily than acid and that an increase of p_H favours the uptake of cations whilst a decrease of p_H favours the uptake of anions. The view is advanced that the uptake of alkaloids, basic dyes, and other cations by the animal cell is dependent on salt formation with acids normally present in the cell, whilst anions when retained combine with the basic constituents. W. O. KERMACK.

Fixation of intravenously injected calcium by the tissues. L. CONDORELLI (Arch. Farm. sperim., 1927, 43, 88—96).—The tissues fix calcium injected into the blood-stream with great rapidity. This property is not exclusive to the reticulo-endothelial system as the blocking of the latter by colloidal silver produces no sensible diminution in the rate of disappearance of calcium from the blood. E. A. LUNT.

Intermediary carbohydrate metabolism. C. G. LAMBIE (J.S.C.I., 1927, 46, 300—304T).—A discussion of the questions as to where the primary disturbance occurs in diabetes and what is the locus of insulin action. It is suggested that the diabetic primarily lacks the power of transforming dextrose into some intermediate product which can readily be oxidised by the diabetic as well as by the normal, and, moreover, that the essential action of insulin is to cause this transformation to take place. The evidence put forward by other workers that this intermediary is dihydroxyacetone, methylglyoxal, acetaldehyde, hexose-mono- or -di-phosphate is discussed. A scheme of the degradation products of carbohydrates, fats, and proteins with dihydroxyacetone as a common intermediary is given. W. ROBSON.

Influence of quantity of food on growth. H. VON HOESSLIN (Z. Biol., 1926, 46, 175—194).—In an experiment extending over 400 days on two pure-bred puppies of equal initial weight on a mixed diet, the one dog receiving continuously only one third of the amount of food supplied to the other, the former dog showed throughout an increase in weight only 0·26 times that shown by the normally fed dog. E. A. LUNT.

Growth of cats. H. VON HOESSLIN (Z. Biol., 1926, 85, 248—264).—The influence of quantity of diet on growth has been investigated in the case of the cat with particular reference to the variation with temperature of the minimum food intake necessary for preservation of life. E. A. LUNT.

Effect of amino-acids on sugar metabolism with respect to their optical activity. W. E. BURGE, G. C. WICKWIRE, A. M. ESTES, and M. WILLIAMS (J. Biol. Chem., 1927, 74, 235—239).—The rate of utilisation of dextrose by *Paramœcium caudatum* was increased by addition to the medium of the natural modifications of the common amino-acids; the racemic amino-acids were without effect. C. R. HARINGTON.

Rate of nitrogen excretion on a protein diet with added carbohydrate. H. FIRGAU, K. HARTMANN, and E. VOIT (Z. Biol., 1927, 85, 557—566).—For the dog the amount of nitrogen eliminated has been measured at two-hourly intervals in the 24 hrs. following a protein meal. The fraction of the total nitrogen which is eliminated at any given interval is independent of the amount of protein administered, and does not change appreciably when a light protein meal is supplemented with much carbohydrate. On a daily diet containing 125 g. of starch, 55 g. of dextrose, 10 g. of fat, and 18 g. of protein, an increase in the frequency of feeding from 1 to 12 times per 24 hrs. results in a decrease of approximately 16% in the daily amount of nitrogen eliminated when determined at intervals of 4 hrs., and the rate of nitrogen elimination then becomes practically constant. E. A. LUNT.

Fate of *iso*propyl alcohol in the human organism. H. KEMAL (Biochem. Z., 1927, 187, 461—466).—*iso*Propyl alcohol, administered to man, is excreted partly as acetone in the urine and in the breath. The amount of acetone excreted is greatly increased by drinking large amounts of water. Aceto-acetic acid was not detected in the urine. P. W. CLUTTERBUCK.

Preparation of borneolglycuronic and glycuronic acids. A. J. QUICK (J. Biol. Chem., 1927, 74, 331—341).—After administration of borneol to dogs 50% is excreted in the urine in conjugation with glycuronic acid; the urine of a dog so treated was cleared with lead acetate and acetic acid and the filtrate treated hot with zinc acetate; the precipitate of zinc borneolglycuronate was dissolved in hot dilute sulphuric acid and the solution, on cooling, deposited an 87% yield of borneolglycuronic acid. On hydrolysis with 0·2*N*-sulphuric acid this yielded a mixture of 70% glycuronic acid and 30% of the lactone. The acid was obtained pure by removal of the lactone by repeated extraction with alcohol in the cold; it had $[\alpha]_D$ +16·5°⟶+36°; on dissolving the above mixture in hot acetic acid and cooling, the lactone separated; it had $[\alpha]_D$ +19°. C. R. HARINGTON.

Excretion of kynurenic acid in bile. Y. KOTAKE and K. ICHIHARA (Z. physiol. Chem., 1927, 169, 1—2).—Considerable amounts of kynurenic acid have been isolated from gall-bladder fistula bile of a dog after the subcutaneous injection of an aqueous suspension of tryptophan (2 g.). A. WORMALL.

Nature of the "inorganic phosphate" in voluntary muscle. C. H. FISKE and Y. SUBBAROW (Science, 1927, 65, 401—403).—When the phosphorus is determined colorimetrically by means of aminonaphtholsulphonic acid, delay in the production of colour occurs. The delay is observed with muscle filtrates from which all the inorganic phosphate has been removed by precipitation with barium or silver salts, and is ascribed to the presence of a labile phosphorus compound. For its determination, the authors' ordinary method is employed, readings being taken at specified intervals, and the concentration of inorganic phosphate found by extrapolation. The normal resting voluntary muscle of the cat contains 60—75 mg. of "labile" phosphorus and 20—25 mg. of inorganic phosphorus per 100 g. The effect of stimulation is to decrease the labile and increase the inorganic phosphorus. The labile substance is considered to be a phosphocreatine compound. A. A. ELDRIDGE.

Physiological significance of phosphagen. P. EGGLETON and G. P. EGGLETON (J. Physiol., 1927, 63, 155—161; cf. this vol., 271).—In the resting gastrocnemius the amount of phosphagen-phosphorus is about 0·055%, in cardiac muscle it is about one tenth of this, and in smooth muscle none was detected. A gastrocnemius tetanised electrically for 2—4 min. lost most of its phosphagen and about two thirds of the phosphorus of the latter appeared as inorganic phosphorus together with rather more than one molecule of lactic acid for every atom of phosphorus. In fatigue more slowly induced the lactic acid production was greater and the loss in phosphagen about the same. There is no restitution of phosphagen anaerobically, but in the presence of oxygen it rapidly reappears and an exact equivalent of inorganic phosphate disappears. Little lactic acid is removed during this synthesis. The role of phosphagen in muscle contraction is discussed. R. K. CANNAN.

Syncholia and syncholics. II. Elimination of substances containing iodine by bile and urine. T. IBUKI (Arch. exp. Path. Pharm., 1927, 124, 370—384).—Iodine administered in the form of benzene derivatives is eliminated to a much greater extent by the urine than by the bile, whilst when administered in the form of aliphatic iodine compounds it is eliminated to a relatively greater extent by the bile. Iodine administered as tetraiodophenolphthalein is also eliminated chiefly by the bile. W. O. KERMACK.

Fate of fat emulsions administered intravenously. R. VON BODÓ and L. SCHEFFER (Arch. exp. Path. Pharm., 1927, 124, 326—333).—'Iodipin," a fat containing iodine, when administered intravenously to a dog as a fine emulsion is taken up largely by the liver and only to a less extent by the lungs and spleen. At the end of 72 hrs. 5% of the iodine administered is still in the blood, whilst 65% has been eliminated in the urine. W. O. KERMACK.

Emulsion therapy. II. Amount and duration of fat storage in the lungs. L. SCHEFFER (Arch. exp. Path. Pharm., 1927, 124, 334—342). When emulsions of "iodipin" are injected intravenously

into a dog the concentration of the fat in the lungs may reach 0·6—1·1%, but after 1½ hrs. it decreases to 0·3%. W. O. KERMACK.

Anæsthetic value of nitrous oxide under pressure. W. E. BROWN, G. H. W. LUCAS, and V. E. HENDERSON (J. Pharm. Exp. Ther., 1927, **31**, 269—289).—Full surgical anæsthesia is not produced by nitrous oxide–oxygen mixtures under pressure unless the partial pressure of oxygen is less than 70 mm. W. O. KERMACK.

Pharmacology of the two 5-phenyl-3-methyl-*iso*oxazolecarboxylic acids and of other related substances. M. DORINI (Arch. Farm. sperim., 1927, **43**, 51—87).—Whilst no attempt is made to explain the nature of the isomerism of the two 5-phenyl-3-methyl*iso*oxazolecarboxylic acids, the pharmacological properties of the two substances are shown to differ. The one isomeride (m. p. 189°) exhibits no toxic action, whilst the lethal dose of the second (m. p. 157°) is 5 g. per kg. body-weight for the frog and 3 g. per kg. for the mouse. The toxic acid appears to be excreted unchanged in the urine, although an extract of liver pulp at 34° will destroy its toxic action in a few hours. The amide corresponding to the acid of m. p. 157° is more toxic than the acid itself and undergoes complete decomposition in the organism. Benzylidenemethyl*iso*oxazolone is less toxic than the acid of m. p. 157°, whilst the oxazole ring is devoid of toxicity and this property appears only on the introduction into the molecule of toxic groups. The physiological effects produced are similar to those produced by strychnine. E. A. LUNT.

Electromotive action of drugs as a cause of their toxicity. I. Extension of Nernst's theory of excitation and demonstration of the sensitiveness of a certain phase boundary potential towards potent alkaloids. R. BEUTNER (J. Pharm. Exp. Ther., 1927, **31**, 305—318).—The *E.M.F.* of the system -Hg|KCl sol. sat. Hg_2Cl_2|10% oleic acid in nitrobenzene|0·02% sodium oleate in 0·85% NaCl|KCl sol. sat. Hg_2Cl_2|Hg^+, which is normally 0·085 volt, is depressed when very small quantities of certain alkaloidal salts are added to the sodium chloride solution. Pilocarpine hydrochloride, atropine sulphate, strychnine sulphate, and cocaine hydrochloride in concentrations of 0·001% reduce the potential by 0·03—0·04 volt, quinine hydrochloride and morphine hydrochloride are slightly less active, whilst caffeine, adrenaline hydrochloride, chloroform, amyl alcohol, chloretone, and veronal have practically no effect at the low concentrations used. W. O. KERMACK.

Effect of polarised light on the pharmacological properties of some drugs. D. I. MACHT and W. T. ANDERSON (J. Amer. Chem. Soc., 1927, 9, 2017—2034).—Irradiation of tincture of digitalis with polarised light of the visible spectrum decreases e potency of the drug, whilst non-polarised light is without effect under similar conditions. Polarised ra-violet light increases the poisoning power of the rug, non-polarised ultra-violet light is without effect. Irradiation of cocaine hydrochloride in aque- s solution, whether by infra-red, visible, or ultra-violet rays, lowers the pharmacological action of the drug only if the light is polarised, the effect being apparently due to hydrolysis, with formation of ecgonine, benzoic acid, and methyl alcohol. Quinine and cinchonidine are similarly affected by polarised light. The deterioration produced in tincture of digitalis by circularly polarised light is greater than that by plane polarised light. F. G. WILLSON.

Hypoglycæmic properties of galegine sulphate. H. SIMONNET and G. TANRET (Compt. rend., 1927, **184**, 1600—1602, and Bull Soc. Chim. biol., 1927, **9**, 908—927; cf. A., 1914, i, 1031).—Subcutaneous injection of galegine sulphate in rabbits (lethal dose, 1 g. per kg. body-weight) gives rise to hypoglycæmia in most cases; in some, however, this state is preceded or replaced by hyperglycæmia. The toxic symptoms are very reminiscent of those of insulin and, like the latter, may be reduced by the injection of dextrose. The pharmacological investigation is rendered difficult, especially in the case of dogs, by the high toxicity of the substance. G. A. C. GOUGH.

Rat-poisoning substance in red squills. F. R. WINTON (J. Pharm. Exp. Ther., 1927, **31**, 123—136).—The rat-poisoning substance present in red squills is relatively thermostable, soluble in water and in concentrations of alcohol and acetone up to 90%. It is destroyed by boiling with dilute acid or alkali. It can be kept for long periods without appreciable deterioration. Administered *per os* to rats this substance induces convulsions and paralysis. Female rats succumb to one half the dose needed to kill males. The technique of determinations of toxicity is discussed. W. ROBSON.

Contrast between actions of red and white squills. F. R. WINTON (J. Pharm. Exp. Ther., 1927, **31**, 137—144).—The cardiac glucoside and rat-poisoning principle in red squills are distinct substances. The former occurs in about equal amounts in red and white squills, whilst the latter is present in significant amounts in red squills only. W. ROBSON.

Chemotherapy of bacterial infections. II. Relation between chemical constitution and chemotherapeutic action in staphylococcic infections. E. L. WALKER and M. A. SWEENEY (J. Pharm. Exp. Ther., 1927, **31**, 87—121).—Introduction of mercury into the benzene nucleus is followed by the systematic modification of the molecule by substitution in the other positions in the ring. An exact relation has been found to exist between chemical constitution and chemotherapeutic action. Two factors are essential, viz., toxophore and chemophore groups. The toxophore group may be either a toxic metallic element or a structural arrangement of non-toxic elements in the molecule, as the quinonoid structure. Eutherapeutic chemophore groups are primary and accessory, the former being radicals which, introduced alone into the mercuribenzene ring, form chemotherapeutically active compounds, the latter, elements or radicals, which, although alone inactive, on introduction into the benzene ring in a definite position relative to a primary eutherapeutic group, enhance the action of the primary group. For staphylococcic infections, primary groups include

NMe_2, NEt_2, OH, and CO_2H, and accessory-primary SO_3H *para* to OH, Cl *ortho* to CO_2H, and NH_2 *ortho* to CO_2H. The efficiency of the authors' series of derivatives is greatly reduced by indirect contact with the microbes through the tissues and blood as compared with their direct action on the organisms. Toxicity, like chemotherapeutic activity, is a function of chemical constitution. It is possible simultaneously to increase chemotherapeutic activity and decrease toxicity by chemical manipulation of the molecule. W. ROBSON.

Oligodynamic action of metallic silver. R. WERNICKE and I. DORTZENBACH (Anal. Asoc. Quím. Argentina, 1927, **15**, 138—147; cf. Wernicke and Sordelli, A., 1921, i, 758).—Under an atmosphere of air mixed with carbon dioxide, distilled water kept in contact with metallic silver acquires marked bactericidal properties. With an atmosphere of hydrogen negative results are obtained. G. W. ROBINSON.

Concentration of lead in the body in lead poisoning. VALLEE (Bull. mens. Mond. Ind., 1927, **54**, 642—645).—The origin, quantity, and location of the lead found in the body as a result of occupational and criminal lead poisoning are reviewed. E. A. LUNT.

Effect of long-continued ingestion of zinc compounds. Relation of zinc excretion to zinc intake. K. R. DRINKER, P. K. THOMPSON, and M. MARSH (Amer. J. Physiol., 1927, **81**, 284—306).—Extensive metabolic studies, *post mortem* examinations, and tissue analyses are reported of the effects of long-continued administration of zinc salts to rats. There was no evidence of any harmful effect. The main part of the zinc is excreted by the intestine and there is no significant storage in the tissues. R. K. CANNAN.

Physiological importance of nickel and cobalt. G. BERTRAND and H. NAKAMURA (Compt. rend., 1927, **185**, 321—324).—Data are given for the growth of 35 young mice on two artificial diets, one free from nickel and cobalt and the other containing 0·00025% of nickel chloride and 0·0001% of cobalt sulphate. The average period of survival on the first diet (14 mice) was 19·7 days, and on the second diet (15 mice) 23·1 days. From the data cited it is claimed that nickel and cobalt have a definite effect on animal metabolism. About one tenth of the nickel and cobalt administered appeared to be retained in the tissues. E. A. LUNT.

Excretion of nickel and cobalt. P. MASCHERPA (Arch. exp. Path. Pharm., 1927, **124**, 356—369).—Finely divided nickel and cobalt administered orally or subcutaneously are absorbed by the organism and excreted partly by the kidneys and partly by the intestine. W. O. KERMACK.

Arginase. K. POLLER (Z. Biol., 1927, **86**, 309—316).—The colour reaction of Sakaguchi (J. Biochem. Japan, 1925, **5**, 13, 133; cf. Poller, A., 1926, 1284), according to which certain derivatives of guanidine including arginine yield a red colour when treated in alkaline solution with sodium hypochlorite and α-naphthol, has been applied to the study of the action of arginase on various guanidine derivatives. Glycerol extracts of liver which readily decompose arginine have no action on agmatine. Agmatine is also resistant to plant extracts, but is decomposed by putrefactive bacteria. Galegine is resistant to ferments generally. W. O. KERMACK.

Optimal hydrogen-ion activities for the enzymic hydrolysis of starch by pancreatic and malt amylases under varied conditions of time and temperature. H. C. SHERMAN, M. L. CALDWELL, and M. ADAMS (J. Amer. Chem. Soc., 1927, **49**, 2000—2005).—In presence of 0·06*M*-phosphate mixtures malt amylase shows optimal activity at p_H 4·4—5·0 at 30—40°, 4·6—5·0 at 50°, and 5·3—5·8 at 70°, whilst in presence of 0·01*M*-acetate-acetic acid mixtures optimal activity is shown at p_H 4·6 at all temperatures between 30° and 60° for a half-hour period of hydrolysis, and at p_H 4·8 for a two-hour period. The period of hydrolysis does not appreciably affect the optimal p_H in the case of the phosphate mixtures. In presence of phosphate or acetate, higher temperatures increase the sensitiveness of malt amylase to change in p_H. Pancreatic amylase shows optimal activity at p_H 7·0—7·2 at 30—50° for hydrolysis periods of from 0·5 to 2 hrs. At 60°, optimal activity for half-hour periods is at p_H 6·9, and for two-hour periods at p_H 6·7. F. G. WILLSON.

Conductivity method and proteolysis. I. Peptone. H. D. BAERNSTEIN (J. Biol. Chem., 1927, **74**, 351—362).—During peptic digestion of egg-albumin the conductivity of the solution decreased when the p_H was less than 3·0, a maximum rate of decrease being observed at p_H 1·3; above p_H 3·0 the conductivity increased. Addition of Witte's peptone, in all except minimal amounts, to solutions of hydrochloric acid has a similar effect on the conductivity. Experiments with lower degradation products of protein indicate that the increase in conductivity is determined by the free carboxyl and the decrease by the free amino-groups present in solution. The conductivity method is not well suited to the determination of the optimum p_H for peptic digestion. C. R. HARINGTON.

Proteases and proteolytic inhibitors. H. H. WEBER and H. GESENIUS (Biochem. Z., 1927, **187**, 410—436).—The solution obtained by digesting to equilibrium a 2·4% caseinogen solution with trypsin-kinase (Waldschmidt-Leitz) retards proteolysis of further amounts of caseinogen and, if present in three times the concentration of the fresh caseinogen, inhibits completely. Glycylglycine, leucylglycine, and alanylglycine inhibit similarly. Alanine, glycylglycine, and the trypsin-digestion solution inhibit in increasing amount when used in equal normal concentrations. A solution obtained by digestion of a 2·55% caseinogen solution inhibits the hydrolysis of a 0·9% caseinogen solution and completely represses hydrolysis of a 0·3% solution. The extent of inhibition appears to be determined by the ratio of the amounts of substrate to inhibitory substance and not merely by the absolute amount of the latter. In the same normality in which hydrolysis is completely repressed by pepsin digestion-products o caseinogen, alanine and leucylglycine have no effect, the inhibitory substances being here much more complex than in trypsin hydrolysis. P. W. CLUTTERBUCK.

Enzymic conversion of hexosediphosphate into hexosemonophosphate and the enzymic synthesis of hexosediphosphate from hexosemonophosphate. C. NEUBERG and J. LEIBOWITZ (Biochem. Z., 1927, **187**, 481—490).—Magnesium hexosediphosphate treated with taka-diastase gives rise to Neuberg's hexosemonophosphate, whilst Robison's sodium hexosemonophosphate treated with bottom yeast forms hexosediphosphate.

P. W. CLUTTERBUCK.

Oxidation-reduction potential of yeast, of *B. coli*, and of the media on which these grow. E. AUBEL and L. GENEVOIS (Compt. rend., 1927, **184**, 1676—1678).—Media containing fermenting yeast show a definite oxidation-reduction potential. The r_H is near 7 and corresponds with an affinity for hydrogen of about 11 g.-cal. There is no affinity of the products of fermentation for hydrogen. The use of vital dyes enables the course of the decoloration of the medium and of the micro-organism to be followed. Results so obtained are in accordance with the hypothesis of Needham (cf. A., 1926, 545) that facultative anaerobes have the power of adjusting their interior oxidation-reduction potential to that of the surrounding medium, a characteristic which differentiates them from strict aerobes.

W. ROBSON.

Comparison between oxido-reduction and carbon dioxide production by yeast-enzymes. R. NILSSON and B. JANSSON (Z. physiol. Chem., 1927, **169**, 73—90).—The ratio between zymase activity or carbon dioxide production and reductase activity is not constant with different preparations of the same yeasts and the processes of drying and washing have some influence. Small quantities of adrenaline have no activating action on fermentation or the rate of decolorisation of methylene-blue by fresh top yeast. No evidence can be obtained that catalase is concerned in the reductase action of these yeast preparations, and the addition of catalase to washed dried bottom yeast, with or without co-zymase (co-reductase), has little or no effect on the decolorisation of methylene-blue. Small amounts of tetrahydro-β-naphthylamine accelerate the reduction of methylene-blue by fresh yeast but not by washed dried yeast; this substance has no activating action on the fermentative powers of dried or fresh yeasts. No explanation of these results can be offered, but tetrahydro-β-naphthylamine does not function as a hydrogen-donator for the mutase, nor can it replace the co-zymase. *o*- and *m*-Phenylenediamine have no activating effect on the reductase of dried bottom yeast. Picric acid, which is used in the purification of co-zymase and is present in the preparations obtained, has an inhibitory influence on yeast fermentation only when present in concentrations greater than $1{\cdot}25 \times 10^{-4}M$.

A. WORMALL.

Co-zymase. XIV. Purification. H. VON ER and K. MYRBÄCK (Z. physiol. Chem., 1927, 169, 1 —122).—Co-zymase is dialysable through collodion membranes, and the active material can be precipitated from the dialysate by various salt solutions. The most active preparations have been obtained from the dialysate by precipitating twice with lead acetate, then with mercuric nitrate, and finally with silicotungstic acid in the presence of sulphuric acid. The precipitate is then decomposed with barium hydroxide solution and the barium removed with sulphuric acid. The purified preparations obtained by various methods give precipitates with mercuric nitrate and solutions of silver and barium salts, phospho- and silico-tungstic acids, and alcohol up to 70%. No precipitation occurs with platinic chloride, ferrocyanic or metaphosphoric acid. The purest co-zymase is practically free from phosphorus (0·01%) but contains appreciable amounts of sulphur. The sulphur content and the positive nitroprusside reaction, however, may be due to the hydrogen sulphide used in the preparation. The ash content is usually very high—often about 10%. The protein reactions and Fehling's test are all negative, but Molisch's test and the pentose tests are strongly positive. The murexide test, special tests for adenine, hypoxanthine, and cytosine, and the pyrrole reaction are all negative. The preparations have no optical activity.

A. WORMALL.

Behaviour of pyrimidine derivatives in organisms. III. Action of yeast extracts on aminopyrimidines. A. HAHN and W. HAARMANN (Z. Biol., 1926, **85**, 275—279).—Extract of yeast contains an enzyme which deaminises 5-methylcytosine with the production of thymine. The free ammonia was neutralised from time to time during the experiment with 0·1*N*-acetic acid; for 3 g. of methylcytosine per 300 c.c. of yeast culture about 70% of the methylcytosine undergoes deaminisation. Similar experiments with *iso*cytosine and 4-methyl*iso*cytosine produced no deaminisation.

E. A. LUNT.

Cytochrome in yeast cells. II. H. VON EULER, H. FINK, and H. HELLSTROM (Z. physiol. Chem., 1927, **169**, 10—51).—The absorption spectra of oxidised and reduced cytochrome in suspensions of top and bottom yeasts have been determined and the absorption curves obtained. Dried top yeast is almost as rich in cytochrome as the fresh yeast, but the drying of bottom yeast causes an appreciable loss. Some relationship may exist between catalase activity and cytochrome content, since cytochrome-rich dried top yeast has a much greater catalase activity than cytochrome-poor dried bottom yeast. The method for the determination of the hæmochromogen content of pyridine extracts of yeast (cf. Euler and Fink, this vol., 379) is fully described and has been applied to various yeasts. In contrast to the cytochrome values, there are only small differences between the hæmochromogen values for top and bottom yeasts, compared either fresh or dried. The hæmochromogen content of yeasts does not run parallel, therefore, with cytochrome content, nor is there any relationship with the intensity of respiration. Copro-yeast has a higher hæmochromogen content than either bottom yeast *H* or top yeast *R*.

A. WORMALL.

Fermentation tube. F. F. NORD and M. G. WHITE (J. Amer. Chem. Soc., 1927, **49**, 2118—2119).—A stopcock is added to the longer arm of an Einhorn saccharimeter, whilst the end of the shorter arm is fitted with a single-holed rubber stopper, to enable a

current of any desired gas to be bubbled through the medium with which the apparatus is filled, so that the behaviour of micro-organisms can be observed in varying atmospheres. F. G. WILLSON.

Enzymic metabolism of bacteria. IV. Application of the biological determination of dextrose. P. RONA, D. NACHMANSOHN, and H. W. NICOLAI (Biochem. Z., 1927, **187**, 328—343).—The anaerobic decomposition of dextrose by *B. coli* is followed by the authors' manometric method (A., 1926, 868) and by the Hagedorn–Jensen method, the results agreeing within ± 4%. Similar results are obtained with lævulose and galactose, but maltose, sucrose, and lactose are unattacked. The hydrolysis of starch to dextrose by the combined action of salivary and pancreatic amylase (Pringsheim and Leibowitz, A., 1926, 715) was not confirmed. P. W. CLUTTERBUCK.

Cellulose as a source of "humus" in the soil. S. A. WAKSMAN (Cellulosechem., 1927, **8**, 97—103).—The decomposition of cellulose by various groups of soil fungi and bacteria is accompanied by the formation of considerable amounts (20—30% of the cellulose decomposed) of cell-substance, involving the conversion of inorganic nitrogen into complex organic nitrogen compounds. When the cell-substance is itself decomposed, certain resistant constituents remain, resembling lignins and "humic acids" in their chemical reactions, easily soluble in alkali and containing 3—5% of nitrogen. The author restates his view that soil humus is composed of two groups of substances of different origin, viz., (*a*) plant materials, such as lignin and cutin, which are resistant to decomposition, and (*b*) resistant constituents of the cell-substance formed by the activity of micro-organisms using cellulose, pentosans, sugar, and protein as sources of energy. C. T. GIMINGHAM.

Carbon nutrition of some algæ isolated from soil. B. M. B. ROACH (Ann. Bot., 1927, **41**, 509—517; cf. this vol., 176).—A study of five species of soil algæ, grown in pure culture on media containing mineral salts with 1% of various sugars, shows that all the species were capable of growth in complete darkness, provided that a suitable organic compound was present. The requirements of the individual species and their responses to different conditions were, however, widely different, and it is not justifiable to regard the soil algæ as a homogeneous physiological unit. C. T. GIMINGHAM.

Preparation of insulin. A. SORDELLI (Anal. Asoc. Quím. Argentina, 1927, **15**, 57—61).—Details are given for the preparation of insulin from the pancreas of sheep. G. W. ROBINSON.

Effect of insulin injected intrathecally. J. V. SUPNIEWSKI, Y. ISHIKAWA, and E. M. K. GEILING (J. Biol. Chem., 1927, **74**, 241—246).—Whilst subcutaneous injection of insulin is followed by reduction of the sugar and phosphate content of the cerebrospinal fluid, intrathecal injection causes, if anything, an increase in the sugar and phosphates of the blood. Incubation of insulin together with cerebrospinal fluid has no effect on the physiological properties of the former. C. R. HARINGTON.

Effect of insulin on hypophysectomised dogs. E. M. K. GEILING, D. CAMPBELL, and Y. ISHIKAWA (J. Pharm. Exp. Ther., 1927, **31**, 247—268).—Completely hypophysectomised dogs and also animals in which the posterior lobe secretion is absent or greatly diminished are hypersensitive to insulin, the sensitivity increasing with time. Removal of the anterior lobe alone does not make a dog more sensitive to insulin. Extracts of the posterior lobe injected into hypophysectomised dogs protect them against insulin hypoglycæmia, whilst extracts of the anterior lobe are inactive. The antagonistic action of the pituitary to insulin is attributable to the hormone of the posterior lobe, and possible explanations of this are put forward. The difference in sensitivity of animals towards insulin is probably partly due to the varying degrees of pituitary activity as well as to variations in thyroid activity (cf. Burn and Marks, J. Physiol., 1925, **60**, 131). W. ROBSON.

Action of insulin on the aseptically perfused heart. R. BODO and H. P. MARKS (J. Physiol., 1927, **63**, 242—248).—The increase in the disappearance of sugar from the blood of the perfused heart which has been observed by other workers still occurs under aseptic conditions. R. K. CANNAN.

Utilisation of dextrose, lævulose, and galactose by animal and plant cells, and the antagonistic action of insulin to thyroxine. W. E. BURGE and M. WILLIAMS (Amer. J. Physiol., 1927, **81**, 307—314).—The rates at which *paramœcia* and *spirogyra* consume these hexoses from solution in the presence of oxygen are in the order dextrose > lævulose > galactose. Addition of insulin increases but thyroxine diminishes these rates in the case of all three hexoses. Moreover, thyroxine antagonises the stimulating effect of insulin. R. K. CANNAN.

Effect on cell metabolism of the hormone of the thyroid gland. Experiments with leucocytes. W. FLEISCHMANN (Biochem. Z., 1927, **187**, 324—327).—The respiratory and glycolytic powers of exudate leucocytes of thyroidectomised rabbits are the same as for normal leucocytes. Addition of thyroxine or "thyreoid-opton," *in vitro*, to exudate leucocytes does not affect cell respiration but considerably increases anaerobic glycolysis. P. W. CLUTTERBUCK.

Effect of adrenaline on phosphorus partition in muscle. J. SACKS (Amer. J. Physiol., 1927, **81**, 276—279).—Injection of adrenaline into rabbits resulted in a fall in the lactacidogen of the muscles to less than half that of normal muscle together with the production of an equivalent amount of inorganic phosphate. This effect was found to be independent of the carbohydrate reserve of the animal. R. K. CANNAN.

Iron content of the liver, spleen, and blood during scurvy. (MME.) L. RANDOIN and (MLLE.) A. MICHAUX (Compt. rend., 1927, **185**, 365—368).—Experiments on 65 guinea-pigs have shown that there is no sensible diminution in the amount of iron in the spleen and in the blood during scurvy. In the liver the mean amount of iron is 9·0 mg. per 100 g. of the fresh organ for guinea-pigs on a complete artificial diet; this value falls to a mean of 5·8 mg. per 100 g.

of the fresh organ during the period from the fifteenth to the twenty-fifth day of feeding on a diet free from vitamin-*C*. On the twenty-seventh day of the experiment a value of 2·9 mg. is recorded, thus showing that the reserve of cellular iron in the liver is depleted during scurvy. E. A. LUNT.

Effect of vitamin-*D* on phosphorus, calcium, and p_H of the intestinal tract. L. YODER (J. Biol. Chem., 1927, **74**, 321—329).—Transference of rats from a complete diet to one deficient in vitamin-*D* caused an increased intestinal excretion of calcium and phosphorus; restoration of vitamin-*D* at once reduced the excretion of calcium, whilst that of phosphorus was at first increased and later decreased; the acidity of the intestinal tract was increased throughout by administration of cod-liver oil, and in the lower part by irradiation; there is thus a relationship between efficient absorption of calcium and phosphorus and a sufficiently acid reaction of the gut. C. R. HARINGTON.

Buffering capacity and plant juices. F. LEUTHARDT.—See this vol., 937.

Plant colloids. XIX. Starch dextrins. M. SAMEC (Biochem. Z., 1927, **187**, 120—136).—During the hydrolysis of starch by maltase or by taka-diastase, the phosphorus content of the colloidal residue increases continuously; synthetic amylo-phosphoric acids are hydrolysed with much greater difficulty than natural starch by these enzymes to give again products richer in phosphorus than the starting material; it thus appears that the increase of phosphorus in the unhydrolysed residue is responsible for the inhibition of the hydrolysis. Extracts of yeast, muscle, bone, and soya bean are able to eliminate phosphorus both from natural starch and from synthetic amylophosphoric acids. The dextrins prepared by Lintner's method contain phosphorus; the amylodextrin could be separated by electrodialysis into a phosphorus-containing gel and a phosphorus-free sol; although the erythro- and achroo-dextrins could not be so separated, it is probable that they also consist of two similar fractions. The dextrin obtained by the action of *Bacterium macerans* on starch is a phosphorus-containing degradation product of amylopectin, of high mol. wt. C. R. HARINGTON.

Lactic acid in phanerogams. G. B. VAN KAMPEN (Biochem. Z., 1927, **187**, 180—182).—Lactic acid occurs in beech-nuts, soya beans, and cotton seeds in the form of magnesium lactate.

C. R. HARINGTON.

Plant phosphatides. V. Aqueous dialysate of soya bean. V. GRAFE and K. OSE (Biochem. Z., 1927, **187**, 102—113).—The qualitative reactions of the solution obtained by dialysing soya beans against water at 20° are described. The phosphatides of the soya bean differ from those hitherto investigated in having a higher content of alkaline earths.

C. R. HARINGTON.

barley. I. Proteins. Y. NAKAMURA (Bull. Agric. Chem. Soc. [Japan], 1926, **2**, 155—158).—ogen distribution in three varieties of brewing barleys has been determined.

CHEMICAL ABSTRACTS.

Presence of sparteine in the flowers of *Spartium junceum*, L. A. SANNA and G. CHESSA (Annali Chim. Appl., 1927, **17**, 283—284).—Like those of *Spartium scoparium*, the flowers of *S. junceum* (Spanish broom) contain sparteine.

T. H. POPE.

Presence of polygalitin in the leafy stems of *Polygala vulgaris*. P. PICARD (Bull. Soc. chim. Biol., 1927, **9**, 692—696).—A compound $C_6H_{12}O_5$, m. p. 141·5—142°, $[\alpha]_D$ +41·1°, extracted from the stems of *P. vulgaris* has been identified as polygalitin isolated by Chodat from *P. amara* (Arch. Sci. Phys. Nat. Genève, 1888, **19**, 290; cf. Berkhout, Diss., Geneva, 1918). W. O. KERMACK.

Sapucainha. R. A. D. DA SILVA (Rev. Brasil. med. pharm., 1926, **2**, 627—646).—The seed oil of sapucainha (*Carpotroche brasiliensis*, Endl., or *Mayna brasiliensis*, Raddi) has d^{25} 0·95, f. p. below 16°, acid value 1·2—4, saponification value 180—190, iodine value (Hanus) 105—112, n_D^{40} 1·4718—1·4760, $[\alpha]_D^{25}$ +52° to 56°. The Reichert–Meissl–Polenske values of the soluble and insoluble volatile acids, respectively, are 1·21 and 0·6. The constants and odour resemble those of chaulmoogra oil. The fatty acids consist chiefly of chaulmoogric and hydnocarpic acids; "carpotrocholeic acid" was not found. Peckolt's alkaloid carpotrochine, on evaporation of an ethereal solution with dilute sulphuric acid, yields a green residue giving a chestnut-coloured aqueous solution.

CHEMICAL ABSTRACTS.

Dragon's blood. S. FRÄNKEL and E. DAVID (Biochem. Z., 1927, **187**, 146—158).—The pigment obtained by ethereal extraction of dragon's blood (from *Dracaena Draco*) is a red amorphous powder, $C_{17}H_{18}O_4$, m. p. 147° (decomp.); with bromine in acetic acid it gives a *tribromo*-derivative, m. p. 131° (decomp.). With ozone it gives a *dicarboxylic acid*, $C_{12}H_{22}O_5$, and, on oxidation with dilute nitric acid, (i) a *monocarboxylic acid* (*dracaenic acid*), $C_{12}H_{12}O_3$, m. p. 120° (p-*nitrophenylhydrazone*, m. p. 204°; *ethyl* ester, m. p. 104°), which on reduction with sodium in alcohol gave a *substance* $C_{12}H_{14}O_3$, m. p. 188°, and was therefore a ketododecoic acid, and (ii) a *monocarboxylic acid* (*draconic acid*), $C_5H_6O_5,4H_2O$, m. p. 178° (*ethyl* ester, m. p. 154°).

C. R. HARINGTON.

***Fabiana imbricata*.** G. R. EDWARDS and H. ROGERSON (Biochem. J., 1927, **21**, 1010—1014).—The following substances have been isolated from the aerial stems of *F. imbricata*: a neutral essential oil by distillation in steam; an ester of m. p. 77·7—78°; palmitic acid; a phytosterol of m. p. 134°; an unsaturated *alcohol*, $C_{26}H_{42}O$, b. p. 145°/25 mm.; traces of unsaturated acids and arachidic acid; scopoletin; a basic compound which gave an amorphous picrate, m. p. 125° (decomp.); a sugar giving *d*-phenylglucosazone; a *glucoside* of scopoletin, $C_{16}H_{18}O_9,2H_2O$, m. p. 226—228°, designated *fabiatrin*, and a saponin.

S. S. ZILVA.

Reactions of wood with aromatic amines and with phenols. E. HÄGGLUND and T. JOHNSON (Biochem. Z., 1927, **187**, 98—101).—On heating at 100° for 24 hrs. in dilute hydrochloric acid in presence of excess of naphthylamine or of guaiacol, pine wood

combined with 11·5% of the former and 10·3% of the latter. Assuming the reaction to depend on the presence of a carbonyl group in the lignin molecule this indicates that the wood contains 27% of lignin of mol. wt. 338. At the ordinary temperature, at which the glucoside linking of the lignin is stable, the amounts of amine or phenol bound by the wood are minimal, and may be due to the presence of carbonyl compounds other than lignin. C. R. HARINGTON.

Influence of plant injury and root rot disease on the physical and chemical composition of maize grain. G. H. DUNGAN (Illinois Agric. Exp. Sta. Bull., 1926, No. 284, 254—281).—There is no definite correlation between kernel "starchiness" and quantity of starch in the grain. The percentage of total nitrogen, hemicellulose, and non-hydrolysable material is higher in ears on broken than on sound shanks; mutilation of the shanks reduced the proportion of ether extract and starch in the grain. Differences in the chemical composition between sound grain and grain from plants inoculated with root rot are not significant. Horny and floury maize of the Leaming variety do not differ chemically, but on germination the former contains more soluble starch and dextrin than the latter. CHEMICAL ABSTRACTS.

Fungicidal activity of furfuraldehyde. H. H. FLOR (Iowa State Coll. J. Sci., 1927, **1**, 199—223).—The furan nucleus appears to be a minor factor in the toxicity of furfuraldehyde towards *Puccinia coronata holci*, *Ustilago hordei*, and *Sphacelotheca sorghi*. The toxicity of metallic furoate accords with that of the metal. The effects of various fungicides on wheat, oats, and barley are described.

CHEMICAL ABSTRACTS.

Oxidation quotients. H. MULLER (Biochem. Z., 1927, **186**, 451—460).—The oxidation quotient of a substance or solution is the ratio between the nitrogen content and the "oxygen requirement" (the amount of oxygen which is required for the complete oxidation of the organic matter to the end-products of animal combustion). The substance is oxidised by heating with strong sulphuric acid and a known amount of potassium iodate, the free iodine driven off, and the amount of iodate remaining and the nitrogen are determined in the solution. The oxygen requirement calculated from the amount of iodate decomposed during the oxidation agrees very closely with that calculated from the formula, on the assumption that the carbon, hydrogen, and sulphur are oxidised to carbon dioxide, water, and sulphuric acid respectively, and the nitrogen is reduced to ammonia. When chlorides are present, the amount of chloride must be determined and a special correction made; if volatile acids are present in appreciable amounts, the method is not applicable. Preliminary applications of the method to urine are described, and it is considered that the oxidation quotient gives a more accurate record of the oxidation processes than does the C : N ratio.

A. WORMALL.

Determination of carbon dioxide and of carbonates in solution. Determination of carbon dioxide in whole blood, plasma, serum, corpuscles, bile, urine, and mineral waters. M. NICLOUX (Bull. Soc. Chim. biol., 1927, **9**, 758—771).—The author's method for the determination of carbon dioxide (cf. this vol., 436) affords a very convenient and rapid method in the case of body-fluids and other solutions of biochemical interest. The error of the determination is less than 1·5%.

W. O. KERMACK.

Determination of carbon dioxide in fermenting mixtures. A. L. RAYMOND and H. M. WINEGARDEN (J. Biol. Chem., 1927, **74**, 189—202).—The carbon dioxide evolved (evolution being facilitated by mechanical agitation) is passed, with the aid of a stream of air, into barium hydroxide solution, and determined by the resulting change in conductivity of the latter. Figures are given for the specific resistance of solutions of barium hydroxide at 25°, 30°, and 37°. C. R. HARINGTON.

Determination of chlorides in body-fluids. W. R. BOND and H. B. HAAG (Bull. Med. Coll. Va., 1926, No. 23, 9—13).—A direct titration method is based on measurement of the potential difference established between a silver electrode and solutions of silver salts. CHEMICAL ABSTRACTS.

Determination of cysteine, cystine, and their derivatives in tissues and biological fluids. Y. OKUDA (Proc. Imp. Acad. Tokyo, 1927, **3**, 287—290).—10 G. of tissue paste are treated with 20 c.c. of *N*-sulphosalicylic acid so as to precipitate the proteins. The residue after filtration is extracted with 0·5*N*-sulphosalicylic acid and the combined filtrates are made up to 100 c.c. In order to determine cysteine in this filtrate water is added to 40 c.c. of it to make the concentration of acid equal to 0·5*N*, and 5 mg. of cysteine contained in 5 c.c. of 0·5*N*-sulphosalicylic acid are then added. To 20 c.c. of this resultant solution are added 2 c.c. of approximately 5% potassium iodide solution and 2 c.c. of *N*-sulphosalicylic acid solution and the mixture is titrated with 0·002*M*-potassium iodate solution until a blue colour is produced, starch having been added as indicator. The temperature is then read and the quantity of cysteine corresponding with a given amount of potassium iodate at this temperature is obtained from a curve previously prepared by carrying out determinations of a definite amount of cysteine at various temperatures. The total cystine and cysteine is determined by adding 0·5 g. of zinc dust to 40 c.c. of the original filtrate and boiling for 10 min. The filtrate is adjusted so as to contain 0·5*N*-sulphosalicylic acid and the total cysteine then determined by the above method.

W. O. KERMACK.

Bang's method for micro-determination of nitrogen. K. SUTO (Biochem. Z., 1927, **187**, 78—83).—A condenser of hard glass may be substituted for the quartz or platinum condenser recommended by Bang ("Micromethoden zur Blutuntersuchung," 1920, 15); a silver condenser is not suitable. C. R. HARINGTON.

BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

NOVEMBER, 1927.

General, Physical, and Inorganic Chemistry.

Revision of Rowland's preliminary tables of solar spectrum wave-lengths. C. E. St. John (Proc. Nat. Acad. Sci., 1927, **13**, 678—683).—An account is given of the methods adopted in fixing standard wave-lengths, and of the scheme in operation at Mount Wilson Observatory, for the accurate determination of solar wave-lengths in the international system. R. A. Morton.

Intensity and width of spectral lines. B. Trumpy (Z. Physik, 1927, **44**, 156).—By using in error the number of atoms instead of the number of resonators in earlier work (this vol., 179) when calculating the radius r_0 of mercury atoms, values slightly too low were obtained. R. W. Lunt.

Intensities in the hydrogen fine structure. W. V. Houston (Physical Rev., 1926, [ii], **28**, 428).—Sommerfeld and Unsold's treatment of the intensities of the hydrogen fine structure components is criticised. The forbidden components $2p_1$—$2p_1$, $3p_2$—$2p_2$, and $3s$—$2s$ are to be expected in this order of decreasing intensity, and the current in a discharge tube is likely to produce them in hydrogen. These components will increase with an increase in current, and will also show a resultant polarisation. A. A. Eldridge.

Doublet separation and fine structure of the Balmer lines of hydrogen. N. A. Kent, L. B. Taylor, and H. Pearson (Physical Rev., 1927, [ii], **30**, 266—283).—The wave-length difference between the components λ' and λ'' ($\lambda'>\lambda''$) of H_α, H_β, and H_γ are determined as 0·1370, 0·0791, and 0·0666 A., respectively. Another component in λ' in H_α, H_β, and H_γ is present, and there are indications of other components in λ''. The magnitudes of the components agree with those given theoretically by the new quantum mechanics with the spinning electron. A. A. Eldridge.

Spectral intensity distribution in a hydrogen discharge. E. W. Tschudi (J. Franklin Inst., 1927, **204**, 219—225).—A cold cathode discharge tube has an auxiliary tube attached from which cathode rays are projected against the main cathode. The relative intensity distributions of H_γ and H_β were measured, by means of a photo-electric cell, from the main cathode through the cathode dark space into the negative glow, with and without excitation of the auxiliary tube. The intensity of spectral illumination in the negative glow is increased by about 20% when the main cathode is bombarded by the electron stream. This increase is attributed to the production of soft X-rays in the gas which are capable of exciting the gas molecules. W. E. Downey.

Emission of light from hydrogen atoms. R. d'E. Atkinson (Proc. Roy. Soc., 1927, **A**, **116**, 81—103).—Experiments are described in which a non-luminous beam of canal rays, some distance after their entry into the vacuum, were made to emit the Balmer lines by excitation at approximately one point only, so that any interval between excitation and emission could be directly measured. The method of point-excitation used was to pass the canal rays across the mouth of one or more fine jets, from which air, or some other gas, was streaming, and to rely on rapid pumping to keep the general pressure low. It was found impossible to confine the excitation region to less than about 1·5 mm. in length, but the distribution of excitation over the region could be definitely determined, and the position of its maximum fixed within one or two hundredths of a mm. The distribution of intensity in the Balmer lines was measured photographically and compared near the maximum with that to be expected on the assumption that the intensity due to strict point-excitation would begin at the point and would fall off exponentially from the start. The results obtained support this assumption, and are in direct disagreement with the conclusions reached by McPetrie (A., 1926, 652). Several considerations arising out of this result are discussed. It is suggested that the process of excitation consists in an instantaneous placing of the hydrogen ion (or atom) into a definite, and preferably fairly deep, quantised state. A number of further experiments made possible by the success of the method are outlined, including a proposal for observing the "negative radiation effect" postulated by Einstein. L. L. Bircumshaw.

Origin of the nebulium spectrum. I. S. Bowen (Nature, 1927, **120**, 473).—The behaviour of the nebulium lines accords with their identification as regards wave-length, source, and series designation, as follows: 7235·0, O II, ^2D—^2P; 6583·6, N II, $^3P_2$—^1D; 6548·1, N II, $^3P_1$—^1D; 5006·84, O III, $^3P_2$—^1D; 4958·91, O III, $^3P_1$—^1D; 4363·21, O III, ^1D—^1S; 3728·91, O II, ^4S—$^2D_3$; 3726·16, O II, ^4S—$^2D_2$. A. A. Eldridge.

Origin of the nebulium spectrum. A. Fowler (Nature, 1927, **120**, 582—583).—The author's observations lend support to the view (preceding abstract) that the two green lines of the nebular spectra are due to O III. On the whole, the numerical evidence

also supports the assignment of nebular lines to N II and O II. A. A. ELDRIDGE.

Transition probabilities in the lithium atom. B. TRUMPY (Z. Physik, 1927, 44, 575—584).—The transition probabilities associated with the $1s-4p$ to $1s-12p$ lines of the principal series of the lithium spectrum have been calculated from experimental determinations of the intensities and widths of these lines as absorbed by lithium vapour. For $1s-9p$ to $1s-12p$ the values agree well with those calculated by Pauli according to Schrodinger's theory, whilst those for $1s-4p$ to $1s-9p$ agree well with those calculated by Sugiura in which Pauli's treatment is modified. R. W. LUNT.

Nitrogen series in the ultra-violet. J. J. HOPFIELD (Physical Rev., 1926, [ii], 27, 801).—Two new series of triplets probably converging to a common head and belonging to the quadruplet system, and two series of doublets also having a common limit and belonging to the doublet system, have been observed in nitrogen. The short wave-length lines of one of the triplet series are given by: $117353-109677\,(m+0{\cdot}845685-0{\cdot}022749/m^2-0{\cdot}026562/m^4)^{-2}$, where $m-1$, 3, and 4 (known) and 2 (new), and $1S=117353$ (14·48 volts) is the lowest energy level yet observed in neutral nitrogen. A. A. ELDRIDGE.

First spark spectrum of aluminium, Al II. R. A. SAWYER and F. PASCHEN (Ann. Physik, 1927, [iv], 84, 1—19).—The lines of the spectrum of Al II have been photographed, measured, and analysed into series. The source of the aluminium spectrum was a cylindrical cathode of aluminium in a discharge through pure helium. Complete freedom from water vapour was necessary to obtain the higher members of the series. Spectra were photographed on a quartz prism apparatus, on two grating apparatus, and on a vacuum spectrograph. The observations extend from 7471 to 933 Å. The term-scheme has been worked out for Al II. The ionisation potential of Al^+ is 18·744 volts. W. E. DOWNEY.

Spectral relationships of lines arising from the atoms of the first row of the periodic table. R. A. MILLIKAN and I. S. BOWEN (Phil. Mag., 1927, [vii], 4, 561—579).—The work of Millikan, Bowen, and others on the determinations of the types of spectra arising from different electron configurations is recapitulated and it is shown that the recently developed rules of Russell, Pauli, Heisenberg, and Hund have been of extreme importance in the interpretation of the problems. The rules originally developed from a study of the elements of the first long period of the periodic table have been shown to apply equally well for the spectra produced by the atoms of the first row of the periodic table. The application of the spectroscopic rules to systems comprising from 1 to 7 electrons in the first row of the periodic table is discussed in detail. A. E. MITCHELL.

Arc spectra of metals in chlorine. M. MIYANISHI (Japan. J. Phys., 1927, 4, 119—131).—In the arc spectra of mercury, cadmium, zinc, magnesium, calcium, strontium, and barium in chlorine a number of combination lines which are forbidden by the selection principle have been observed and classified. The broadening of some of the mercury and calcium lines was found to be similar in nature to that produced by the Stark effect. Since the effects observed in chlorine at a constant arc current are approximately reproducible in air with four times the arc current, it is concluded that the marked broadening and the appearance of enhanced and forbidden lines now recorded are due to the presence of chlorine ions in the arc. R. W. LUNT.

Anomalous dispersion in the principal series of potassium. Ratio of the dispersion constants of the red and violet doublets. W. PROKOFIEV and G. GAMOV (Z. Physik, 1927, 44, 887—892).—The ratio of the dispersion constants of the red and violet doublets of potassium is $111{\cdot}5+1{\cdot}5$ and is independent of the vapour density over a wide range (1 : 65). The ratio of the probabilities of the transition $2p_1-1s$ to the transition $3p_1-1s$ is 30·7. R. W. LUNT.

Extreme ultra-violet spectrum of titanium. R. C. GIBBS (Physical Rev., 1926, [ii], 27, 799).—The hot spark spectrum of titanium was photographed from 192 to 1718 Å. Lines not due to titanium were eliminated; Lang's 25 titanium lines, and 90 others, were observed. A. A. ELDRIDGE.

New lines in the arc spectrum of manganese at normal pressure between 2300 and 2000 Å. S. PINA DE RUBIES and J. DORRONSORO (Anal. Fís. Quím., 1927, 25, 374—377).—Data are given for a new series of lines in the arc spectrum of manganese at normal pressure between 3100 and 2000 Å. They are all reversible and have, hitherto, been unclassified. G. W. ROBINSON.

Ultra- and extra-ultra-violet spectrum of iron as developed by the inverse photo-electric effect. O. STUHLMAN, jun. (Physical Rev., 1926, [ii], 27, 799).—The following spectral regions were reproduced: spark spectrum of iron (Exner and Haschek, Tabellen), pronounced lines between 2456 and 2213 Å., new lines between 2211 and 2154 Å.; Millikan, Bowen, and Sawyer's spark spectrum, 2152—880 Å. A. A. ELDRIDGE.

Spark spectrum of nickel (Ni II). A. G. SHENSTONE (Physical Rev., 1927, [ii], 30, 255—265).—The wave-lengths (4362—1812 Å.) and classification of the lines in the spectrum of Ni II are tabulated, as well as the Zeeman effect of 44 lines. The important atomic structures are d^8s and d^8p. The low set of terms comprises $^4F'$, $^2F'$, $^4P'$, $^2P'$, ^2D, ^2G, of which $^4F_5'$ is the lowest. The calculated ionisation potential from d^8s to d^8 is 17·4 volts. The g-sum rule is not confined to terms built on the same ion term. A. A. ELDRIDGE.

Spectrum of ionised krypton. P. K. KICHLU (Nature, 1927, 120, 549).—Three groups of terms, A, B, and C, are tabulated for the spark lines of krypton, such that A combine with B, and B with C; the values given are arbitrary. A. A. ELDRIDGE.

Hyperfine structure of the terms of the cadmium spectrum. A. SCHRAMMEN (Ann. Physik, 1927, [iv], 83, 1161—1199).—Details are given of the use of a quartz Lummer plate. The best position for the plate is found to be between the collimator

and the prism. The optical axis of the plate must be within $\pm 10'$ of the perpendicular to the direction of the radiation in order to obtain parallel interference bands. The ultra-violet spectrum of cadmium and the mercury line at 2537 Å. have been examined and the plates measured by means of a registrating photometer. The structure of the lines and the hyperfine structure of the terms are discussed.

W. E. Downey.

Structures of the arc spectra of elements of the oxygen group. J. C. McLennan, A. B. McLay, and J. H. McLeod (Phil. Mag., 1927, [vii], 4, 486—495).—The wave-lengths in the tellurium arc spectrum have been re-measured in the spectral range 3200—1640 Å. Forty lines of wave-length less than 2080 Å. have been measured for the first time. The lines at 2259·02, 2142·75, 2385·76, and 2383·24 Å. previously observed by Zumstein (A., 1926, 650) have been classified as $5^3P_2-6^5S_2$, $5^3P_2-6^3S_1$, $5^3P_1-6^3S_1$, and $5^3P_0-6^3S_1$, respectively. From the observation of Kimura (this vol., 601) that the lines at 2259·02 and 2142·75 Å. were absorbed by the normal tellurium vapour whilst the other pair were not, it is assumed that the lines at 2385·76 and 2383·24 Å. originate in transitions involving metastable states. The absence of $5^1D_2-6^5S_2$ is explained by the rare observance of singlet–quintuplet intercombination lines. The authors were unable definitely to identify any terms of higher energy than 6^3S_1. In the investigation of the tellurium arc spectrum five wave-lengths were observed that were due to the presence of selenium as an impurity. In accordance with the results of Kimura (*loc. cit.*) these have been classified as the most fundamental lines of the Se I spectrum. The results obtained show that in so far as they are known the Se I and Te I spectra are analogous to those of O I and S I. All four spectra have been shown to conform to the theoretical structures predicted from the Pauli–Heisenberg–Hund theory.

A. E. Mitchell.

Intensity ratio of the blue cæsium doublet. C. F. Hagenow and A. L. Hughes (Physical Rev., 1927, [ii], 30, 284—287).—Redetermination of the intensity ratio of the members of the blue doublet of cæsium (4555, 4593 Å.) gives results ranging from 2·3 to 3·8 : 1, instead of that (2 : 1) anticipated from Burger and Dorgelo's rule (Z. Physik, 1924, 23, 258).

A. A. Eldridge.

Intensity ratio for doublets with large frequency differences. L. S. Ornstein, (Frl.) M. Coelingh, and (Frl.) J. G. Eymers (Z. Physik, 1927, 44, 653—654).—Intensity determinations in the spark spectrum of barium have shown that the addition rule for *ps* and *pd* doublets is valid if the observed intensity is divided by the fourth power of the emission frequency.

R. W. Lunt.

Quenching of mercury resonance radiation by foreign gases. P. D. Foote (Physical Rev., 1927, [ii], 30, 288—299).—The mechanism of the quenching of mercury resonance radiation by the rare gases or nitrogen differs from that of the quenching by hydrogen. Absorption of radiation 2537 Å. produces $^3P_1$ Hg′ atoms, some of which return to the $1S_0$ state by radiating, and some undergo collision of the second type with foreign gas molecules giving $^3P_0$ atoms. Many of these return to the $^3P_1$ state by collision of the first type with high-speed gas molecules; others return to the normal state through collision with traces of hydrogen impurities, whilst yet others collide with normal mercury atoms producing Hg_2' excited molecules.

A. A. Eldridge.

Depolarisation of resonance radiation. P. D. Foote (Physical Rev., 1927, [ii], 30, 300—304).—Depolarisation and quenching of mercury resonance radiation are phenomena of different types. Two effects producing depolarisation are described.

A. A. Eldridge.

Selective displacement of 0·0153 A. in *X*-ray spectral lines. X. F. H. Loring (Chem. News, 1927, 135, 183—185; cf. this vol., 707).—Theoretical. A revision of the calculation of the atomic weight of silver and of other atomic constants.

W. E. Downey.

General characterisation of phenomena associated with *X*-rays as a function of frequency. R. Glocker (Z. Physik, 1927, 43, 827—838).—Earlier experiments on the energy of photo- and Compton-electrons as a function of the incident *X*-radiation led to a law that the intensity of any effect due to *X*-rays was directly proportional to any given frequency, and to the product of the electron exchange concerned and the intensity of the incident *X*-radiation. The validity of this relationship has now been examined in a number of phenomena associated with *X*-rays.

R. W. Lunt.

***X*-Ray absorption spectra and chemical linking.** S. Aoyama, K. Kimura, and Y. Nishina (Z. Physik, 1927, 44, 810—833).—The absorption limits for the K_1-line of calcium, the K_1- and K_2-lines of chlorine, and for the K_1-, K_2-, and K_3-lines of sulphur have been determined from observations on a large number of compounds containing these elements. The results are discussed at length with reference to the grating energies of these compounds and thus to the nature of the linking of these atoms in the compounds investigated.

R. W. Lunt.

Spatial distribution of the intensity of *X*-rays scattered by copper. G. E. M. Jauncey and A. W. Coven (Physical Rev., 1926, [ii], 28, 426).—The total mass scattering coefficient per unit solid angle in a direction ϕ for *X*-rays λ 0·41 Å. when scattered by copper is determined for various values of ϕ, and the ratio of the experimental to Thomson's value is determined for carbon and copper. The ratio for a given angle and wave-length increases with the atomic number of the scatterer.

A. A. Eldridge.

***X*-Ray absorption in heated silver.** H. S. Read (Physical Rev., 1926, [ii], 27, 795).—For silver, the transmission is a complex function of the wave-length, increasing or decreasing with the temperature; the results are considered theoretically.

A. A. Eldridge.

Higher multiplets in *X*-ray spectra [of the rare earths]. J. H. van der Tuuk (Z. Physik, 1927, 44, 737—744).—The $M\alpha$-, $M\alpha$ -, $M\beta$-, and $M\beta'$-lines of the following elements have been determined: tungsten, tantalum, hafnium, lutecium, ytterbium, thulium,

erbium, holmium, dysprosium, terbium, gadolinium, europium, and samarium. The $M\alpha_1,\alpha_2,\beta$ doublet degenerates in these elements and changes its structure from element to element. This is discussed with reference to the filling up of the fourth quantum orbit with electrons. R. W. LUNT.

Spectrographical measurements in the intermediate region (*K*-, *L*-, *M*-, *N*-series). J. THIBAUD and A. SOLTAN (Compt. rend., 1927, **185**, 642—644).—Thibaud's method (this vol., 803) has been applied to the photography of additional new lines in the intermediate region, viz., the *K*-lines of nitrogen and boron, and the *N*-doublets of tantalum, tungsten, platinum, and gold. In most cases the maximum error is 0·5—1%. Very soft *X*-rays are shown to obey the laws established by Drude for optical and ordinary *X*-ray frequencies. The inaccuracy of Bragg's law for high wave-lengths, however, involves a difficulty in measurements in which the diffracting properties of crystals are used. J. GRANT.

Relative intensities of *X*-ray lines in the *L*-spectrum of thorium. S. K. ALLISON (Physical Rev., 1927, [ii], 30, 245—254).—The relative intensities of the thorium *L*-series lines were measured at 31·8 kilovolts, and the results, together with the relative intensities at high voltage, and those of *L*-doublets, are tabulated. The additional lines, $L\eta$, $L\beta_7$, and $L\gamma_2$ were found, but not γ_5 or γ_4; observed wave-lengths were 854, 772, 641X, respectively. A. A. ELDRIDGE.

Azimuthal intensity of scattered *X*-rays. W. FRIEDRICH and G. GOLDHABER (Z. Physik, 1927, 44, 700—707).—The azimuthal intensity of an *X*-ray beam scattered by water contained in a thin-walled glass vessel has been determined by an ionisation method. The angular distribution of intensity thus observed agrees fairly well with that calculated by Compton's theory. R. W. LUNT.

Quantum theory of the Zeeman effect for band lines. E. C. KEMBLE (Physical Rev., 1926, [ii], 27, 799—800).—Assuming an electronic angular momentum with fixed components σ and ε along and perpendicular to the axis of figure of a diatomic molecule, the Zeeman term formula $E=E_0+rh\Delta\nu_n[\sigma^2+\varepsilon(j^2-\sigma^2)^{\frac{1}{2}}]/j^2$, where r is the magnetic quantum number, $\Delta\nu_n$ is the Larmor frequency, and j is the total angular momentum, holds. It is inferred that the Zeeman pattern for lines adjacent to a band origin will normally be simple, and the scale may be similar to that for an atomic line; that the outer lines of a band will have very complicated patterns, usually on a scale too small to detect; that if the initial and final values of ε are different, the outer lines of a band will seem to be diffusely broadened in a magnetic field; and that the direction of rotation for the Faraday effect in the neighbourhood of a band line will frequently be different for the *P* and *R* branches of the same band. A. A. ELDRIDGE.

Ratio of intensities of modified and unmodified rays in the Compton effect. Y. H. WOO (Physical Rev., 1926, [ii], 28, 426).—The intensity ratios for silver $K\alpha$ rays (scattering angle 120°) are: lithium ∞, beryllium 8·72, boron 7·02, carbon 5·48, sodium 3·04, magnesium 2·78, aluminium 2·61, silicon 2·33, sulphur 1·91, potassium 1·72, calcium 1·71, chromium 0·75, iron 0·51, nickel 0·40, copper 0·21. A. A. ELDRIDGE.

Disappearance of the unmodified line in the Compton effect. Y. H. WOO (Physical Rev., 1926, [ii], 28, 426—427).—The unmodified peak is present, although faint, in the scattered radiation when silver $K\alpha$ rays are scattered by beryllium at 105° and 120°, by boron at 120° and 135°, and by carbon at 140°. The results are not in accord with the theory or results of Jauncey. A. A. ELDRIDGE.

Intensity distribution in the $K\alpha$-doublet of the fluorescence *X*-radiation. Y. H. WOO (Physical Rev., 1926, [ii], 28, 427).—Assuming each component of the α-doublet to be a single line of the same width, the relative intensities α_1/α_2 are: (third order) zinc 2·00, arsenic 1·98; (fourth order) strontium 1·96, zirconium 1·96, molybdenum 2·00, silver 2·06, tin 2·00, iodine 2·05. A. A. ELDRIDGE.

Ionisation potential and radius of the atom. A. S. EVE (Physical Rev., 1926, [ii], 27, 515).—For the rare gases, the ionisation potential is approximately inversely proportional to the radius of the atom, whether Bragg's or the kinetic theory value is selected. A. A. ELDRIDGE.

Critical potentials of copper by electron impacts. H. B. WAHLIN (Nature, 1927, **120**, 585).—Critical potentials for copper were observed at 7·7, 1·61, 3·80, 4·84, 5·65, 6·08, 6·73, 8·26, 8·73, 9·40, 10·07, and 10·91 volts; a critical potential at 2·6 volts does not correspond with any spectroscopic transition, and may be due to impurity. A. A. ELDRIDGE.

Critical potential of iodine. V. KONDRATÉEV and A. LEIPUNSKI (Z. Physik, 1927, 44, 708—712).—The critical potential of molecular iodine has been determined by allowing a narrow beam of iodine molecules to flow through the ionisation space so that practically no iodine molecules come in contact with the emitting filament. The values so found are 2·5, 3·8 (very weak), and 5 ±0·4 volts. That these potentials are due only to the iodine molecule has been established in a second series of determinations in which the beam of iodine molecules was heated at 800° before entering the ionisation chamber. At this temperature about half the iodine is monatomic; the potentials observed were: 1, 2·5, 5 (very weak), and 6·5 volts. Dymond and Kuhn have shown that 4995 Å. is the limiting wave-length producing one excited and one neutral iodine atom, and corresponds with 2·47 volts. The work of dissociation of the iodine molecule corresponds with 1·53 volts, and the transition $^2P_2$—$^2P_1$ with 0·94 volt; the potential observed at 3·5 volts therefore corresponds with the production of two excited iodine atoms.

The observed critical potential at 1 volt in the second series of experiments is identified with the transition $^2P_2$—$^2P_1$ in the iodine atom (0·94 volt), and that at 6·5 is thought to be the resonance potential with the value of 6·92 predicted by Turner from spectroscopic data in the Schumann region. R. W. LUNT.

Ionisation potential of terbium. L. Rolla and G. Piccardi (Atti R. Accad. Lincei, 1927, [vi], **5**, 818—819).—The ionisation potential of terbium determined by the flame method (cf. A., 1926, 769) is 6·74 volts. This again confirms the earlier observation that the ionisation potential of members of the rare-earth group increases with increasing atomic number (cf. A., 1926, 1187). M. Carlton.

Determination of critical potentials and the ionisation potential of mercury vapour. E. O. Lawrence (Physical Rev., 1926, [ii], **27**, 515).—A method of high precision gave a value of 10·4 (±0·5%) volts for the ionisation potential of mercury vapour. A. A. Eldridge.

Voltage-intensity relations of mercury lines below ionisation. D. R. White and H. W. Webb (Physical Rev., 1926, [ii], 27, 243—244).—The voltage–intensity relationship for each of 20 mercury lines between 2500 and 5800 Å. is primarily a function of the outer energy level involved. Abrupt changes of slope of the curves apparently correspond with certain critical potentials. A. A. Eldridge.

Ionisation by collision and a "photo-electric theory" of the sparking potentials. J. Taylor (Phil. Mag., 1927, [vii], **4**, 505—511).—A reply to criticisms by Huxley (this vol., 709) of the author's theory of sparking potentials (Proc. Roy. Soc., 1927, **A**, **114**, 73; Phil. Mag., 1927, [vii], **3**, 753).
A. E. Mitchell.

Photoelectric emissivity and sparking potentials. J. Taylor (Nature, 1927, **120**, 477—478).—Evidence in favour of the author's photoelectric theory of sparking potentials (preceding abstract) is adduced. A. A. Eldridge.

Diffusion of slow electrons (2—30 volts) in hydrogen and argon. E. Zachmann (Ann. Physik, 1927, [iv], **84**, 20—60).—Electrons of velocities between 30 and 11 volts in argon undergo an increase in diffusion with decreasing velocity. Between 11 and 7 volts velocity the diffusion decreases rapidly and at 6·5 volts it is not noticeable. Between 6·5 and 2 volts velocity, no diffusion is detectable. In hydrogen the diffusion increases with decrease of electron velocity between 30 and 2 volts.
W. E. Downey.

Heats of condensation of electrons and positive ions on molybdenum in gas discharges. C. C. Van Voorhis (Physical Rev., 1927, [ii], **30**, 318—338).—A new calorimetric method for measuring the electronic work function of a metal in a gas discharge is described. Values of the heat of electron condensation for molybdenum in argon, hydrogen, and nitrogen are: 4·76; 4·04, 4·35; 4·77, 5·01 volts, respectively, according to the treatment of the surface. The heating effect on molybdenum due to the surface neutralisation of an argon positive ion is about 1 volt. The presence in a low-pressure gas discharge of Langmuir's high-speed "secondary" electrons is indicated. A. A. Eldridge.

Collisions of the second kind in activated ozone. H. D. Smyth (Physical Rev., 1926, [ii], **27**, 108—109).—With ozone some experimental evidence was obtained in support of the view that if an electron collides with an activated molecule, the energy of activation of the molecule may be converted into kinetic energy of the electron by a collision of the second kind. A. A. Eldridge.

Ionic mobility in gaseous mixtures. H. Mayer (Physikal. Z., 1927, **28**, 637—644).—The presence of a trace of impurity in a gas frequently brings about a sudden large change in the mobility of one ion. The values at 760 mm. for k_+ and the mobilities in pure, dry hydrogen, have been determined as 6·00 and 10·07 cm./sec. per volt/cm., respectively. The addition of chlorine in amounts 0·3, 0·9, 1·5, and 3·0% resulted in the values for k_+ of 5·55, 5·35, 4·95, 4·25, respectively, whereas the corresponding values for k_- were 5·15, 4·60, 4·40, 4·12. A large decrease is thus shown in with the addition of quite small amounts of chlorine, but larger amounts do not maintain the rapid alteration. With small quantities of chlorine in oxygen the mobility of the negative ion decreases fairly rapidly until the chlorine concentration reaches 2% and after this point it falls much more slowly. Water vapour decreases the mobilities in oxygen. For 0, 1·6, 2·4, and 3·0% of water vapour the values of k_+ were 1·38, 1·38, 1·35, and 1·25, respectively, and of k_- 2·11, 2·00, 1·85, and 1·63. Hydrogen–oxygen mixtures have been investigated. For 2·2% of oxygen k_+ is 5·6, k_- 9·3; for 99·3% of oxygen k_+ is 1·44, k_- 2·15. The results are discussed in terms of the cluster theory. R. A. Morton.

Ionisation in flames of various organic substances. J. A. J. Bennett (Trans. Faraday Soc., 1927, **23**, 307—311).—To study the relation between ionisation and detonation the ionisation in flames of hexane, coal-gas, "B.P. petrol," benzene, pentane, acetone, etc., and the effect of adding carbonyls, amyl nitrite, aromatic bases, halogens and halogen compounds, and other substances which alter the highest useful compression ratio of a fuel, have been determined. Although in many cases knock-inducers increase and anti-knocks decrease the ionisation of flames, this is not general. Thus, although ionisation accompanies detonation, there is no simple relation between them, and ionisation does not appear to be either a cause or an effect of detonation, but mainly a temperature effect. This is not in agreement with either Wendt and Grimms' theory (B., 1924, 856) or that of Charch, Mack, and Boord (B., 1926, 570). M. S. Burr.

Ionisation processes in hydrogen, nitrogen, and argon. K. E. Dorsch and H. Kallmann (Z. Physik, 1927, **44**, 565—574).—Previous experiments (this vol., 604) have shown that the ratio of the concentration of H^+ ions to H_2^+ ions formed in hydrogen is approximately constant when produced by electrons of energies corresponding with 16—50 volts. The variation of this ratio produced by the addition of argon, and by increasing the ionisation space, has now been examined over a 1 : 10 pressure range. At any given pressure the ratio is unaffected by these factors, but the ratio $H_3^+ : H_2^+$ is increased by increasing the ionisation space at all the pressures examined. These results show that the primary ionisation process is the formation of H_2^+ ions (no other primary process takes place which is more than

0·5% of this process), that H_3^+ ions are formed in considerable amount according to the reaction $H_2^+ + H_2 = H_3^+ + H$, and that the reaction $H_2^+ = H^+ + H$ takes place only in the neighbourhood of the electrodes.

From measurements of the ionisation in argon–hydrogen, argon–nitrogen, and hydrogen–nitrogen mixtures as function of the electron energies (14—19 volts) relative values of the ionisation potentials have been obtained. By assuming Meissner's recent value for argon, 15·6 volts, computed from optical evidence (this vol., 177), the values 16—16·5 and approximately 16·5 volts are assigned to nitrogen and hydrogen, respectively. R. W. LUNT.

Effect of the medium on gas ion mobility. H. A. ERIKSON (Physical Rev., 1927, [ii], **30**, 339—348).—Addition of carbon dioxide or water vapour to the air through which air ions move diminishes the mobility, that of hydrogen increases the mobility, that of ethylene or chlorine has no effect, whilst that of ammonia results in the formation of a single positive ion of the same mobility as that of the negative ion, which is not affected. Acetylene gives rise to an ion which has a mobility only slightly less than that of the initial air ion. When acetylene remains in air a substance is formed which, when it becomes charged, has a lower mobility. A. A. ELDRIDGE.

Impact of slow cations on lithium chloride in a high vacuum. E. BADAREU (Physikal. Z., 1927, **28**, 634—637).—When canal rays impinge on a metal collector the galvanometer readings increase rapidly at first and then more slowly as the voltage increases between 0 and 900. If, however, a surface of lithium chloride is used, the galvanometer deflexion becomes constant at about 500 volts if the experiments are conducted in a high vacuum. On the other hand, experiments at pressures of about 0·1—0·5 mm., instead of showing deflexions of the same order of magnitude for the metal and salt surfaces, disclose wide differences; *e.g.*, a copper collector gave at 462 volts a deflexion twenty times as great as that with a collector covered with lithium chloride. The differences between the experiments at relatively low pressure and with high vacuum are ascribed to the fact that the emission of positively-charged particles from the salt increases with increasing current density in the exciting current (cf. Volker, A., 1919, ii, 43).

R. A. MORTON.

Ionisation probability in collisions between electrons and atoms. F. M. PENNING (Physica, 1926, **6**, 290—297).—A lecture.

CHEMICAL ABSTRACTS.

Divergence of magnetic electrons. W. BOTHE (Z. Physik, 1927, **44**, 543—546).—A mathematical analysis of the effect of the magnetic moment of electrons on the divergence of a cathode beam.

R. W. LUNT.

Charged state of atoms before light emission. E. RUPP (Ann. Physik, 1927, [iv], **84**, 154—160).—It is shown that the majority of hydrogen atoms emitting light in canal rays are positively charged before the emission. W. E. DOWNEY.

Luminescence of canal rays. H. RAUSCH VON TRAUBENBERG and R. GEBAUER (Z. Physik, 1927, **44**, 762—767).—An improved technique is described for examining the fine structure of the hydrogen spectrum emitted by canal rays. The changes produced as the beam moves from the region of an electric field to a region where no field exists are recorded and discussed.

R. W. LUNT.

Polarisation of the light from canal rays. II. E. RUPP (Ann. Physik, 1927, [iv], **84**, 94—110; cf. *ibid.*, 1926, [iv], **81**, 615).

Structure of the radioactive atom and origin of the α-rays. (SIR) E. RUTHERFORD (Phil. Mag., 1927, [vii], **4**, 580—605).—For the first time a theory of the structure of the nucleus of a radioactive atom is put forward and discussed in terms of the experimental data. In the radioactive atom one of the neutral α-satellites is regarded as circulating in a quantised orbit round the central nucleus. When for some reason this becomes unstable the satellite escapes from the nucleus, losing its two electrons, and the electric field falls to a critical value. It escapes as a doubly-charged helium nucleus with a velocity which is a function of the quantum orbit and the nuclear charge. The two electrons liberated from the satellite fall towards the nucleus and probably circulate close to the central nucleus and inside the region occupied by the neutral satellites with a speed of the order of that of light. On the occasion of one of these being hurled from the system a disintegration electron results. The disturbance of the neutral satellite system by the liberation of an α-particle or a swift electron may lead to a rearrangement involving the transition of one or more satellites to a different quantum orbit and the emission in the process of γ-rays of frequency determined by quantum relations. It is pointed out that before further progress in the solution of the problem of the origin of the γ-rays can be obtained a knowledge of the precise frequencies of the main γ-rays and their intensities is essential.

A. E. MITCHELL.

Possible mechanism of atomic disintegration. G. PICCARDI (Nature, 1927, **120**, 442—443).—The "excess weight" (Harkins' "isotope weight"), $P-2N$, where P is the atomic weight and N the atomic number, is regarded as constituted of $P-2N$ dipoles, externally to the atomic nucleus, formed by one positive and one negative electron sufficiently close together to form an electrically neutral complex. For the inactive gases, and for zinc, cadmium, and mercury, the maximum excess weight (that of the higher isotope of each element) is doubled each time a given atomic structure is repeated, values being: neon 2, argon 4, krypton 14, xenon 28, radon 50, zinc 10, cadmium 20, mercury 44. These elements are also in maximal positions on the curve of ionisation potentials; hence the excess weight is definitely related to the atomic structure.

A. A. ELDRIDGE.

Actinium series and the order of stability of radioactive isotopes. A. S. RUSSELL (Nature, 1927, **120**, 402—403).—Protoactinium is identified as the most stable isotope of element 91 and actinium as the second stablest isotope of element 89, from relations between atomic mass and stability deducible from Aston's results on non-radioactive elements. It

follows that actinium may not have the mass 227 which has been ascribed to it by all of those who consider that the masses of members of the actinium series are of odd number; it follows also that the mass of protoactinium is 233 and therefore that of actinium 229. On the basis of these results the masses of all the actinium products are known unless it can be shown either that one or more α-particles have been overlooked or that a massive particle other than an α-particle is expelled by some member of the series. Two rules, also, are deducible. (1) For a radio-element of even atomic number the masses of its α-ray and of its β-ray isotopes are in decreasing order of stability when arranged in the orders x, $x-2$, $x-1$, $x-4$, $x-3$, etc., and x, $x+2$, $x+1$, $x+4$, $x+3$, etc., respectively, x being an even number and the atomic mass of the stablest isotope. (2) For an element of odd atomic number the masses are in decreasing order of stability when arranged in the same order as the β-ray isotopes of an element of even number. Applied to the isotopes of non-radioactive elements these rules are partly successful only they are inapplicable to the isotopes of tin, magnesium, and silicon, but apply better to those of xenon, cadmium, mercury, sulphur, selenium, krypton, neodymium, and lead. On the theory put forward the end-product of the actinium series has a mass of 209. A. S. Russell.

Radioactive haloes. Possible identification of "hibernium." A. S. Russell (Nature, 1927, **120**, 545—546).—Observations of Joly (Proc. Roy. Soc., 1922, **A**, **102**, 682) and of Iimori and Yoshimura (A., 1926, 990) on the rings of radioactive haloes are considered in the light of Marckwald and Russell's work (A., 1911, ii, 360) on the alteration of radioactive minerals by agencies like percolating water and of Russell's view (preceding abstract) of the atomic masses of the products of the actinium disintegration series. Iimori and Yoshimura ascribed their *Z*-haloes, Joly's *X*-haloes, and possibly Joly's so-called radon haloes to the products of the actinium series. They regard the actinium series as independent of the uranium–radium series; two inner rings sometimes found in *Z*-haloes are ascribed by them to two uranium isotopes at the head of the actinium series. The author criticises this. If uranium minerals have been altered by chemical agencies in the past, different radioactive products may have been isolated from the rest depending on their solubility, etc. From these products three different kinds of haloes should result: the uranium halo resulting from uranium or ionium or radium, the actinium halo resulting from protoactinium, and a lead halo resulting from the end-product of the actinium series if it should be feebly radioactive. Similarly from thorium minerals two haloes may be obtained: the thorium halo and a lead halo due to a possible feebly radioactive end-product. It is concluded that the radius of the ring made by the α-particles from the thorium end-product (mass 208) should be smaller than that from the actinium end-product (mass 209). The hibernium ring is ascribed to the first of these; an unnamed ring discovered by Joly to the second. Some *Z*-haloes are ascribed to protoactinium isolated from uranium minerals; other *Z*-haloes and *X*-haloes to protoactinium and lead separated either from uranium or uranium–thorium minerals. There is no need to regard hibernium, as did Rosseland (Nature, 1922, **109**, 711), as a radioactive element of atomic number approximately 40. If the views put forward are correct the radioactive series are partly extended to mercury; hibernium is identified as thorium-Ω.

A. S. Russell.

Mode of disintegration of radium-*D*, -*E*, and S. Kikuchi (Japan. J. Phys., 1927, **44**, 143—158).—The tracks of rays from an equilibrium mixture of radium-*D*, -*E*, and -*F* have been examined by the Wilson cloud method. Each atom of radium-*E* emits one β-particle only on disintegrating, and the heterogeneous nature of the β-particles so produced cannot be traced to encounters with planetary electrons. The β-particles from radium-*D* are of secondary origin; this substance emits, in addition to radiation of 0·264 Å., radiation of mean wave-length 0·4 Å. which is possibly homogeneous; the *L*-radiation of this element was also detected. R. W. Lunt.

Ionisation produced by radon in spherical vessels. G. Glockler (J. Physical Chem., 1927, **31**, 1322—1331).—Theoretical. A comparison is made of the ionisation produced by radon and its decomposition products as calculated by the average path law (cf. Lind, A., 1912, ii, 1027) and by the method of Mund (A., 1925, ii, 732). For spherical vessels of a diameter up to 10 cm., the two methods give similar results, which are also in agreement with the experimental value obtained by Lind (A., 1919, ii, 210). A new derivation of Mund's original equation is given, but the assumption that the whole of the radium-*A* and the radium-*C* decomposes on the wall of the vessel is modified. Using the experimental value of Lind and Bardwell (A., 1924, ii, 11) for the average path (0·61 × radius of the reaction vessel), it is calculated that 30% of the radium-*A* and 7% of the radium-*C* decompose in the gaseous phase. Mund's efficiency factor is recalculated on this basis and the new values are tabulated.

L. S. Theobald.

Scattering of α-particles by helium. (Sir) E. Rutherford and J. Chadwick (Phil. Mag., 1927, [vii], 4, 605—620).—Investigations of the collisions of α-particles with helium have shown that in general the collision relations for these particles are similar to those representing the collisions between α-particles and hydrogen nuclei. For large collision distances the forces between the particles are given by Coulomb's law, but with closer approaches (less than $3{\cdot}5\times10^{-13}$ cm. for central collisions and less than 14×10^{-13} cm. for glancing collisions) powerful additional forces are involved. It is suggested that these additional forces originate in the magnetic fields of the nuclei.

A. E. Mitchell.

Probability law and the α-particle emission of polonium. W. Kutzner (Z. Physik, 1927, 44, 655—683; cf. A., 1924, ii, 226).—The α-particle emission of polonium has been re-examined, and it is found that Bateman's expression for the time probability of emission gives values of the emission probability the agreement of which with experiment

diminishes as the thickness of the polonium preparation is increased. The discrepancies cannot be accounted for by recoil atoms, and are thought to be due to impurities in the polonium preparation which impede the emission of the true total emission of polonium. R. W. LUNT.

Scattering and absorption of the γ-rays of radium. H. M. CAVE and J. A. GRAY (Physical Rev., 1926, [ii] 27, 103).—γ-Rays filtered through 2 cm. of lead have an effective wave-length in the neighbourhood of 0·012 Å. A. A. ELDRIDGE.

Internal conversion of γ-rays. (MISS) B. SWIRLES (Proc. Roy. Soc., 1927, A, **116**, 491—500).—Theoretical. The results of Ellis and Wooster (this vol., 393) are discussed on the lines of quantum mechanics. An expression is obtained for the coefficient of absorption in the K-levels. W. E. DOWNEY.

Variation of radioactivity of hot springs. K. SHIRATORI (Sci. Rep. Tohoku Imp. Univ., 1927, **16**, 613—620).—A comparison is made between the radioactivity of a number of hot springs in Japan before and after a period of eleven or twelve years during which earthquakes have taken place. Changes in temperature are also recorded. M. S. BURR.

Transmutation of elements. A. SMITS (Nature, 1927, **120**, 475—476).—Renewed experiments indicate that the mercury found in the earlier experiments, in which a discharge was maintained between lead electrodes under carbon disulphide, originated partly, if not entirely, from the carbon disulphide. Thus there is still no conclusive evidence of the reproducible conversion of lead into mercury. A. A. ELDRIDGE.

Failure of the mercury-to-gold transmutation experiment. H. H. SHELDON and R. S. ESTEY (Physical Rev., 1926, [ii], 27, 515).—A repetition of Miethe's experiments failed to produce any transmuted gold. A. A. ELDRIDGE.

Radiation arising from the formation of helium from hydrogen. G. E. M. JAUNCEY and A. L. HUGHES (Physical Rev., 1926, [ii], 27, 509).—Four processes are considered: (1) The protons and electrons initially at rest produce a helium nucleus recoiling in the opposite direction of the quantum. (2) The protons and electrons all initially having velocity βc produce a helium nucleus at rest. (3) One proton with velocity βc meeting 3 protons and 2 electrons at rest produces a helium nucleus at rest. (4) One electron with velocity βc meeting 4 protons and one electron at rest produces a helium nucleus at rest. In (1), (2), and (3), $\lambda=0{\cdot}0004$ Å.; in (4), $\lambda=0{\cdot}0008$ Å. In (1) and (2), $\beta=0{\cdot}008$; in (3), $\beta=0{\cdot}03$; in (4), $\beta=0{\cdot}9995$. The reverse of (4) is the photo-electric effect. By analogy with X-rays, 0·004 Å. and 0·0008 Å. may be considered as critical absorption wave-lengths. A. A. ELDRIDGE.

Radiation from the mutual annihilation of protons and electrons. A. L. HUGHES and G. E. M. JAUNCEY (Physical Rev., 1926, [ii], 27, 509—510).—The collision of two electrons and one proton results in a recoil electron moving with a minimum velocity $0{\cdot}9999995c$ and a quantum of wave-length $2{\cdot}6\times10^{-5}$ Å., or less. The collision of two protons and one electron results in a recoil proton moving with a minimum velocity $0{\cdot}6c$ and a quantum of wave-length $1{\cdot}9\times10^{-5}$ Å. or less. A. A. ELDRIDGE.

Application of Schrodinger's wave functions to the calculation of transition probabilities for the principal series of sodium. Y. SUGIURA (Phil. Mag., 1927, [vii], 4, 495—504).—In accordance with the result of Kramers (Z. Physik, 1926, **39**, 828) that a rational first approximation to the quantum-mechanical calculation may be obtained by using an orbital model fixed by the usual quantum conditions, if in these half-number values are introduced for the radial and azimuthal quantum numbers, the proper functions according to Schrodinger (Ann. Physik, 1926, [iv], **79**, 361) have been found for the 3_1, 3_2, and 4_2 states of the sodium atom. These functions have then been used for the calculation of the transition probabilities and the number of dispersion electrons for the principal series of sodium. The result so obtained for each D-line of sodium is in close agreement with that deduced from the experimental results of Minkowski (A., 1926, 650). A. E. MITCHELL.

Intensities in the secondary spectrum of hydrogen at various temperatures. J. C. MCLENNAN, H. GRAYSON-SMITH, and W. T. COLLINS (Proc. Roy. Soc., 1927, **A**, **116**, 277—312).—The intensities of the lines of the secondary spectrum of hydrogen have been studied. A specially constructed discharge tube was arranged in a liquid-air flask with the capillary vertical. Special precautions were taken to obtain pure hydrogen. Photographs were taken at the ordinary temperature and at the temperature of liquid air, nothing else being varied. The intensities were obtained by a Moll self-registering microphotometer and most of the lines measured by Merton and Barratt were examined. Richardson's series system is thereby included and the variation of intensity with temperature is in good agreement with theory. The alternation of intensity between the odd and the even members of the series was observed. Other regularities have been examined and are discussed. W. E. DOWNEY.

Intensity distribution among the lines of certain bands in the spectrum of the hydrogen molecule. O. W. RICHARDSON (Proc. Roy. Soc., 1927, A, **116**, 484—491).—Theoretical. The results of McLennan, Grayson-Smith, and Collins (preceding abstract) are discussed. W. E. DOWNEY.

Bands in the secondary spectrum of hydrogen. II. H. S. ALLEN and I. SANDEMAN (Proc. Roy. Soc., 1927, **A**, **116**, 312—327; cf. this vol., 394).—Theoretical. Further work on the system attributed to triatomic hydrogen is described. Further bands have been added and it is concluded that these are only the strongest in an extensive system. The spacing in groups with a difference of 92 wave-numbers is not attributed to the vibration quantum number but possibly is dependent on a new quantum number. W. E. DOWNEY.

Interpretation of the continuous spectrum of hydrogen. Y. TAKAHASHI (Japan. J. Phys., 1927, 4, 103—108).—It is claimed that the difficulties

which face the explanation of this spectrum by Bohr's theory are obviated by assuming that it arises from the recombination of two hydrogen atoms of which one at least is excited. R. W. LUNT.

Hydrogen band spectrum in the extreme ultra-violet. T. HORI (Z. Physik, 1927, 44, 834—854).—The band spectrum of hydrogen excited by the glow discharge has been examined with a vacuum spectrograph of dispersion 8·28 Å. per mm. in the range 1027—1249 Å. A large number of lines have been recorded, and arranged according to the term scheme of Dieke and Hopfield. The moment of inertia of the hydrogen molecule in the normal state is found to be $4{\cdot}67\times10^{-41}$ g. cm.^{2}, and the nuclear spacing $0{\cdot}75\times10^{-8}$ cm.; for the excited state the corresponding values are $9{\cdot}2\times10^{-41}$ g. cm.^{2} and $1{\cdot}06\times10^{-8}$ cm. R. W. LUNT.

Structure of the hydrogen molecule. H. C. UREY (Physical Rev., 1926, [ii], 27, 800).—Dieke's and Takahashi's arrangements of the Fulcher bands of hydrogen are reconsidered. It is assumed that the molecule is symmetrical about the median plane, and that it has no angular momentum in the electron system. It appears necessary to assign the steady states involved to the vibration electron orbits of the median plane. This would give no first-order Zeeman effect as required, and a diamagnetic model for the normal state. A. A. ELDRIDGE.

Structure of the hydrogen molecule ion. H. C. UREY (Physical Rev., 1926, [ii], 27, 800—801).—The energy levels of the vibrational model of the hydrogen molecule ion have been calculated, including the energy contributed by the vibration and rotation of the nuclei. The emitted bands should consist of single band systems, each band having a zero branch only. A. A. ELDRIDGE.

Combinations in the ultra-violet spectrum of the hydrogen molecule. G. H. DIEKE and J. J. HOPFIELD (Physical Rev., 1926, [ii], 28, 849).—Between 1050 and 1650 Å. there are two systems of bands degraded towards the red, and all are of similar structure; they have the same final states, which are the states of lowest energy of the hydrogen molecule. The first system includes a progression which, in a mixture of argon and hydrogen, appears without the rest of the spectrum. In the initial electronic state of this system the nuclei are more tightly bound than in the initial state of the other system, although their distance apart is larger. A. A. ELDRIDGE.

Zero-zero band of the second positive band spectrum of nitrogen. G. NAKAMURA (Japan. J. Phys., 1927, 4, 109—117).—The band has been analysed by examining the spectrum of a low-tension arc in nitrogen between tungsten electrodes. It is found that the formulæ of Zeit and Lewis (Z. wiss. Phot., 1922, 21, 1) are not applicable to the high members of the band lines. R. W. LUNT.

Structure of the atmospheric absorption bands of oxygen. G. H. DIEKE and H. D. BABCOCK (Proc. Nat. Acad. Sci., 1927, 13, 670—677).—The lines in the *A*-band (7624·493—7594·970) and the *A'*-band (7622·998—7603·212), the *B*-band (6886·743—6869·626), and the α-band (6289·397—6277·533) have been remeasured and Rowland's values for the α'-band have been corrected by subtracting 0·216 Å., so that the wave-lengths given are all expressed on the neon scale. The empirical structure of the bands is worked out in the form

$$\left.\begin{aligned} P_i(j) &= F_i(j) - F_i''(j+1) \\ R_i(j) &= F_i'(j) - F_i''(j-1) \end{aligned}\right\},$$

which makes the bands analogous to other well-known bands. The significance of the empirical structure is not fully elucidated, but the relation $B=h/8\pi^2cJ$ leads to values for the moment of inertia J for the O_2 molecule in the normal and in the excited state of 19·27 and $19{\cdot}93\times10^{-40}$, respectively, corresponding with 1·205 and $1{\cdot}225\times10^{-8}$ cm. as distances between the nuclei in the two states.

R. A. MORTON.

Half-integral vibrational quantum numbers and rotational energy data for the MgH bands. W. W. WATSON (Physical Rev., 1926, [ii], 27, 801).—The magnitude of the isotope effect in the 5211 Å. band accords with the assumption that and $n''=\frac{1}{2}$; the zero points of this band system are represented by the equation $\nu-19217+(1603{\cdot}5n'-34{\cdot}75n'^2)-(1493{\cdot}5n''-31{\cdot}25n''^2)$, where n' and n'' assume half-integral values from $\frac{1}{2}$ to $3\frac{1}{2}$. For the final state in the 5211 Å. band, the rotational energy $F-Bm^2+Dm^4+Fm^6$, where $m=j+\frac{1}{2}-\varepsilon$ ($\varepsilon=0{\cdot}47$). The presence of a Kramers and Pauli effect is indicated. The value of ε for the initial state is approx. 0·43.

A. A. ELDRIDGE.

Fine structure of the 4842 Å. band of AlO. W. C. POMEROY (Physical Rev., 1926, [ii], 27, 640).—The doublet separation of band lines is represented as a function of k (a half integer representing the resultant molecular momentum) of the initial state for both P and R branches by the equation $\Delta\nu=0{\cdot}0116k+12\times10^{-6}k^2-7\times10^{-11}k^4$. Attributing the doublets to a double energy level in the initial state, $(F')^{+-}=(0{\cdot}6019\pm6\times10^{-6})m^2-(1{\cdot}1630\times10^{-6}\pm3{\cdot}5\times10^{-11})m^4+0{\cdot}54\times10^{-12}m^6$, where $m-k-0{\cdot}0074\pm0{\cdot}00482$; $(F'')=0{\cdot}6386m^2-1{\cdot}1094\times10^{-6}m^4-0{\cdot}43\times10^{-12}m^6-5{\cdot}2\times10^{-18}m^8$. A. A. ELDRIDGE.

Colouring of glass [containing manganese] in ultra-violet light. C. L. CROSS (Physical Rev., 1926, [ii], 27, 108).—The effective light has a wave-length only slightly greater than 2900 Å., the absorption limit of the glass. The tinting takes place only near the surface, and is hastened by heating. Decolorisation is accelerated by heat or visible light.

A. A. ELDRIDGE.

Band spectrum of silicon fluoride. R. C. JOHNSON and H. G. JENKINS (Proc. Roy. Soc., 1927, A, 116, 327—351).—The discharge through silicon fluoride has been examined. Purified and dry silicon fluoride was streamed through a discharge tube at 1 mm. pressure. The discharge is of a strong blue colour, due to a system of intense bands in the blue region. Several groups of bands have been measured, some being favoured by high current density, others by low. Special precautions were taken to eliminate impurities and it is concluded that the bands are due to SiF_4. The structures of the α-, β-, and γ-systems of bands have been determined. The heat

of dissociation as calculated from the vibrational states is found to be 116,000 g.-cal. W. E. Downey.

Structure of Fraunhofer's lines and the dynamics of the sun's chromosphere. A. Unsold (Z. Physik, 1927, **44**, 793—809).—From an analysis based on the theory of dispersion and on Schwarzschild's theory of radiation equilibria, and by making the assumption that the partial pressure of calcium in the chromosphere is 5×10^{-8} atm., which is in satisfactory agreement in order of magnitude with St. John's data (Astrophys. J., 1910, **32**, 36), the structure of the *H*- and *K*-lines of the singly-ionised calcium atom in the chromosphere has been deduced. R. W. Lunt.

Photochemical absorption of iron salts. J. Plotnikov and M. Karschulin (Z. Elektrochem., 1927, **33**, 212—217).—The absorption bands of potassium ferricyanide and of green and brown ferric ammonium citrate extend into the infra-red, but the region of photochemical sensitiveness does not extend into the infra-red. The use of gelatin coated on glass instead of sized paper as the medium for the light-sensitive substances results in a shift of the sensitivity maximum towards the longer wave-lengths and an alteration in the general sensitivity. The results indicate the invalidity of the Einstein photochemical equivalent law. A simple method of demonstrating the photochemical absorption is given. The photochemically active region of "Ozalid" paper extends from 4750 to 2470 Å., with a maximum at 4000 Å. W. Clark.

Absorption spectra of aragonite and strontianite in the near infra-red. F. I. G. Rawlins and E. K. Rideal (Proc. Roy. Soc., 1927, **A**, **116**, 140—152; cf. this vol., 5).—The absorption spectra of aragonite and strontianite have been examined in the near infra-red by means of two types of apparatus: (*a*) an infra-red spectrometer, thermopile, and moving-magnet galvanometer of the Hill–Downing pattern, and (*b*) an infra-red spectrometer (Littrow principle) and a modified Boys radiomicrometer. From the results it has been found possible to compare the two allotropic modifications of calcium carbonate, and the bi-axial crystals of the alkaline-earth carbonates. In the former case, definite displacements of the three fundamental frequencies of the carbonate ion occur in the two crystal forms. From the overtones of the fundamental at 7 μ it is shown that the frequencies do not follow the order ν_1, $2\nu_1$, $3\nu_1$, but that a correction must be used analogous to the Kratzer correction for an harmonic coupling in gases (Z. Physik, 1920, **3**, 289). This correction is greatest for the less symmetrical form of calcium carbonate. In the bi-axial group, it appears that whereas at the absorption wave-lengths increase with the molecular volume, the reverse holds for the bands at ν_2 and ν_3, and the same is true for calcite and aragonite. The values of have been determined for the various bands with the help of Schaefer's data for $\lambda_{ref.}$ (cf. this vol., 5). These are generally positive, in confirmation of Schaefer's results, but are smaller than the values obtained by him. L. L. Bircumshaw.

Theory of colour on the basis of molecular strain. II. S. Dutt (J. Indian Chem. Soc., 1927, **4**, 99—109; cf. A., 1926, 830).—The results of a study of the absorption spectra of a number of coloured substances are found to be in agreement with their unsaturation as measured by the ease of hydrogenation in the presence of hydrogen and colloidal palladium. In benzene derivatives, a chromophore is regarded as a seat of strain which may be partly absorbed by dynamic equalisation in the ring, unless the structure is made static by the introduction of an auxochrome. The latter point is illustrated by the comparison of the absorption spectrum of alizarin (dynamic structure) with that of the potassium salt (static, quinonoid structure). The loading effect of substituents in dyes on their absorption spectra is shown to be the greater, the nearer the substituent is to the point of strain. G. A. C. Gough.

Theory of colour on the basis of molecular strain. III. Decomposition of dyes under the influence of solar radiation. K. K. Barat and S. Dutt (J. Indian Chem. Soc., 1927, **4**, 265—270; cf. A., 1926, 830, and preceding abstract).—The absorption spectra of aqueous solutions of a number of typical dyes have been determined during various stages of bleaching by solar radiation. The measurements indicate that the dyes are decomposed to colourless substances without the intermediate formation of less coloured substances. In accordance with the authors' theory, the dyes which absorb the longer wave-lengths decompose most rapidly. G. A. C. Gough.

Vibration frequencies of organic compounds. W. Herz (Z. anorg. Chem., 1927, **166**, 110—112).—The vibration frequencies of the molecules of numerous organic compounds have been calculated by the method previously applied to inorganic compounds (this vol., 817). The frequency decreases on ascending a homologous series and when hydrogen is replaced by the halogens, and for analogous compounds with the same number of carbon atoms is greatest for the one containing a triple linking and smallest for that with single linkings only. R. Cuthill.

Series due to halogens in infra-red absorption spectra of organic compounds. J. W. Ellis (Physical Rev., 1926, [ii], **27**, 639).—The absorption spectra of methylene dichloride and chloroform contain, in addition to the C–H series, bands which fit a linear series starting at 16·8 μ, and bands accounted for by combinations. Similar bands are observed with methylene dibromide and bromoform (17·2 μ) and with methyl iodide and methylene di-iodide (17·5 μ), as well as with more complex molecules containing halogen and hydrogen atoms, but not with carbon tetrachloride or tetrachloroethylene. A. A. Eldridge.

Spectrochemical studies of hydroxyazo-compounds. IV. T. Uemura and S. Tabei (Bull. Chem. Soc. Japan, 1927, **2**, 229—236; cf. this vol., 396).—The absorption spectra of neutral and alkaline solutions of the dyes obtained by coupling diazotised toluidines with each of the three cresols have been examined. The colour changes observed on addition of alkali are due to the change of the substance from the *A*- to the *R*-form. There is but one absorption

band when the hydroxyl group in the cresol ring occupies the *p*-position with respect to the azo-group, and two when it occupies the *o*-position. Comparison of the present absorption curves with those of the corresponding hydroxyazobenzenes and benzeneazocresols shows that the methyl group has a hyperchromic influence only when introduced into a non-methylated compound. The effect of a methyl group is apparently independent of its position.

J. S. CARTER.

Absorption of ultra-violet rays by the ten isomerides of dichloronaphthalene. H. DE LASZLO (Compt. rend., 1927, **185**, 599—601).—The absorption curves and m. p. of the ten dichloronaphthalenes fall into three groups according as the chlorine atoms are in the αα-, ββ-, or αβ-positions. As with the *p*-substituted benzene derivatives, the m. p. are highest when the substituents are symmetrically placed, and as far apart as possible. With the exception of that of the 1 : 2-compound, the spectra all show a large electronic interval in the region of about 1420 cm.$^{-1}$, and this is most clearly marked with the ββ- and αβ-derivatives. The absorption bands of the vapours indicate two different states of electronic activation. J. GRANT.

Infra-red absorption of fluids. E. N. GAPON (Z. Physik, 1927, **44**, 600—602).—If ν_c denotes a characteristic infra-red frequency of a liquid defined so that $u = 2\pi r\nu_c$, where u is the velocity of a molecule of mass m in orbital rotation at a radius r about its centre of gravity, then $mr^2\nu_c^2 = \text{constant} \times T$, where T is the temperature of the liquid. Since Stefan's law gives $PV_T = \text{constant} \times T$, where P is the internal pressure and V_T the molecular volume of the fluid, the above expression can be written $mr^2\nu_c^2 = \text{constant} \times V_T/\beta_T$, where β is the coefficient of compressibility. By substituting $m = M/N$ and $r = \text{constant} \times \sqrt[3]{V_T}$, where N is Avogadro's number, the following expression for ν_c is obtained: $\nu_c = k(V_T^{\frac{1}{3}}/M\beta)^{\frac{1}{2}}$, where the constant $k = 0{\cdot}34 \times 10^{12}$. The values of ν_c have been thus calculated for the following substances: benzene, toluene, *o*-, *m*-, and *p*-xylene, hexane, mesitylene, chloroform, and chlorobenzene. The values so obtained agree fairly well with those calculated from known spectroscopic data by Marton's equation (A., 1925, ii, 1025) for the frequency ν_i of the absorption bands: $\nu_i = \nu_c\sqrt{n}$, where n is an integer and ν_c an infra-red frequency which is identified with that defined by the author.

R. W. LUNT.

Time interval between excitation and emission for fluorescein. L. G. HOXTON and J. W. BEAMS (Physical Rev., 1926, [ii], **27**, 245).—The time elapsing between the beginning of incidence and the beginning of fluorescence emission was $3{\cdot}2 + 0{\cdot}3 \times 10^{-8}$ sec. for an aqueous solution, and $3{\cdot}7 \pm 0{\cdot}4 \times 10^{-8}$ sec. for an alcoholic solution, of fluorescein containing $2{\cdot}5 \times 10^{-5}$ g. per c.c. A. A. ELDRIDGE.

Absorption and fluorescence of silver bromide and of silver chloride vapour. J. FRANCK and H. KUHN (Z. Physik, **44**, 607—614).—From an analysis of the absorption and fluorescence spectra of the vapours of silver bromide and chloride it is shown that the size of the nuclear vibrational quanta decreases with increasing quantum number, and that therefore in the vapour state the molecules of these substances are compounds of atoms, as has been established previously for silver iodide. R. W. LUNT.

Fluorescence yield of solutions [of sodium fluorescein]. S. SZCZENIOVSKI (Bull. Int. Acad. Polonaise, 1927, *A*, 127—174).—The absorption spectra of solutions of sodium fluorescein in glycerol and in water have been determined over the range 4000—6000 Å. by a photo-electric method. The curves exhibit maxima at 4850—4900 Å. and absorption coefficients near 600, whilst an inflexion near 4600 Å. shows itself most clearly in the glycerol solutions; it is considered that the observed curve is due to the summation of at least two simple bands. Over the concentration range 1×10^{-4}—8×10^{-4} g./litre Beer's law is not obeyed since the absorption increases more slowly with increasing concentration than the law requires, whilst the wave-length of maximum absorption is shorter for the more concentrated solutions. In glycerol solutions the maximum is some 100 Å. nearer the red than is the corresponding aqueous solution.

In order to study the fluorescence it was necessary to prove that Wien's law for the spectral distribution of intensity applies to the visible spectrum from a carbon-filament lamp; the spectral sensitivity curve of the potassium photo-electric cell had also to be determined. It was then possible to measure the fluorescence yield for monochromatic radiations between 4400 and 5100 Å. The yield was independent of concentration over the range of aqueous solutions, but it showed an increase with longer exciting wave-lengths, which was most marked with the glycerol solutions. The fluorescence spectrum exhibits a maximum at approx. 5140 for the aqueous, and 5220 Å. for the glycerol solutions. The fluorescence yield at 5100 Å. for the 4×10^{-4} g./cm.^{3} solution is 0·71, but for the glycerol solution it is nearly 1·00.

R. A. MORTON.

Photometric and spectrophotometric studies. VI. Light-intensity measurements in the silent electric discharge. K. SCHAUM and R. TRAUTLUFT (Z. wiss. Phot., 1927, **24**, 416—423).—Since chemical change in the silent electric discharge occurs at the brush discharge, a correlation between the intensity of electroluminescence, the electrical conditions, and the chemical reactions seems desirable. Experiments have been carried out on the minimum voltage in a Siemens tube containing oxygen, carbon monoxide, carbon dioxide, ammonia, (*a*) for the discharge merely to pass and (*b*) for it to run continuously. Measurements of the brightness of the luminescence show that this is greater for the streaming gases than for the stationary gases. Alternative mechanisms for the ozonisation process are discussed in connexion with the luminescence. R. A. MORTON.

Luminescence of solid nitrogen under cathode-ray bombardment. J. C. MCLENNAN, H. J. C. IRETON, and K. THOMSON (Proc. Roy. Soc., 1927, **A, 116**, 1—15).—Two types of apparatus are described for the examination of the phosphorescence spectrum of solid nitrogen and the spectrum of the light emitted by solid nitrogen when irradiated by cathode rays.

In the phosphorescence spectrum the band N_2 was found to have the components 5240, 5235, 5229, 5224, 5220, 5214, 5210, and 5204 Å., 5214 having the strongest intensity. The band N_4 was shown to be composite and to have the components 5944·47, 5938·8, and 5932·0 Å., the strongest being 5944·47 Å. In addition to the bands N_2 and N_4, the luminescence spectrum contained three diffuse bands, N_1, which shaded into each other and had the mean wave-lengths 5554, 5617, and 5658 Å. A number of faint diffuse bands were also observed, each shaded off towards the red in the blue and violet spectral region between 4573 and 2480 Å. The N_1 bands were found to decrease in intensity after the solid nitrogen had been irradiated for some time, but the groups N_2 and N_4 did not show this phenomenon. The view is held that the solid nitrogen initially deposited in a form *A* is rapidly transformed into a form *B* under electronic irradiation, the phosphorescence investigated being due to form *B*. No trace was observed of the group of wave-lengths N_3 obtained by Vegard (A., 1924, ii, 436). From a study of the structures of the bands N_2 and N_4 the moment of inertia of the molecular system involved in the phosphorescence of solid nitrogen is shown to be 3×10^{-40} g. cm.^{2} approx. It is not considered possible on the evidence obtained to decide whether the band observed by Vegard in the auroral spectrum near 5230 is identical with the band N_2 in the spectrum of solid phosphorescent nitrogen, or with the band 5228, the fourth member in the first negative band system of gaseous nitrogen.

L. L. Bircumshaw.

Spectra of high-frequency discharges in super-vacuum tubes. R. W. Wood and A. L. Loomis (Nature, 1927, 120, 510).—If a discharge tube, while being exhausted with a Holweck molecular pump, is excited by an oscillating circuit giving a 3-metre wave, a blue hydrogen discharge at first appears, being replaced by the olive-green discharge characteristic of pure oxygen. The walls of the tube phosphoresce with a brilliant ruby-red light. The spectrum includes the line and band spectra of oxygen (possibly from silica) and many carbon lines (doubtless from stop-cock grease). A. A. Eldridge.

Heat of dissociation of N_2 and N_2^+. H. Sponer (Physical Rev., 1926, [ii], 27, 641).—The ω^n/n curve for the final state of the first positive group gives $E_e+E_n=11·87$ volts, approx.; for N_2^+, $Q'=9·06$, 9·7 volts, the second value being probably too great. If $I=16·5$ volts, $I'=14·16$ volts. A. A. Eldridge.

Heat of dissociation of O_2 and O_2^+. R. T. Birge (Physical Rev., 1926, [ii], 27, 641).—The true heat of dissociation, Q, of the molecule O_2 is calculated from the ω^n/n curve for the excited state to be $7·05\pm0·03$ volts, and from the curve for the stable state to be $6·666+0·5$ volts. Values of Q' are obtained from the O_2^+ bands as 6·46 volts from the curve for the stable state and 6·49 volts from that for the excited state. The ionisation potential of the atom is 13·54 volts, and that of the molecule 14·1 volts.

A. A. Eldridge.

Critical potentials of nitrogen and the nature of active nitrogen. A. S. Levesley (Trans. Faraday Soc., 1927, 23, 552—560).—An apparatus for determining the nature of the collisions between nitrogen molecules and electrons, for a range of accelerating voltages from 2·0 to 15·0, is described. The collisions become inelastic when the electrons attain an energy of 6·30 volts, and are then inelastic up to 9·3 volts. The addition of hydrogen produces practically no effect, hence the effect observed is probably due to nitrogen alone, and not to nitric oxide present as an impurity. The wave-length corresponding with 6·3 volts is 1940, and with 9·3 volts 1318, so that the inelastic collisions are probably associated with the excitation of a system of bands in the ultra-violet, having for the final state the normal state of the nitrogen molecule. Down to 2·0 volts, no critical potential was observed which might be associated with the surplus energy of metastable molecules of active nitrogen (cf. Willey and Rideal, A., 1926, 893).

M. S. Burr.

Variation of dielectric constants of certain organic substances with temperature. M. Velasco Durantez (Anal. Fís. Quím., 1927, 25, 252—305).—On the supposition that a molecule has no permanent electrical moment the relation of Mossotti and Clausius, $(\varepsilon-1)/(\varepsilon+2)\rho=$constant, follows. If a permanent electrical moment be assumed, the relation of Debye, $(\varepsilon-1)/(\varepsilon+2)\rho=b+a/T$, follows. The dielectric constants of benzene, toluene, xylene, cymene, chlorobenzene, and *cyclo*hexanol have been determined at different temperatures. The dielectric constant of all the compounds studied is a quadratic function of temperature, the coefficient being positive except for benzene. Benzene, toluene, and xylene give results in agreement with the equation of Mossotti and Clausius. The remaining compounds, except *cyclo*hexanol, satisfy Debye's equation. As the constant a in Debye's formula is negative for benzene, toluene, and xylene, it is inferred that the molecules of these compounds have no permanent electrical moment.

The effect of asymmetry produced by substitution in the benzene nucleus on electrical moment is discussed. It is concluded that the molecules of the compounds studied which have asymmetric formulæ are electrically bipolar. G. W. Robinson.

Electrical conductivity of vapours and liquid drops during incipient combustion. J. A. J. Bennett (Trans. Faraday Soc., 1927, 23, 295—301).—To obtain some insight into the mechanism of the chemical action immediately preceding detonation in an engine cylinder, the electrical conductivity with rise of temperature of mixtures of air with various vapours, viz., ether, *n*-hexane, phenol, aniline, iodine, toluidine, or mixtures of these, has been determined. With rich mixtures of the less volatile substances marked ionisation was obtained above 400° when fogging occurred in the combustion tube. Gold electrodes were used in place of platinum, since the latter caused surface combustion. Similar experiments were carried out in liquid drops–air systems containing mixtures of undecane with a large number of other organic compounds, *e.g.*, alcohols, nitrogen compounds, aromatic bases, and phenols, and also some miscellaneous anti-knockers. The behaviour was similar to that observed in the former systems after fogging had taken place. The conductivity

increases exponentially with temperature. The action of ultra-violet light is to lower the temperature of initial combustion without affecting the conductivity. It is suggested that the slow combustion of a disperse system of liquid drops of organic substances in air is accompanied by profuse liberation of electrons, whilst few electrons are present in mixtures of air and vapours. Recombination of electrons and ions may be the source of the energy which causes ignition at a lower temperature in mixtures of gaseous fuels containing liquid drops than in a completely vaporised mixture. M. S. BURR.

Optical dissociation of metallic halides. A. TERENIN (Z. Physik, 1927, 44, 713—736).—The limiting frequencies at which lines characteristic of the metal atoms are emitted when the vapour of the halide is irradiated with intense ultra-violet light have been determined for sodium and thallium iodides: 2450±50 and 2080±20 Å. for the sodium *D*-line and the thallium 3776 line, respectively. The optical dissociation corresponds thus with the formation of an excited metal and a neutral halide atom. The vapours of mercuric chloride, bromide, and iodide and of the iodides of cadmium, zinc, and lead emit a band spectrum when irradiated with light of wave-length shorter than a given limiting value characteristic of the substance. For these substances it is shown that the optical dissociation corresponds with the formation of an excited diatomic molecule and a neutral or an excited halogen atom according to the general equation $MX_2=(MX)'+X$. The band spectra of the mercuric halides observed are given in tabular form with an accuracy of 1—2 Å. R. W. LUNT.

Molecular scattering of light in a binary liquid mixture. C. V. RAMAN (Phil. Mag., 1927, [vii], 4, 447—448).—A reply to a criticism by Kar (this vol., 295) of the paper by Raman and Ramanathan (Phil. Mag., 1923, [vi], 45, 213) in which the author's improvement on Einstein's equation for the molecular scattering of light in a binary liquid mixture is justified in that whilst Einstein finds merely the work necessary to change the concentration by an infinitesimal amount from one value to another, both differing from that of the bulk of the mixture, they evaluate directly the total work necessary to change the concentration of a small volume of the mixture from its mean value to one slightly different, the work being done in a strictly reversible manner. It is shown that Kar's assumptions involve a process which is not reversible. A. E. MITCHELL.

Valency and additive compounds. J. PERRIN (Compt. rend., 1927, 185, 557—561).—The current theories of valency and of atomic structure are reviewed and correlated with a developed form of Kekulé's conception that chemical action between two substances involves the formation of an intermediate additive compound, which then breaks down in a different sense. Such intermediate compounds are held together by a single electron linking (semivalency), which is weaker than a double electron linking (valency), and is characteristic of a rigid system built up from two octets, or from two closed electronic systems, having in common one instead of two electrons. The theory explains the existence of the Cl_3 molecule and is applied to a few simple reactions. A trimeric formula for polymerised water is obtained, which has the hexagonal symmetry of ice crystals. J. GRANT.

Variability of valency. (SIR) P. C. RAY (J. Indian Chem. Soc., 1927, 4, 89—95).—A discussion of modern conceptions of valency with special reference to the compounds of auric chloride with mercaptans. G. A. C. GOUGH.

Intramolecular rearrangements in the complex cobalt compounds. A. USPENSKI and K. TSCHIBISOV (Z. anorg. Chem., 1927, 164, 326—334).—It is suggested as a general rule that if a reaction gives rise to stereoisomerides which can be represented by the formula $[Co(NH_3)_4R_1R_2]R_3$ or $[Co\,en_2R_1R_2]R_3$, where R_1, R_2, and R_3 are negative groups, then in the system in equilibrium in the solution a preponderance of the *trans*-form exists. If, however, R_1 and R_2 are electropositive groups, the *cis*-form predominates. The transformation of *trans*-dichlorodiethylenediaminecobaltic chloride into the *cis*-form on evaporation of the aqueous solution, which appears to conflict with the above generalisation, does not, however, occur quantitatively, and is complicated by the unequal solubilities of the two forms. Absorption spectrum observations show that when a strongly acid solution of the *trans*-form is warmed, there is no marked tendency for the formation of the *cis*-form, and on warming an aqueous solution of the aquochlorosulphate an equilibrium with the diaquo-salt is set up. In general, the ratio between the amounts of two stereoisomerides produced in a reaction does not appear to be influenced by their relative solubility, unless the solution becomes saturated in respect of one form. R. CUTHILL.

Substitution reactions in the inner sphere of complex compounds. A. USPENSKI and K. TSCHIBISOV (Z anorg. Chem., 1927, 164, 335—340).—The absorption spectra of oxalato-, carbonato-, and diaquo-compounds of the cobalt-tetrammines have been examined. For each of the first two groups, the spectra of the various members are qualitatively similar, being only slightly dependent on the nature of the anion, and with increase in concentration the molecular absorption coefficient increases. If carbon dioxide is passed into a solution of diaquotetramminocobaltic sulphate, the spectrum of the carbonatosulphate is ultimately obtained, but the mechanism of the change is not clear. The action of sulphuric acid on the carbonato-compounds gives absorption curves corresponding with those of the aquo-salts. R. CUTHILL.

Optical absorption and constitution of complex salts. H. LEY (Z. anorg. Chem., 1927, 164, 377—406).—Solutions of the nickel, cobalt, and cupric salts of the amino-acids, which may be regarded as simple salts with internal complexes, have been investigated by measurements of the conductivity and optical absorption. The dissociation of copper, nickel, and silver aminoacetates as derived from conductivity measurements increases in this order. *E.M.F.* measurements with solutions of the copper salts indicate very low concentrations of the metal ion, but are not wholly conclusive. The behaviour of such

compounds in solution depends, not only on the strength of the primary valency between the metal and the group with which it is associated, but also on the character of the subsidiary valency between the metal and the nitrogen, so that as a rule metals giving highly-dissociated ammonia complexes manifest but little tendency to form stable internal complexes with amino-acids. There is no general relation, however, between the degree of dissociation of the internal complex salt and the strength of the acid from which it is formed. Conversion of the copper aquo-complex, [Cu4H_2O], into the corresponding ammino-complex, [Cu4NH_3], displaces the maximum absorption towards shorter wave-lengths and increases the extinction. The wave-length of maximum absorption of the internal complex with aminoacetic acid is practically the same as that of the ammine, whilst the extinction is intermediate between those of the ammino- and aquo-complexes. Measurements with ammoniacal solutions of copper sulphate indicate that these solutions contain complexes such as [Cu6NH_3] and [Cu2$NH_3$2H_2O] in addition to the tetrammino-complex. The absorption of nickel sulphate closely resembles that of the acetate. Ammoniacal solutions of the sulphate, which appear from distribution experiments to contain a hexammino-complex, vary in colour with the ammonia concentration. The internal complex with aminoacetic acid occupies an intermediate position between the aquo-complex and the ammino-complex. Both the cupric and nickel salts of aminoacetic acid obey Beer's law over a considerable concentration range, indicating the presence of very stable complexes. Addition of ammonia to solutions of the copper salt, however, increases the extinction, new complexes being formed by the expulsion of aminoacetate ions by ammonia. Determination of the distribution coefficient of ammonia between chloroform and an aqueous solution of cupric aminoacetate points to the addition of two ammonia molecules to the salt. The constitution of such a salt is, however, uncertain. Nickel aminoacetate shows a similar unsaturated character in respect of ammonia. It is suggested in explanation of the optical variability of these internal complex salts that the groups bound by two principal and subsidiary valencies are arranged about the central atom in a plane, in which there is sufficient space for the introduction of, *e.g.*, ammonia molecules. The internal complexes of cobalt, on the other hand, are remarkably inert both chemically and optically, which may be ascribed to an octahedral configuration protecting the metal atom. A complex *compound* of cupric aminoacetate and ethylenediamine, $Cu(C_2H_4O_2N)_2$,2 en,2H_2O, has been prepared.

R. CUTHILL.

Electronic structure of atoms. I. The periodic classification. J. D. MAIN SMITH (J.C.S., 1927, 2029—2038).—It is shown that the feature of the classification of most importance to chemists is the octet arrangement of the elements into eight valency groups, and that modifications of the classification most serviceable in chemistry must give greater prominence to this octet arrangement. It is proposed to abridge the periodic classification by the relegation of the transition elements to a separate transition classification, the abridged classification then including only elements most closely related to the typical elements of the short periods, and consisting of a primitive period of two elements, 5 simple periods of 8 elements each, and a final incomplete period assumed to be also a simple period. The transition elements then form a separate table of 4 periods, each period consisting of 8 valency groups but beginning with Group III and ending with Group II. Each transition period consists of 10 elements, 3 being allotted to Group VIII, but to effect the reduction to 10 elements in the third long period containing 24 transition elements, 14 rare-earths proper to Group III are relegated to a transition sub-series which is not capable of being arranged in a period of 8 groups. The abridged and the transition classifications are then recombined to form a complete periodic classification embodying all the features of the two. The foregoing arrangements and the allocation of the various elements to their proper classifications, periods, groups, and series are discussed, and detailed experimental evidence is cited in support. It is indicated that this classification of the elements is to be the basis of a complete scheme of the distribution of electrons in atomic structures.

F. S. HAWKINS.

Rare earths. J. D. MAIN SMITH (Nature, 1927, **120**, 583—584).—The rare earths have no real relation to any other series of elements, and the observed colour resemblances are fortuitous. The sequence of colours of the (tervalent) salts of the first eight rare earths is identical with that of the last eight in the reverse order. Dysprosium salts are yellow; terbium salts are faintly rose in thick layers; illinium salts should be yellow. The identity in the colour sequences indicates that the same colour is obtained in two different ions when one has as many electrons (after deducting 54) more than zero as the other has less than 14, and that the 14 electrons concerned are arranged in only two sub-groups. It is further inferred that gadolinium has electrons in both sub-groups, but also that the second sub-group begins when the first is complete. The author's law of uniform atomic plan is supported.

A. A. ELDRIDGE.

Analogies of scandium with the rare-earth elements and with the tervalent elements of the iron family. G. URBAIN and P. B. SARKAR (Compt. rend., 1927, **185**, 593—596).—The resemblance between scandium and the other tervalent elements of the periodic system is discussed. Apart from its simple, anhydrous salts, scandium compounds always differ in composition from the corresponding salts of the rare earths, and no case of isomorphism is known. Scandium acetonylacetate and salts of the types $M_3[ScF_6]$ and $K_3[M(C_2O_4)_3]$,5H_2O, however, strongly resemble those of the tervalent elements of the iron family, and the author furnishes evidence of this analogy in the following new *compounds* which are isomorphous with the corresponding compounds of the iron family: $(NH_4)_3[Sc(SCN)_6]$,4H_2O, $K_3[Sc(SCN)_6]$,4H_2O, and $Na_3[Sc(SCN)_6]$,12H_2O. True scandium alums could not be obtained, but microcrystalline double salts with the sulphates of potassium, rubidium, cæsium, and ammonium, which had the com-

position of anhydrous alums, were prepared. The salt $Tl_3[Sc(SO_4)_3]$, also, is analogous to Étard's salt, $K_3[Cr(SO_4)_3]$. J. GRANT.

Electron distribution in sodium chloride. A. H. COMPTON (Physical Rev., 1926, [ii], **27**, 510—511).—The electron density falls to zero for the sodium ion 1·1 Å. and for chlorine at 2·0 Å. from the centre. Sodium has a group of eight electrons (probably K and $L2_2$) near the centre, with two electrons (probably $L2_1$) at 0·9 Å. from the centre. Near the centre of the chlorine ion are 10 electrons (K and L) outside which are 8 others, resolvable into 4 ($?3_3$) at 0·74 Å., 2 ($?3_2$) at 1·14 A., and 2 ($?3_1$) at 1·60 Å. A. A. ELDRIDGE.

Relationship of classical stereochemistry to the new work of Weissenberg. M. VON STACKELBERG (Z. angew. Chem., 1927, **40**, 1023—1027; cf. A., 1926, 459, 934).—The fundamental postulates of classical stereochemistry are (1) the valencies of the carbon atom are directed towards the corners of a tetrahedron, (2) a substituent group or atom can rotate freely about a single linking; whereas those of Weissenberg are (1) the valencies have no fixed direction or length, but the substituents so arrange themselves that their potential energy is a minimum, (2) every symmetrical arrangement corresponds either with a stable (energy minimum) or a labile (energy maximum) configuration, (3) of the large number of theoretically possible symmetrical arrangements, only those occur in practice in which identical atoms occupy similar positions, and different atoms dissimilar positions. These postulates are difficult to apply, however, since only in the case of the simplest substituents can the symmetry arrangements be definitely worked out, and also it is not always possible to distinguish labile from stable configurations. Further, there are often several configurations giving energy minima.

Optical activity is due to the fact that a plane of symmetry will be absent where the four substituent groups are dissimilar; racemisation is explained by the existence of an " energy mountain " between two equally stable configurations, so that a powerful shattering effect (*e.g.*, thermal agitation) will enable the molecules to surmount the mountain and fall in equal numbers on both sides; the Walden inversion is similarly easily explained.

Since free rotation is no longer present, a great number of isomerides are theoretically possible, but are not experimentally observable, owing to the smallness of the " mountains " and " valleys " of the " energy surface "; the possibility of finding such isomerides at low temperatures is thus still open. The final test of the theory lies in X-ray measurements, but since the atomic numbers of the atoms composing organic compounds lie so closely together, the spectrographs are difficult to interpret.

S. J. GREGG.

Effective cross-sectional area [of molecules] and molecular structure. E. BRÜCHE (Ann. Physik, 1927, [iv], **83**, 1065—1128; cf. this vol., 492).—The previously described experiments have been extended to include oxygen, methane, carbon monoxide, carbon dioxide, nitrous oxide, and nitric oxide. The Ramsauer effect is not characteristic of the rare gases alone, but appears in all the gases examined. The results are plotted as before and the curves can be divided into three groups. Argon, krypton, xenon, hydrogen chloride, and methane all have eight outer electrons and each yields an area against electron velocity curve which slowly rises to a maximum and then more slowly falls away again. Nitrogen and carbon monoxide with ten outer electrons yield curves which rise very sharply to a maximum, followed by an equally sharp descent, which in turn is followed by a very flat maximum. Nitrous oxide and carbon dioxide with sixteen outer electrons yield curves having a small, sharp maximum, followed by a similar but very flat maximum.

W. E. DOWNEY.

Effective cross-sectional area of the carbon dioxide molecule against slow electrons. C. RAMSAUER (Ann. Physik, 1927, [iv], **83**, 1129—1135; cf. preceding abstract).—It is concluded that the difference between total and absorbing cross-section is in part due to definition and experimental difficulties. The total cross-section would appear to be that given by Lenard. W. E. DOWNEY.

Periodicity of molecular numbers. L. W. TIBYRIÇA (Nature, 1927, **120**, 585).—Curves indicating the percentage of occurrence in each of four groups of molecular numbers, 4, 12, 20, 28; 6, 14, 22, 30; 0, 8, 16, 24; 2, 10, 18, 26, of a number of gases, acids, bases, and ions exhibit significant differences, which are considered theoretically. A. A. ELDRIDGE.

Activated molecules. L. J. WALDBAUER and I. J. PATTON (J. Physical Chem., 1927, **31**, 1433—1434).—The hypothesis is put forward that molecules are in an activated condition when the valency electrons are at their greatest distance from the nucleus and at their lowest speed in their elliptical orbits. Absorption of radiation quanta, on this view, merely moves the valency electron to an outer orbit further removed from the nucleus, and produces a higher degree of activation. The temperature coefficient of a reaction can be explained by an increase in the number and in the force of molecular collisions arising from the increase in velocity of the molecules with a rise in temperature.

L. S. THEOBALD.

Constitution of homogeneous acids. A. HANTZSCH (Ber., 1927, **60**, [*B*], 1933—1950).—All homogeneous acids, available for investigation, are not " true " acids in the sense of Werner's complex formulæ, $[XO_2]H$, $[XO_3]H$, and $[XO]_4H$ with ionically-combined hydrogen atoms, which are therefore in themselves heteropolar substances and consequently electrolytes, but are rather homopolar hydroxy-compounds, $OX{\cdot}OH$, $O_2X{\cdot}OH$, and $O_3X{\cdot}OH$. Free, ionically-combined hydrogen and free hydrogen ions do not exist. In the unimolecular state, the acids are homopolar non-electrolytes with structurally united hydrogen atoms, and hence are pseudo-acids in accordance with a nomenclature which has become superfluous. This is strictly true only for hydrogen chloride, bromide, and iodide, which are unimolecular as liquids and therefore non-electrolytes; for other acids, it holds only in the gaseous state at a sufficiently high temperature. In the liquid con-

dition the oxygen acids, with certain exceptions, are more or less strongly associated; since the association has an optically bathochromic effect it is not brought about by participation of the oxygen atoms of the acid radical but, as in the case of water and the alcohols, solely by means of the hydroxyl groups; as dimerides they correspond with the formula $OX—O<^{H}_{H}>O—XO$. Like bimolecular hydrogen fluoride, they are partly converted into electrolytes by association, since, in consequence of a restricted displacement of the hydrogen atoms according to the scheme $(OX·OH)_2 \longrightarrow [X(OH)_2]^+[O_2X]^-$, they yield acylium salts, which are dissociated in the unchanged portion and thus convert such pseudo-homogeneous acids (regarded previously as equilibrium acids from true and pseudo-acids) into electrolytes. Free halogeno-acids do not exist, since, by reason of the non-existence of ionogenic hydrogen, they decompose spontaneously into halogen hydride and the halogen compound of the corresponding element. Their "hydrates" or "alcoholates," like other strong acids, are oxonium salts. All acids behave towards water as "pseudoclectrolytes," since they are more or less completely transformed by addition of water to the "acid" hydrogen atoms into hydroxonium salts and dissociated. The phenomena can be most definitely expressed electrochemically by the phrase "only salts and not acids are electrolytes." Acids are compounds of hydrogen with negative atoms or atomic complexes; oxy-acids are at the same time derivatives of water in which a hydrogen atom is replaced by more negative atoms or atomic complexes. Consequently, acids have the tendency to replace their hydrogen atoms by more positive atoms (metals) or atomic complexes and thereby to pass into salts. Their degree of acidity (strength) is measured by their tendency towards salt formation. The acidity of the acids XH or X·OH increases with increase in the negative nature of the substituent X and is also determined by the differingly strong tendency of the acids towards salt formation or, conversely, by the differing stability of their salts. The strength of acids is most certainly determined by comparison of their tendencies towards additive salt formation with unsaturated substances, particularly with water and related oxides in the production of oxonium salts.

The absorption curves of tetrahydronaphthalene-2-sulphonic acid, its salts and *ethyl* ester, m. p. 35°, are incidentally recorded. H. WREN.

Electron lattice theory of metals. B. E. WARREN (Physical Rev., 1926, [ii], 27, 797—798).—It is predicted that the metals of Groups I and III should utilise a complete lattice of the rock-salt type, the sub-lattice of the positive ions being face-centred cubic; exceptionally, the sub-lattice of the alkali metals should be face-centred tetragonal. The sub-lattice of the metals of Groups II and IV should be either face-centred cubic or hexagonal close-packed; that of and VI should be body-centred cubic. The lattice of a Group VII metal should not be of a simple type. The predictions are in agreement with the experimental results. A. A. ELDRIDGE.

Determination of crystal orientation in metallic single crystals. Y. SHIMIZU (Sci Rep. Tohoku Imp. Univ., 1927, 16, 621—625).—A simple method of determining the crystal orientation of a metallic single crystal, without the use of *X*-rays, is described. The crystal is etched and the direction of brightest reflexion observed. M. S. BURR.

Intensity measurements of *X*-ray reflexions from fine powders. J. BRENTANO (Phil. Mag., 1927, [vii], 4, 620—629).—Measurements of the *X*-ray reflexion from finely-powdered rock salt have been made and the results compared with those of Compton and others obtained from single crystals and from coarse powders. In general, the measurements are in good agreement except that for the most powerful reflexions the present measurements give slightly higher values. This indicates a small amount of primary extinction in the measurements from larger crystals. In general, it is concluded that the reduction of a crystal to a coarse powder is sufficient to eliminate secondary but not primary extinction, and it is only with such substances as sodium chloride, the crystal units of which are initially sufficiently small, that grinding can reduce materially primary extinction. A. E. MITCHELL.

Size of the ideal synthesised lattice-range in true crystals. A. SMEKAL (Ann. Physik, 1927, [iv], 83, 1202—1206).—Polemical against Kast (this vol., 816). W. E. DOWNEY.

Orientation of aluminium crystals. K. TANAKA (Japan. J. Phys., 1927, 4, 137—140).—The orientation of long crystals in commercial aluminium wire in relation to the axis of the test piece has been examined. The (210) axis is more favoured than others for the orientation of crystals, a result not in agreement with the results of Elam (A., 1925, ii, 945).
R. W. LUNT.

Crystallite orientation in aluminium. G. TAMMANN and A. HEINZEL (Z. Metallk., 1927, 19, 338—341).—When commercial aluminium ingots are rolled down to sheet the proportion of cube planes in a section parallel to the direction of rolling gradually decreases to zero with a 66% reduction in thickness, whilst the proportion of octahedral and dodecahedral planes remains practically constant or falls slightly up to a 90% reduction, and the proportion of eicositetrahedral planes rapidly increases. Rolled sheet with 60—90% reduction commences suddenly to develop new crystals with varying orientations after annealing at 350°; the orientation of the new grains remains practically unchanged at higher temperatures and consists of 40—45% of (111), 35—40% of (110), and 18—21% of (100) planes on the surface of the rolled sheet. No twinned crystals are formed and prolonged annealing at a temperature just below the m. p. does not produce cube planes over the entire surface as is the case with copper. Progressive planes cut parallel to the cooling surface of a sand-cast aluminium ingot show little change in the crystal orientation, the (111) planes predominating and few (100) planes occurring on the cut surfaces. In chill-cast ingots, however, the predominating orientation is (100) followed by (111), except very

close to the cooling surface, where the converse is true. A. R. POWELL.

Rhombic sulphur isolated from volcanoes. F. RANFALDI (Mem. Accad. Lincei, 1927, [vi], **2**, 266—318).—A comprehensive comparative survey of existing crystallographic data referring to the rhombohedral sulphur produced by volcanic eruption. R. W. LUNT.

Lattice constant of metallic cobalt. S. SEKITO (Sci. Rep. Tohoku Imp. Univ., 1927, **16**, 545—553).—*X*-Ray examination of annealed cobalt by the powder-photographic method, at ordinary temperatures, indicates that it has a hexagonal close-packed arrangement of lattice constant 2·498 Å. and axial ratio 1·622. At about 700°, however, it has a face-centred cubic lattice with lattice constant 3·558 Å. This confirms Masumoto's conclusion (this vol., 21) that there are two allotropic modifications of cobalt which have a transition point lying between 400° and 500°. Electrolytic cobalt may also consist wholly of the hexagonal form, although Hull found a mixture of the two forms in the powder obtained by rapid electrolysis (A., 1922, ii, 624). The amount of discontinuous change at the transition point, calculated from the lattice constant, is in satisfactory agreement with the result obtained by Masumoto from his elongation–temperature curve. M. S. BURR.

Coherence of the reflected *X*-rays from crystals. G. E. M. JAUNCEY and A. H. COMPTON (Nature, 1927, **120**, 549).—For the $K\alpha$ line of molybdenum reflected from the (100) planes of rock-salt in the nth order, the ratio of the energy of recoil (given to a sodium atom by the impulse imparted by the reflected quantum) for each order to the energy of a quantum of Reststrahlen is 0·017, 0·067, 0·15, 0·27, 0·42, 0·60, 0·82, respectively, for values of n from 1 to 7. The fact that the ratio is always less than unity indicates that the energy of recoil is always less than that of a quantum of thermal agitation; hence the impulse is imparted to the crystal as a whole, and there is no reason to anticipate an absence of coherence in the reflected rays. A. A. ELDRIDGE.

***X*-Ray analysis of hafnium.** K. KIMURA (Z. physikal. Chem., 1927, **128**, 394—398).—The hafnium content of a mixture of hafnium and zirconium oxides or phosphates may be determined by mixing the substance with sufficient lutecium oxide or phosphate to cause the hafnium $L\beta_1$ line and the cassiopeium line to appear of equal intensity. Such a mixture corresponds with a Lu_2O_3/HfO_2 ratio of $2{\cdot}5_5$ for an oxide mixture, and $2{\cdot}7_5$—$2{\cdot}8_5$ for a phosphate mixture. The application of the method to the analysis of alvite is described, together with the method of calculation when other metallic oxides are present. H. F. GILLBE.

***X*-Ray study of the β-transformation in copper–zinc alloys.** A. PHILLIPS and L. W. THELIN (J. Franklin Inst., 1927, **204**, 359—368).—Diffraction data have been obtained for β-brasses at the ordinary temperature and at 520°. The lattice of β-brass is body-centred and the lattice parameter increases with zinc content. Above the transformation temperature β-brass retains a body-centred lattice, but the parameter has the value d_{100} 3·007 Å. against d_{100} 2·956 Å. at the ordinary temperature. The values are for brass containing 51·1% of copper. W. E. DOWNEY.

Hexagonal structure of thallium crystals. G. R. LEVI (Z. Physik, 1927, **44**, 603—606).—The contention of Becker (this vol., 503) that crystalline thallium has a tetragonal structure is contradicted by photographs and crystallographic measurements of actual crystals, which show that the structure is hexagonal. R. W. LUNT.

Crystal structure of magnesium telluride. W. ZACHARIASEN (Z. physikal. Chem., 1927, **128**, 417—420).—The crystals of magnesium telluride belong to the wurtzite type, with $a=4{\cdot}52\pm0{\cdot}02$, $c=7{\cdot}33\pm0{\cdot}04$ Å.; u is approx. $\frac{3}{8}$; $d_{calc.}$ is 3·86. The distance between neighbouring magnesium and tellurium atoms is 2·76 Å. H. F. GILLBE.

Crystal structure of potassium dihydrogen phosphate. S. B. HENDRICKS (Amer. J. Sci., 1927, [v], **14**, 269—287).—The space-group of ammonium and potassium hydrogen phosphates is D_{2d}^{12} (Hassel, A., 1925, ii, 1130). The unit cell of the potassium salt contains 4 molecules. Using Wyckoff's notation, the phosphorus atoms are at (*a*), the potassium atoms at (*b*), and the oxygen atoms at (*e*), the locations of the latter being fixed by the parameter ranges: $x=0{\cdot}045$—$0{\cdot}075$; $y=0{\cdot}120$—$0{\cdot}135$; $z=0{\cdot}145$—$0{\cdot}165$ Å. The eight hydrogen atoms are at (*c*) and (*d*), the parameter u not being determined. This structure offers evidence against the assumption that the shape of a phosphate group is independent of its ionic surroundings. In the rotating-crystal method of analysis the duration of exposure varies for different parts of the photographic plate. The method of calculating the effective times of exposure is described. S. K. TWEEDY.

Crystal structures of ammonium, potassium, and rubidium cupric chloride dihydrates. S. B. HENDRICKS and R. G. DICKINSON (J. Amer. Chem. Soc., 1927, **49**, 2149—2162).—*X*-Ray methods indicate that the unit cell contains 2 molecules of hydrate, the space-group symmetry probably being D_{2h}^{14} with $u=0{\cdot}213$, $v=0{\cdot}217$ for the potassium and rubidium salts and 0·217 and 0·221 for the ammonium salt. The 2Cu are probably at (*a*), 4K at (*d*), 4Cl at (*f*), 4Cl at (*g*), and $4H_2O$ at (*e*) (Wyckoff's notation). This structure, which is in agreement with the behaviour of the substances in solution as double rather than complex salts, represents a new type. S. K. TWEEDY.

Crystal structure of zirconium oxide. W. P. DAVEY (Physical Rev., 1926, [ii], **27**, 798).—Of the several forms in which zirconium oxide may crystallise, one is a face-centred cubic lattice of ZrO_2, $a=5{\cdot}098$ Å.; the second is a triangular close-packed lattice of ZrO_2, $a=3{\cdot}598$, $C=1{\cdot}633$. Both structures give d 6·13. A. A. ELDRIDGE.

Oxides. Density and crystal structure of the oxides of antimony, and the nature of the oxygen linking. IV. A. SIMON (Z. anorg. Chem., 1927, **165**, 31—40).—The oxides Sb_2O_3, Sb_2O_4, Sb_6O_{13},

and Sb_2O_5 all have approximately the same type of lattice. The elementary antimony tetroxide cell contains eight double molecules; antimony tetroxide and the oxide Sb_6O_{13} have a similar type of lattice to the trioxide, whilst the Debye diagram of the pentoxide indicates that this substance is partly colloidal; the fifth atom of oxygen is held much more loosely than the others, and its introduction into or removal from the molecule has but little influence on the dimensions of the lattice. These facts accord with the chemical properties of the pentoxide and its derivatives, notably with the influence of heat on the hydrated form, and with the production of the tetroxide from antimony by the action of nitric acid. The density of antimony trioxide, determined pyknometrically, is 5·19, whilst the *X*-ray method gives the value 5·49. That of the tetroxide increases with increase of time of heating, at 840°: after 1 hr., the density is 5·99, and after 150 hrs., 7·50. The change is ascribed to the production of the crystalline form from the amorphous. Similar irregularities are found when the densities of Sb_6O_{13} and antimony pentoxide are determined; the values from the *X*-ray diagrams are 7·52 and 7·86, respectively. H. F. GILLBE.

Crystal structure of palladium oxide (PdO). W. ZACHARIASEN (Z. physikal. Chem., 1927, **128**, 412—416).—Palladous oxide crystallises in the tetragonal system, with $a=3·029\pm0·005$, $c=5·314\pm0·005$ Å. The elementary cell contains two atoms of palladous oxide, the palladium atoms forming a body-centred lattice; the positions of the oxygen atoms have not been determined on account of the smallness of the scattering. Palladous oxide is probably isomorphous with stannous oxide and red lead monoxide. H. F. GILLBE.

Crystal structure of tetramethylammonium chloroplatinate. M. L. HUGGINS (Physical Rev., 1926, [ii], 27, 638).—The structure has cubic symmetry; $a_0=12·65$ Å. Each platinum atom is surrounded by six chlorine atoms (24*a*) at the corners of a regular octahedron, and each nitrogen atom by four carbon atoms (32*a*) at the corners of a regular tetrahedron. The symmetry is that of the space-group O_h^5 or O^3. The platinum–chlorine distance is 2·35 Å. if the nitrogen–carbon distance is assumed to be 1·47 Å. A. A. ELDRIDGE.

Crystal structure of mercuric oxide. W. ZACHARIASEN (Z. physikal. Chem., 1927, **128**, 421—429).—Powder measurements of the rhombic form of mercuric oxide indicate the existence of two molecules in the elementary cell, of dimensions $a=3·296$, $b=3·513$, and $c=5·504$, with an error of $\pm0·006$ Å.; $d_{calc.}=11·22$. The mercury atoms form a body-centred lattice, but it is not possible to differentiate between the numerous possible positions of the oxygen atoms on account of the small scattering. H. F. GILLBE.

Crystal structure of heteropolar compounds of the composition $MG_6{\cdot}LR_6$, $MG_5D{\cdot}LR_6$, and $MG_4D_2{\cdot}LR$ which crystallise in the trigonal system. O. HASSEL and J. R. SALVESEN (Z. physikal. Chem., 1927, **128**, 345—361).—The crystal structures of the following compounds have been determined; *b* is the semidiagonal of a face of the rhombohedron and *D* is the diagonal through the crystal in Å.: magnesium fluosilicate, $b=9·56$, $D=9·89$; manganous fluosilicate, $b=9·66$, $D=9·75$; ferrous fluosilicate, $b=9·62$, $D=9·68$; cobaltous fluosilicate, $b=9·31$, $D=9·69$; nickelous fluosilicate, $b=9·62$, $D=9·50$; zinc fluosilicate, $b=9·32$, $D=9·64$; magnesium titanium fluoride, $b=9·77$, $D=9·85$; zinc titanium fluoride, $b=9·55$, $D=9·88$; zirconium zinc fluoride, $b=9·77$, $D=10·11$; magnesium fluostannate, $b=9·77$, $D=10·02$; zinc fluostannate, $b=9·71$, $D=10·19$. Measurements for other co-ordination compounds are:

$Co(NH_3)_6Co(CN)_6$, $b=10·89$, $D=10·81$;
$Co(NH_3)_6Cr(CN)_6$, $b=11·15$, $D=10·90$;
$Co(NH_3)_5H_2OCo(CN)_6$, $b=10·74$, $D=10·85$;
$Co(NH_3)_5H_2OFe(CN)_6$, $b=10·74$, $D=10·84$;
$Co(NH_3)_4(H_2O)_2Co(CN)_6$, $b=10·62$, $D=11·01$.

These compounds are all of very similar structure, one ion being at the corner and the other at the centre of a rhombohedron of about 96° inclination. The arrangement of the six surrounding groups is probably such that the true elementary cell is a rhombohedron of four times the size of the simple one and of inclination about 112°. Replacement of one or two of the ammonia molecules in the hexammine compounds by water produces very little alteration in the *X*-ray diagram. H. F. GILLBE.

Structure of xenotime and the relation between chemical constitution and crystal structure. L. VEGARD (Phil. Mag., 1927, [vii], 4, 511—525).—The structure of xenotime has been investigated by means of the powder method and the previous result that xenotime and zircon have practically identical space lattices confirmed. Both belong to the space-group D_{4h}^{19}. In the xenotime lattice all four oxygen atoms are of equal consequence, whilst the old chemical constitution formula would assign to one of them a singular position. On the octet theory of molecular structure the atomic arrangement in the solid state is in agreement with the constitutional formula. The close packing necessary for the stability of a lattice of the zircon type indicates that such crystals may be stable under high pressures. Xenotime is gradually changing its crystal structure with maintenance of its external form, and it is concluded that crystals of this type have probably been formed under very high pressures. A. E. MITCHELL.

Quartz. A. MEISSNER (Physikal. Z., 1927, **28**, 621—625).—If a quartz plate cut at right angles to one of the electric axes is subjected to high-frequency oscillations of variable frequency, two characteristic oriented oscillations manifest themselves at 1665 and 1160 metres. By dusting the quartz surface with lycopodium powder a clear pattern appears on excitation, and a photograph of the pattern discloses orientation in two directions from the optical axis, $\alpha=-48\pm2°$ (1160 metres), $\beta=+71\pm2°$ (1665 metres). The effect is connected with the inclination of planes of like atoms against the optical axis and the values $\alpha=-44\pm2°$ and $\beta=+63\pm2°$ are calculated from the not unequivocal *X*-ray data. Piezo-electric observations considered in the light of the foregoing

lead to values for the modulus of elasticity of E—$7{\cdot}8\times10^{11}$ and $15{\cdot}6\times10^{11}$ cm.$^{-1}$ sec.$^{-2}$ for the conditions corresponding with the angles β and α, respectively, the separations of the planes concerned in the phenomena being 2·3 and 3·4 Å., respectively.

R. A. MORTON.

Equilibrium position of the atoms in β-quartz and its relation to double refraction and optical rotation. E. A. HYLLERAAS (Z. Physik, 1927, **44**, 871—886).—The following values of the oxygen parameters α and u in β-quartz have been computed from an electrostatic evaluation of the grating energy and from data referring to double refraction and to optical rotation, respectively: 77·9°, 0·216; 77·4°, 0·215; 77·1°, 0·214. The values are in satisfactory agreement with those of Bragg, but those of Wyckoff are thought to be in error.

R. W. LUNT.

Structure of silicates. W. L. BRAGG (Proc. Roy. Inst., 1927, **25**, 302—310).

Crystal structure of tetrahedrite. J. PALACIOS (Anal. Fis. Quím., 1927, **25**, 246—251).—Data are given for the crystal structure of tetrahedrite by the methods of Bragg and of Debye and Scherrer, respectively. The unit cell contains four molecules in a cube, $a=10{\cdot}39$ Å.; it is considered that the formula should be $3Cu_2S,Sb_2S_3$, and not $4Cu_2S,Sb_2S_3$, as supposed by Rose, Dana, and Moissan.

G. W. ROBINSON.

Crystal structures of anatase and rutile. M. L. HUGGINS (Physical Rev., 1926, [ii], **27**, 638).—Vegard's and Greenwood's results for rutile, and Vegard's for anatase, have been verified. Anatase has a_0 3·78, c_0 9·50 Å., with titanium atoms at $(0,0,0)(0,\frac{1}{2},\frac{1}{4})(\frac{1}{2},0,\frac{3}{4})(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ and oxygen atoms at $(0,0,u)(0,\frac{1}{2},u+\frac{1}{4})(\frac{1}{2},0,u+\frac{3}{4})(\frac{1}{2},\frac{1}{2},u+\frac{1}{2})(0,0,u)(0,\frac{1}{2},\frac{1}{4}-u)(\frac{1}{2},0,\frac{3}{4}-u)(\frac{1}{2},\frac{1}{2},\frac{1}{2}-u)$, where $u=0{\cdot}20\pm0{\cdot}01$; space-group D_{4h}^{19}. Rutile has $a_0=4{\cdot}58$, $c_0=2{\cdot}95$ Å., with titanium atoms at $(0,0,0)(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ and oxygen atoms at $(u,u,o)(u,u,o)(\frac{1}{2}-u,u+\frac{1}{2},\frac{1}{2})(u+\frac{1}{2},\frac{1}{2}-u,\frac{1}{2})$, where $u=0{\cdot}30\pm0{\cdot}01$; space-group D_{4h}^{14}.

A. A. ELDRIDGE.

X-Ray diffraction in liquids. Primary normal alcohols. G. W. STEWART and R. M. MORROW (Physical Rev., 1927, [ii], **30**, 232—244).—Two significant distances are measured by the molybdenum $K\alpha$ X-ray diffraction curves for the primary normal alcohols containing from 1 to 11 carbon atoms; the first is linearly dependent on the number of carbon atoms, and the second is the distance of separation perpendicular to the chain. The first distance increases about 1·3 Å. for each carbon atom, the second is 4·6 Å. for lauryl alcohol, decreasing slowly to 4·4 Å. for butyl alcohol, and then rapidly to 3·8 Å. for methyl alcohol. It is concluded that the diffraction is produced by planes containing the polar groups, which are not perpendicular to the direction of the parallel chain molecules. The effect is not caused by crystal fragments, but is ascribed to a non-crystalline molecular space array termed "cybotaxis." The cybotactic state permits mobility, but not random motion; the molecules have the same orientation in groups too small to produce optical anisotropy. The universality of cybotaxis in liquids is not, however, claimed. Computed values of the densities of the alcohols are recorded.

A. A. ELDRIDGE.

X-Ray diffraction in liquids. C. V. RAMAN and C. M. SOGANI (Nature, 1927, **120**, 514).—A general account of experiments being described elsewhere. When the benzene ring is unsymmetrically loaded there is a broadening of the halo. Acetic acid and glycerol each give two haloes, corresponding respectively with the mean distance between neighbouring molecules which lie side by side, and that between those lying end to end.

A. A. ELDRIDGE.

Electrolytic crystallisation processes. I. V. KOHLSCHUTTER. **II. Aggregation forms of incoherent metal deposits.** V. KOHLSCHUTTER and A. GOOD. **III. Formation and properties of coherent metallic films.** V. KOHLSCHUTTER and F. JAKOBER (Z. Elektrochem., 1927, **33**, 272—277, 277—289, 290—308).—I. In characterising cathodic metal deposits, the mode of arrangement of the individual crystals to form the aggregate (aggregation form) must be considered as well as the form, habit, and size of the individuals. As in other crystallisation processes, growth of existing crystals and formation of new nuclei are differently affected by changing conditions, and wide variations in the character of such deposits are possible. In reviewing theories as to the mechanism of the formation of cathodic metal deposits, it is shown that numerous factors may possibly operate in determining their character, the growth of the deposit being affected, not only by the forces of crystallisation (cf. Blum and Rawdon, A., 1923, ii, 732), but also probably by forces in the solution. An attempt is to be made to determine the dependence of the character of electrodeposited metals on the nature of the metal and the conditions of deposition.

II. The electrodeposition of metals giving incoherent, outgrowing deposits (cadmium, zinc, tin, silver, and thallium) has been investigated with reference to the character and rate of formation of the outgrowths. In previous work (A., 1924, ii, 528) Kohlschutter and Uebersax showed that under suitable conditions lead is deposited from nitrate solutions in the form of thread-like chains of minute octahedra attached to one another by their apexes. This form is favoured by high current density, low electrolyte concentration, and low temperatures. Raising the temperature leads eventually to the formation of leafy structures difficult to characterise. The chains of octahedra probably arise by the convergence of current lines at the apex of the octahedron, resulting in the formation of a new nucleus at that point. From a comparison of the forms exhibited by various metals under various conditions it is concluded that the deposits obtained with a given metal belong to a characteristic morphological type by which the metal can be recognised, in spite of modification due to variation of conditions. The size of the individual crystals is determined by the relation between rate of crystal growth and rate of nucleus formation, which in turn depends on current density, electrolyte concentration, and temperature. High chemical polarisation is known to be an accom-

paniment of low rate of crystal growth, but this effect cannot be referred to complex formation, since the latter is found to favour crystal growth in some cases. High rate of crystal growth favours regular orientation of the crystals in the chains. The attachment of one to another occurs in a favoured crystallographic direction and depends therefore on the habit of the individuals, which is itself largely determined for a given metal by the composition of the electrolyte. The development of regular chains seems to be favoured by a certain current density and is, no doubt, connected with the chemical polarisation, the magnitude of which affects the distribution of current lines. With silver, chains of crystals were not obtained, there being no favoured direction of growth of the crystals, and probably a suitable relation between rate of growth and rate of nucleus formation was not attained under the experimental conditions. It is concluded that even incoherent cathodic metal deposits exhibit definite regularities and that their formation can be referred to the operation of forces at the crystal surface and in the electrolyte. The observations are discussed in detail and are compared with the results of Glocker and Kaupp (A., 1924, ii, 518) on the *X*-ray examination of coherent metallic deposits possessing a fibrous structure.

III. Mechanical strains developed during the cathodic deposition of thin films of nickel have already been investigated by the "contractometer" method (A., 1922, ii, 648). This method has now been improved and applied to the deposition of other metals which give very fine-grained coherent deposits. The magnitude of the "contraction" developed during the deposition of films of nickel, cobalt, iron, chromium, and palladium on platinum cathodes has been determined under various conditions of current density, temperature, and composition of electrolyte. Deposits obtained on platinum cathodes previously coated electrolytically with very thin films of copper or silver were coarser grained and exhibited a smaller contraction. Cathodic evolution of hydrogen at a contracted nickel deposit causes it to expand. The effect of superimposing alternating current on the direct current during metal deposition has also been examined. In the deposition of zinc and lead, metals which tend to give coarse-grained deposits, expansion was observed instead of contraction under all conditions. With silver deposited from cyanide solutions, contractions occur only when the current density is very high or when the solution contains a large excess of potassium cyanide: these conditions are the reverse of those leading to fine-grained, coherent deposits, and in the formation of such deposits a notable expansion occurs. The various factors which may determine the observed contraction and expansion phenomena are discussed in the light of theories of the mechanism of cathodic metal deposition.

H. J. T. Ellingham.

Recrystallisation of silver and platinum. O. Feussner (Z. Metallk., 1927, 19, 342—345).—As is the case with most other metals, there is a lower temperature limit below which platinum and silver will not recrystallise on annealing. This limiting temperature is higher the smaller is the amount of deformation to which the metal has been subjected; for silver, the minimum temperature lies between 250° and 300° and for platinum it is about 650°. Annealing at temperatures just above the limit yields a fine grain which becomes rapidly coarser with rise of temperature. For silver the relation between annealing temperature and grain size is almost linear above 350°, whereas for platinum the curve is hyperbolic and concave to the axis of temperature, *i.e.*, a relatively small rise in temperature between 800° and 900° causes a large increase in the size of the crystals, but a similar rise of temperature between 1200° and 1500° has a very slight effect on the size of the crystals. By plotting the grain size against the logarithm of the deformation a straight line is obtained in both cases for all temperatures.

A. R. Powell.

Tyndall's experiments on magne-crystallic action. (Sir) W. Bragg (Proc. Roy. Inst., 1927, 25, 162—184).

Grating theory of the electrolytic conductivity of rock salt. W. Braunbek (Z. Physik, 1927, 44, 684—699).—From a statistical analysis of the energy distribution of sodium ions in the rock-salt grating an expression is derived for the probability that an ion will move from the grating, *i.e.*, for the number of ions crossing a given boundary per sec. A consideration of this movement in a uniform electric field leads to an expression for the ionic conductivity, χ, in the following form: $\log\chi=\log 2e^2/3\tau ac\phi_0-\phi_0/kT$, where e is the electronic charge, τ the time period of the ions in the grating, a the grating constant, c a grating distortion factor, k the gas constant per mol., T the temperature Abs., and ϕ_0 the minimum shearing energy per unit cell. The value of c has been calculated from grating theory, that of τ from the frequency of residual rays, and that of ϕ_0 from the melting temperature. The above expression then becomes $\log\chi=27{\cdot}7-10{,}400/T$, from which values of the conductivity χ have been calculated in the range 20—500°, which agree well with those observed by von Seelen (Z. Physik, 1924, 29, 125) for which the relationship $\log\chi=25{\cdot}9-10{,}700/T$ obtains.

R. W. Lunt.

Magnetic susceptibility of some binary alloys. J. F. Spencer and (Miss) M. E. John (Proc. Roy. Soc., 1927, A, 116, 61—72).—The magnetic susceptibilities of silver, lead, cadmium, tin, gold, aluminium, bismuth, and a number of their alloys have been measured by means of the Curie–Cheneveau magnetic balance. The values for the pure metals agree with those obtained by Honda (Ann. Physik, 1920, [iv], 32, 1027). The susceptibility values are plotted against composition in the case of the alloys (silver–lead, gold–lead, gold–tin, gold–cadmium, aluminium–tin, bismuth–tin, cadmium–tin, and lead–tin), and well-defined maxima and minima are obtained, the compositions at which correspond in a number of cases with compounds, and in a few cases with compounds known to exist from a study of f.-p. curves. The magnetic susceptibility of an alloy system may lie well inside the paramagnetic region although both constituents are diamagnetic (lead–

silver). The susceptibility curve for the lead–tin system is almost linear. L. L. BIRCUMSHAW.

Magnetic susceptibility of the alkali metals. J. C. MCLENNAN, R. RUEDY, and (MISS) E. COHEN (Proc. Roy. Soc., 1927, A, 116, 468—483).—The magnetic susceptibilities of sodium, potassium, cæsium, and rubidium have been determined. The metals were purified by distillation in a vacuum. The cæsium and rubidium were prepared by the action of calcium on the halides; sodium was also prepared by electrolysis through glass. The susceptibility was measured by weighing the metals in the presence and absence of a strong uniform magnetic field. The atomic susceptibilities of sodium, potassium, rubidium, and cæsium were found to be 14×10^{-6}, 19×10^{-6}, 17×10^{-6}, and 28×10^{-6}, respectively. The susceptibilities of sodium and cæsium were found to be constant down to —190°. The theoretical bearing of these results is discussed. W. E. DOWNEY.

Distortion of crystals of aluminium under compression. II. Distortion by double slipping and changes in orientation of crystal axes during compression. III. Measurements of stress. G. I. TAYLOR (Proc. Roy. Soc., 1927, A, 116, 16—38, 39—60).—II. Changes in the orientation of crystal axes during compression of a disc cut from a single aluminium crystal are found to be in accordance with the prediction made on the assumption that the crystal slips as determined by distortion measurements. The bearing of the results on the structure of rolled sheets of metal is discussed, and distortions of cubical blocks of material, due to various types of double slipping, are compared, to discover which is most likely to occur.

III. Experiments are described for measuring the internal shearing stresses in a compressed disc. Formulæ are developed for analysing shear stresses parallel to slip planes and distortion due to double and single slipping. It is shown that the material hardens more rapidly when a given total amount of slipping is divided equally between two planes than when it is all on one plane. The experiments cover a large range, and indicate that the resistance to shear increases steadily up to the greatest amounts of distortion used. L. L. BIRCUMSHAW.

Nickel–chromium solid solutions. F. C. BLAKE and A. E. FOCKE (Physical Rev., 1926, [ii], 27, 798).—The amount of distortion of the nickel lattice by substitution of chromium, and *vice versa*, has been determined. A. A. ELDRIDGE.

Influence of time and temperature on the mechanism of the mechanical fracture of large crystals of iron, aluminium, copper, and brass. F. SAUERWALD and G. ELSNER (Z. Physik, 1927, 44, 36—57).—Measurements have been made of the extensibility, tensile strength, and shearing strength of rods of iron, aluminium, copper, and brass, each containing at most two or three single crystals, at temperatures from 0° to 1000°. The crystalline nature of the fracture produced by stretching and by shearing has been examined, and recorded photographically. The results show that the general statement that at lower temperatures the fracture is crystalline and at higher temperatures intercrystalline does not represent experimental observation. R. W. LUNT.

Sub-grain boundaries in nickel. E. S. DAVENPORT (Nature, 1927, 120, 478).—An example of the formation of sub-boundaries in nickel is described and illustrated. A. A. ELDRIDGE.

Synthesis of nematic fusions. W. KAST (Ann. Physik, 1927, [iv], 83, 1200—1201).—A correction.

Mol. wt. of gelatin in cresol. R. O. HERZOG and H. COHN (Z. physiol. Chem., 1927, 169, 305).—Owing to the difficulty in obtaining trustworthy results with the cryoscopic method (cf. Troensegaard and Schmidt, this vol., 785; Cohn and Conant, A., 1926, 891), the rate of diffusion of gelatin dissolved in cresol is used. A. WORMALL.

Metal crystals. V. Thermal and electrical conductivity of crystals belonging to the regular system. E. GRUNEISEN and E. GOENS (Z. Physik, 1927, 44, 615—642; cf. A., 1926, 784).—The thermal and electrical conductivities of gold, copper, platinum, rhodium, aluminium, iron, and tungsten in the finely-crystallised state and as single crystals have been determined at 0°, —190°, and —252°. For metals of high conductivity the thermal conductivity is determined principally by the purity and to a small extent only by the crystal size. The thermal resistivity, w, can be expressed by $w=w_i+\rho/ZT$, where ρ is the electrical resistivity, Z a constant, T the absolute temperature. The quantity w_i is identified as the non-metallic component of the resistivity, and, at temperatures at which superconductivity occurs, is the predominating term; its value is approximately constant for the metals examined, and is thus independent of purity, hardness, and crystal size. The quantity ρ/ZT is termed the metallic component of the resistivity and predominates except at very low temperatures; for pure, or nearly pure, metals Z has the value $2{\cdot}2\times10^{-8}$; it is therefore in this component that the basis of the Wiedemann–Franz–Lorenz law is to be sought. R. W. LUNT.

Measurement of light absorption. H. VON HALBAN and J. EISENBRAND (Proc. Roy. Soc., 1927, A, 116, 153—162).—The relative merits of the photographic and photo-electric methods for the measurement of light absorption in the ultra-violet are discussed. The photographic method is characterised by a definite absolute difference in extinction, not by a definite relative error. The accuracy with which the extinction coefficient can be determined depends on the absolute magnitude of the extinction used, and the error may be made very small by employing a sufficiently large extinction. In the photo-electric method it is possible, under favourable conditions, to make the sensitivity to differences of extinction about a hundred times as great as that of the photographic method. The photo-electric method is thus superior to the photographic method for the qualitative or quantitative determination of small changes in light absorption, and is to be preferred as an instrument for the elucidation of problems in chemical dynamics. The method is not so suitable

for absolute measurements, since the purity of the light and the degree of definition in respect of wave-length are much poorer than in the photographic method, owing to the high intensity of light needed. The photographic method is entirely suitable for the quantitative exploration of absorption spectra, and on account of its greater rapidity is preferable to the photo-electric method. The large differences which have been found between the results of the two methods at wave-lengths below 300 $\mu\mu$, especially for solutions of nitrates (cf. Baly and Riding, this vol., 183), have been traced to a systematic source of error in the photo-electric measurements, due to the use of a glass relatively opaque to short-wave light in the cells employed in the measurements. The results of the two methods are now found to be in satisfactory agreement. L. L. Bircumshaw.

Specific heat of hydrogen. G. H. Dieke (Physical Rev., 1926, [ii], 27, 639).—The assumptions necessary in a recalculation of the specific heat of hydrogen on the basis of the new development in band spectra are considered. A. A. Eldridge.

Relation between the difference of the specific heats at constant pressure and constant volume and properties of liquids. W. Herz (Z. anorg. Chem., 1927, 166, 155—160).—Combination of Trouton's rule with the rule that the molecular heat at constant pressure of a liquid exceeds that at constant volume by 10 g.-cal. (Tyrer, A., 1914, ii, 425; Schulze, A., 1915, ii, 221) leads to the relation $c_p - c_v = L/2T$, where c_p and c_v are the specific heats at constant pressure and constant volume, respectively, and L is the latent heat of evaporation at the b. p. (Abs.), T. Somewhat similar relationships can be deduced connecting $c_p - c_v$ and the internal pressure at the b. p., zero volume, capillary constant, critical data, molecular elevation of the b. p., surface tension at the b. p., and the molecular refraction, and, in general, these are in satisfactory agreement with the experimental data. R. Cuthill.

True specific heats at high temperatures by heating with thermionic electrons. H. Klinkhardt (Ann. Physik, 1927, [iv], 84, 167—200).—The effect of thermionic emission in raising the temperature of various substances has been used to determine specific heats at high temperatures. The substance was heated in a vacuum furnace to any desired temperature. The heating effect of the controlled emission from a tungsten wire on the hot body was measured by means of a thermocouple embedded in the substance. Copper, solid and liquid lead, zinc, ammonium chloride, iron, nickel, and six iron–manganese alloys have been examined. The method is particularly applicable to the determination of specific heats near the m. p. or conversion point of a substance. W. E. Downey.

Calorimetric researches on some salts. E. Cane (Rend. Accad. Sci. fis. mat. Napoli, 1927, [iii], 32, 83—86).—Using Bunsen's calorimeter, the specific heats of various metallic molybdates have been determined and by application of the addition law the specific heat of the group MoO_4 has been deduced. Results indicate that this law holds for molybdates. M. Carlton.

Latent heat of evaporation of sulphur. J. H. Awbery (Proc. Physical Soc., 1927, 39, 417—420).—The quantity of sulphur boiled off from a vessel when a known amount of energy is supplied has been determined. Heat losses were prevented by immersing the vessel in sulphur vapour. Another method of estimating the heat loss, involving the use of a dummy vessel with a smaller heating coil so that the differences in energy and weight evaporated could be equated, proved unsatisfactory. The latent heat was found to be 79 with an estimated accuracy of 2%. R. A. Morton.

Heat of formation of the K_2 molecule. A. Carrelli and P. Pringsheim (Z. Physik, 1927, 44, 643—652).—The concentration of K_2 molecules in potassium vapour at temperatures from 240° to 310° has been determined from the intensity of the red fluorescence band, excited by a constant source of white light, which is assumed proportional to the concentration of K_2 molecules. By providing that the vapour is saturated, these data give the vapour-pressure curve for K_2 molecules from which the heat of vaporisation, λ_2, is obtained. The heat of formation, Q, is then given by $Q = 2\lambda_1 - \lambda_2$, where λ_1 is the heat of vaporisation of monatomic potassium; the value thus found is 0·63 electron volt. The variation of the concentration of K_2 molecules with temperature at constant pressure has been employed to calculate Q directly; the value obtained is 0·53 electron volt; that calculated from the convergence frequency of the band is 0·68 electron volt. R. W. Lunt.

Heat of transformation of nickel and cobalt. S. Umino (Sci. Rep. Tohoku Imp. Univ., 1927, 16, 593—611).—The heat content–temperature curves of nickel and cobalt have been determined by a calorimetric method. The heat of magnetic transformation of nickel has hence been found to be 2·01 g.-cal./g., whilst that of cobalt is 2·00 g.-cal./g. and the heat of transformation of cobalt from the hexagonal close-packed to the face-centred cubic lattice is 1·05 g.-cal./g. The mean and true specific heats at different temperatures have also been calculated. M. S. Burr.

New base point on the thermometric scale and the $\alpha \rightleftharpoons \beta$ inversion of quartz. F. Bates and F. P. Phelps (U.S. Bur. Standards Sci. Paper 557, 1927, 22, 315—327).—The heating and cooling curves for crystalline specimens of quartz from widely-separated sources have been investigated, temperature measurements being made by means of thermocouples inserted in small holes drilled in crystalline plates. It was found that the α β inversion is accompanied by superheating and supercooling. Inversion commences sharply at 573·3$_0$° on heating, and this temperature is always recorded regardless of the origin of the quartz specimen, whilst the inversion on cooling begins at 572·3$_8$°, but the exact temperature varies slightly with conditions in the crystal. The true inversion temperature may be taken as 572·6$_7$°. The heat of transition at the inversion temperature is estimated to be 0·165 g.-cal. The change at 573·3$_0$°, it is suggested, might well replace the m. p. of antimony (630·5°) as a reference point on the thermometric scale, specially suitable

for the standardisation and checking of thermocouples. R. A. MORTON.

M. p. of sodium. J. R. NIELSEN and R. BIEBER (Proc. Oklahoma Acad. Sci., 1927, **6**, 295—296).—Sodium prepared by electrolysis through glass has m. p. 97·6°. CHEMICAL ABSTRACTS.

Vapour pressure of diphenyl and aniline. F. J. GARRICK (Trans. Faraday Soc., 1927, **23**, 560—563).—If, by making use of Jaquerod and Wassmer's vapour-pressure data (A., 1904, ii, 538), the ratio T_1/T_2 is plotted against T_1, where T_1 and T_2 are the temperatures Abs. at which diphenyl and mercury, respectively, have the same vapour pressure, the curve obtained shows a sharp change of slope at about 224°. Measurements of the vapour pressure of diphenyl, between 153° and 254°, have therefore been made by a modification of Ramsay and Young's method. The results are not in agreement with those of Jaquerod and Wassmer, and no discontinuity is observed on plotting in accordance with the Ramsay–Young rule. Vapour pressures of aniline have been determined between 91° and 151°. The results do not agree with those of Kahlbaum (Z. physikal. Chem., 1889, **26**, 603). The Ramsay–Young graph is a smooth curve, the curvature being in the usual direction and more pronounced at the lower temperatures. M. S. BURR.

Influence of insoluble materials on the physical properties of liquids. J. B. PEEL, P. L. ROBINSON, and H. C. SMITH (Nature, 1927, **120**, 514—515).—Baker's observations (J.C.S., 1927, 949) of the change in vapour pressure and surface tension of liquids in presence of insoluble catalysts are substantiated by density determinations. The density of water at 14·1° in contact with carbon increases by 0·000080 in 48 hrs., 0·00019 in 96 hrs., and 0·00020 in 150 hrs.; the increase with ethyl ether and carbon at 14·8° is 0·0009 in 18 hrs., 0·0011 in 42 hrs., and 0·0013 in 90 or 130 hrs. Water at 18·5° in contact with thoria gave the following results: −0·00017 in 24 hrs., −0·00002 in 48 hrs., +0·00001 in 96 hrs., +0·00011 in 192 hrs., +0·00015 in 209 hrs.; at 23·3°, −0·00040 in 24 hrs., +0·00004 in 209 hrs. A. A. ELDRIDGE.

Relation between orthobaric densities. J. HORIUCHI (Bull. Chem. Soc. Japan, 1927, **2**, 213—224; cf. A., 1926, 1198).—The previously-derived relationship between the molecular volumes of a substance in the liquid and gaseous states is shown to be applicable to 22 more substances; the relationships between the quantities A and E and the critical constants are confirmed. The additive nature of the quantity E is established. J. S. CARTER.

Surface tension of molten metals and alloys. Y. MATUYAMA (Sci. Rep. Tohoku Imp. Univ., 1927, **16**, 555—562).—An apparatus is described for determining the surface tension of molten metals by the drop-weight method. The surface tensions of tin, bismuth, cadmium, lead, zinc, and antimony fall linearly as the temperature rises. The surface tension–temperature curves are practically parallel for the range of temperature considered, but Eötvos' law is not obeyed. Surface tension–composition curves are given for the binary alloys of antimony with cadmium, zinc, and lead. There is a break in each of the first two curves, showing that the intermetallic compounds formed, CdSb and Zn_3Sb_2, respectively, have not decomposed in the liquid state. M. S. BURR.

Viscosity of liquids above their b. p. IV. T. TITANI (Bull. Chem. Soc. Japan, 1927, **2**, 225—229; cf. this vol., 819).—The additive nature of the constant B in the author's previously-derived volume relation is established. When expressed in a reduced form by the introduction of critical data the author's volume and temperature relations become $\phi_r = k_r(v_r^{2/3} - b_r^{2/3})$ and $1-\phi_r = c_r(1-t_r)^{1.5}$, respectively, where ϕ_r, t_r, etc. represent reduced quantities or constants. The reduced constants k_r, b_r, and c_r are now independent of the nature of the substance and have the values 1·84, 0·308, and 1·09, respectively. They are related to the original constants and to the critical constants as follows: $k_r = KV^{2/3}/\Phi_c$; $b_r = B/V_c$; $c_r = CT_c^{1/5}/\Phi_c$. Further reduced equations are obtained from a consideration of the dimensions of viscosity. These equations are: $\phi_r' - k_r'(v_r^{2/3} - b_r^{2/3})$ and $\phi_{c_r}' - \phi_r' = c_r'(1-t_r)^{1/5}$, where the reduced constants k_r', c_r', and ϕ_{c_r}' have the values $4{\cdot}03\times10^4$, $2{\cdot}40\times10^4$, and $2{\cdot}19\times10^4$, respectively, and are related to the original constants, critical constants, and mol. wt. by the equations $k_r' = KM^{1/2}T_c^{1\cdot2}V_c^{1/3}$, $c_r' = CM^{1/2}T_c^{7/10}/V_c^{1/3}$, and $\phi_{c_r}' = \Phi_c M^{1/2}T_c^{1/2}/V_c^{1/3}$. J. S. CARTER.

Viscosity of nickel, aluminium, and light alloys. J. COURNOT and M. S. SILVA (Compt. rend., 1927, **185**, 650—652).—The viscosities of commercial nickel, "calypso," aluminium, "alpax," and duralumin wires of varying diameters have been studied at 15—700° by the method previously described (B., 1926, 161). Nickel has a viscosity at 500—600° about double of that of an ordinary soft or semi-soft steel, and the limiting viscosities are low in all cases compared with the ordinary rupture loads. If the diameter of the wire is doubled the limiting viscosity is increased by a constant amount independent of the temperature (500 g./mm.² and 1 kg./mm.² for aluminium and duralumin, respectively). J. GRANT.

Theory of the streaming of an elastic liquid in the Couette apparatus. M. REINER and R. RIWLIN (Kolloid-Z., 1927, **43**, 1—5; cf. A., 1926, 678).—From the equation for the internal tangential tension of a hypothetical "elastic liquid," $\tau = \theta + \eta dv/dr$, the following formulæ have been derived for the relation between the torsion angle of the suspension wire ϕ and the angular velocity Ω in the Couette apparatus: $\phi_0 + 2(\eta/\theta)\phi_0\Omega$ (1) and $\phi = (\eta/n)\Omega + (\phi/n)\log_e R_E/R_A$ (2), where η is the viscosity constant, θ the "flow solidity," $\phi_0 = (2\pi l R_A^2/D)\theta$, $n = D(R_E^2 - R_A^2)/4\pi R_E^2 . R_A^2 l$ (the apparatus constant), R_E and R_A are the radii of the outer and inner tubes, respectively, l is their length, and D the torsion modulus of the suspension wire. The relation (1) holds below the values ϕ_1 and Ω_1, relation (2) above these values, and $. R_E^2/R_A^2$, $(\theta/2\eta)[R_E^2/R_A^2 - (\log_e R_E^2/R_A^2) - 1]$. A criterion for the elasticity of a liquid is that its ϕ–Ω curve cuts off a certain value $\phi_0 > 0$ from the ϕ axis. L. L. BIRCUMSHAW.

Viscosities, electrical conductivities, and specific volumes of acetic acid–stannic chloride solutions. J. D. STRANATHAN and J. STRONG (J. Physical Chem., 1927, **31**, 1420—1428).—The viscosities, electrical conductivities, and specific volumes of solutions of stannic chloride in acetic acid have been measured at 25·2° for concentrations of the former up to a mol. fraction 0·4111 at which two layers are formed. Mixing is accompanied by a large evolution of heat, and by a large contraction in volume which, at a mol. fraction 0·3608 of stannic chloride, is 32·1% of the volume calculated on the additive law. The viscosity–concentration curve shows a pronounced maximum which is 282 times the viscosity calculated additively. The maximum occurs at the concentration corresponding with the compound $SnCl_4$,3AcOH, to the formation of which the change in the properties of the system is attributed.

L. S. THEOBALD.

Constitution of certain salts and acids in solution as determined by observations of critical solution temperatures. S. R. CARTER and N. J. L. MEGSON (J.C.S., 1927, 2023—2028).—The elevation of the critical solution temperature in the systems phenol–water and *iso*butyric acid–water by the addition of other substances (Patterson, A., 1925, ii, 389) is used to detect complex formation in hydrochloric acid solution. For mixtures of hydrochloric acid with sulphur dioxide, selenium dioxide, ferrous chloride, and cupric chloride, the rise of the critical solution temperature is normal and there is no complex formation. Mixtures of hydrochloric acid with ferric chloride, mercuric chloride, and cuprous chloride show, however, considerable complex formation, the compounds $FeCl_3$,3HCl and $HgCl_2$,HCl being indicated.

F. S. HAWKINS.

Interdiffusion of immiscible solid salts. C. TUBANDT and W. JOST (Z. anorg. Chem., 1927, **166**, 27—30).—Immiscible solid salts may diffuse into each other when in contact if the ion carrying the current has the same kind of charge in each, and if each salt is able to form mixed crystals by exchanging its own mobile ion for that of the other salt. These conditions are fulfilled by the forms of cuprous sulphide and silver iodide which are stable at higher temperatures, diffusion occurring in this case by exchange of the metal atoms. Diffusion is slowest at the surface of contact of the solids, indicating a not inconsiderable resistance to the transfer of ions from one lattice to another of a different type.

R. CUTHILL.

Determination of solubilities by potentiometric titration, and the "insoluble" form of silver chloride. F. L. HAHN and R. SCHULZE (Z. anorg. Chem., 1927, **166**, 213—218).—Determinations of the solubility of silver chloride by the potentiometric method previously described (this vol., 743) have failed to confirm the existence of the particularly insoluble form reported by Lorenz and Bergheimer (A., 1924, ii, 757).

R. CUTHILL.

Solubility of cupric sulphide in alkali sulphides in presence of sulpharsenates. C. DAVIES and A. D. MUNRO (J.C.S., 1927, 2385—2386).—The amount of cupric sulphide dissolved by yellow ammonium sulphide increases steadily with the amount of arsenic present, sufficient copper being dissolved to cause an error in qualitative analysis. Colourless ammonium sulphide does not dissolve cupric sulphide under the same conditions. With solutions of sodium polysulphide the influence of arsenic on the solubility of cupric sulphide is much less pronounced.

F. S. HAWKINS.

Effect of one salt on the solubility of another in ethyl alcohol solution. I and II. F. E. KING and J. R. PARTINGTON (Trans. Faraday Soc., 1927, **23**, 522—535).—The influence of lithium iodide and sodium thiocyanate on the solubility of sodium iodide in ethyl alcohol at 25° has been investigated, and conductivities and viscosities of the sodium iodide–sodium thiocyanate solutions have been determined. The solubility data for sodium thiocyanate and those for lithium iodide, at concentrations below one equivalent per litre, may be represented by the ordinary salting-out formula, $\log s/s_0=kc$, where s_0 and s are the solubilities in g./litre of saturated solution of sodium iodide, alone and in presence of an added salt of concentration c equiv./litre, respectively. Methods of calculating the ionised and un-ionised fractions in the mixture of sodium iodide and thiocyanate are described and compared, and certain values adopted. As the concentration of sodium thiocyanate increases, both the concentration of undissociated sodium iodide and the solubility product of the ions decrease at approximately the same rate.

M. S. BURR.

Influence of electrolytes on the solubility of other electrolytes in non-aqueous solvents. C. A. KRAUS and R. P. SEWARD (Trans. Faraday Soc., 1927, **23**, 488—491).—The solubility of sodium chloride in *iso*propyl alcohol in the presence of sodium nitrate and ammonium nitrate, respectively, has been determined at 25°, and also the solubility of sodium bromide in acetone in presence of sodium nitrate. The results show that addition of a second salt with a common ion depresses the solubility, whilst addition of a salt without a common ion increases it. The magnitude of the effects is not in accordance with that required by the Debye–Hückel theory. It is possible that, in solvents of lower dielectric constant, it will be necessary to abandon the assumption that the simple ions are the only molecular species present.

M. S. BURR.

Physico-chemical analysis by ebullition of saturated solutions. E. CORNEC and P. KLUG (Bull. Soc. chim., 1927, [iv], **41**, 1009—1017).—The b. p. of solutions which are saturated with regard to pairs of salts are said to afford information concerning the state of the salts in solution. Sodium and potassium chlorides, or nitrates, do not combine in solution; sodium (or potassium) chloride and bromide form a continuous series of mixed crystals; ammonium and copper sulphates, and ammonium and zinc sulphates, form double salts, $CuSO_4,(NH_4)_2SO_4,2H_2O$ and $ZnSO_4,(NH_4)_2SO_4,6H_2O$, respectively, exhibiting congruent solubility.

S. K. TWEEDY.

Partition coefficients and the influence of salts. W. HERZ and E. STANNER (Z. physikal. Chem., 1927, **128**, 399—411).—The partition coefficients of tri-

methylamine between benzene and aqueous solutions of lithium, sodium, potassium, strontium, and barium chlorides, and sodium and potassium bromides, iodides, and sulphates have been determined at 25°. The salting-out effect is greatest for chlorides and least for iodides, *i.e.*, it decreases with rising atomic volume, whereas the effect of the cations increases with increasing atomic volume. Neutral salts have a corresponding influence on the solubility of dipropylamine in water. Measurements of the partition coefficients of phenol and of benzoic acid between benzene and aqueous salt solutions indicate that in the case of acidic substances the sodium ion has the greatest influence and the potassium ion the least, the other cations giving intermediate values. The salting-out effect for a neutral substance such as acetone is greatest for the sodium and potassium ions. H. F. Gillbe.

Actinium. L. Imre (Z. anorg. Chem., 1927, **166**, 1—15).—Experiments on the distribution of the nitrates of thorium and radioactinium between nitric acid solutions and ethyl ether reveal a close similarity in the behaviour of the two salts. A method of removing cerium from actinium preparations has been worked out (cf. this vol., 844). R. Cuthill.

Dynamics of salting out. E. A. Hafner (Biochem. Z., 1927, **188**, 259—269).—Phenol is salted out of aqueous solution by ammonium sulphate, more readily in presence of glycine, carbamide, and acetone, less readily in presence of glycerol and alcohol, whilst dextrose and sucrose have but little effect. The salting out of euglobulin and total globulin by magnesium, ammonium, and sodium sulphates is investigated and the results are discussed theoretically (cf. A., 1925, ii, 283). P. W. Clutterbuck.

Adsorption of gases on the surface of mercury. M. L. Oliphant and R. S. Burdon (Nature, 1927, **120**, 584—585).—Measurement of the change of the concentration of carbon dioxide in admixture with hydrogen or helium when subjected to a shower of mercury droplets indicates that for 5, 10, and 15% of carbon dioxide a complete unimolecular layer of the gas is formed in 0·2 sec. after formation of the surface. For 0·5% the adsorption is less, and for 50% more, than that which corresponds with a unimolecular layer. It seems possible that the drop-weight method for measuring surface tension gives different values according to whether the liquid wets the tube or not. A. A. Eldridge.

Heats of adsorption on poisoned and heat-treated catalysts. G. B. Kistiakowsky, E. W. Flosdorf, and H. S. Taylor (J. Amer. Chem. Soc., 1927, **49**, 2200—2206).—The curves representing the heat of adsorption of hydrogen by copper catalysts as a function of the amount adsorbed (cf. this vol., 426) exhibit a maximum, which corresponds with a smaller amount of adsorbed gas when the catalyst is partly de-activated (by heat treatment) and disappears when the de-activation is complete. The curve for adsorption by a poisoned copper catalyst is typical of that for adsorption without activation. These results support the theory that a catalyst surface contains variable elementary spaces and that adsorption, accompanied by an endothermic activation process, occurs on the most active spaces. Since, in adsorption, that reaction which involves the smaller free energy decrease is favoured, the question arises as to whether free energy change is a true measure of adsorption velocity. S. K. Tweedy.

Hydrolytic adsorption by spongy platinum and charcoal. A. Frumkin and A. Donde (Ber., 1927, **60**, [*B*], 1816—1820; cf. this vol., 106).—Spongy platinum, prepared by the action of magnesium on chloroplatinic acid and purified by successive washings with hydrochloric acid and conductivity water in an atmosphere of hydrogen, adsorbs alkali from a solution of sodium sulphate; the alkali is not completely removed by washing with a considerable quantity of water, so that the amount of acid liberated is always in excess of that of the alkali. It has not been found possible to prepare spongy platinum in presence of oxygen which adsorbs acid and liberates alkali. Charcoal treated with platinum and activated in air adsorbs acid from potassium chloride solution and liberates alkali, whereas the opposite effect is observed in an atmosphere of hydrogen. Addition of thiocarbamide to the potassium chloride solution poisons the platinum and the charcoal then adsorbs only acid independently of the gaseous atmosphere. H. Wren.

Adsorption of ions and of sols at interfaces and its application to certain problems of colloid chemistry. N. R. Dhar (J. Indian Chem. Soc., 1927, **4**, 173—181).—The adsorption of ions by sols of mercuric and antimony sulphides, aluminium and ferric hydroxides, and vanadium and manganese oxides shows that the greater the valency of the ion the less is the amount of adsorption. No experimental support is found for the view that ions of greater valency have greater coagulating power. Although sols are capable of adsorbing ions carrying the same charge as the sol, the adsorption is greatest when there is chemical affinity between the ion and the sol. Sols of ferric hydroxide, silver and lead chromates, but not sols of manganese oxide, antimony and cadmium sulphides, are adsorbed readily by their respective solids. The theory of Liesegang rings (A., 1925, ii, 959) based on the last observations is extended. G. A. C. Gough.

Physical chemistry of colour lake formation. I. General principles. [Adsorption of anions and hydrogen-ion concentration.] H. B. Weiser and E. E. Porter (J. Physical Chem., 1927, **31**, 1383—1399).—As a preliminary to the study of colour lake formation, the adsorption of sulphate and oxalate ions, both separately and together, by the hydrated oxides of iron, aluminium, and chromium at various hydrogen-ion concentrations has been investigated. Preparation of the oxides in sol form by a special method gave products of much greater purity than the precipitated gels usually employed in adsorption experiments with dyes. The p_H values were measured by means of the hydrogen electrode. An increase in concentration of the hydrogen ion increases the positive charge on the sol particles, thus enhancing their adsorption capacity for anions. The adsorption of the latter diminishes rapidly on the

alkaline side of the neutral point, becoming zero at p_H 9·2. Further, the Γ-adsorption curves show no evidence of the formation of a compound between the ion adsorbed and the hydrous oxide. In the simultaneous adsorption of sulphate and oxalate by hydrous chromic oxide sol, the sulphate is adsorbed more strongly than the oxalate in the alkaline and neutral ranges, but from a basic solution no measurable amount of the former is adsorbed in presence of excess of the oxalate. From a neutral solution, however, the adsorptions are equal when the ratio of sulphate to oxalate concentrations is 128 : 1. In an acid solution this ratio approximates to 1·1—1 at 2·5. The sum of the simultaneous adsorptions of sulphate and oxalate approaches a mean between the separate adsorptions at the same p_H value, which disagrees with the finding of Mehrotra and Sen (this vol., 408) that the sum of the adsorptions of two ions from a mixture is always greater than the adsorption of either when present alone in the solution. The relationship between hydrogen-ion concentration and the precipitation concentrations of sulphate and oxalate has also been investigated, and the conclusion of Miller (A., 1925, ii, 192), that the taking up of anions by hydrous oxides is a solid solution phenomenon, is disputed. Finally, it is pointed out that since both hydrogen and hydroxyl ions are strongly adsorbed by the hydrous oxides, precipitation or adsorption data should be obtained at the same hydrogen-ion concentration if conclusions of any value are to be deduced. L. S. THEOBALD.

Experimental test of Gibbs' adsorption theorem. Study of the structure of the surface of ordinary solutions. J. W. MCBAIN and G. P. DAVIES (J. Amer. Chem. Soc., 1927, 49, 2230—2254).—The experiments of Donnan and Barker (Proc. Roy. Soc., 1911, A, 85, 557) are criticised adversely and a simple quantitative method of determining the absolute adsorption of substances at gas–liquid interfaces, giving results only a few per cent. too large, is described. Results are recorded for the adsorption of *p*-toluidine in the nitrogen–water interface and of camphor and *iso*amyl alcohol in the air–water interface. The adsorption is constant over a fairly wide range of concentration. In every case the amount adsorbed greatly exceeds that required for a unimolecular film, so that the surface of these solutions must consist of such a film resting on a comparatively thick layer of concentrated solution, which is decreasing to the bulk concentration with increasing depth. This thick layer probably consists of chains of oriented, contiguous molecules extending downwards into the solution. The higher the bulk concentration the less is the disparity between it and the unimolecular film at the surface and the less is the interfacial tension. Thus the surface tension of a solution attains a definite value as saturation is approached. The actual adsorption for such solutions is the same as for more dilute solutions, whereas the "simplified" Gibbs adsorption isotherm predicts zero adsorption ($d\sigma/dc=0$). On the whole, this equation represents the observed results only to a first approximation; it requires that only two components are present everywhere in the system, a condition never realised in practice. The fundamental equation of Gibbs provides for more than two components: $(d\sigma)_T=-\Gamma_1 d\mu_1-\Gamma_2 d\mu_2-\ldots$ it is shown, however, that other, electrical, terms should be included in this equation. S. K. TWEEDY.

Displacement of the chemical equilibrium at an interface. I. M. KOLTHOFF (Kolloid-Z., 1927, 43, 51; this vol., 732).—The results obtained by Deutsch have been confirmed, but the phenomena observed are believed to be due to a preferential adsorption of the indicator acid or base at the water–benzene interface. Deutsch's explanation is criticised. L. L. BIRCUMSHAW.

Displacement of the chemical equilibrium at an interface. D. DEUTSCH (Kolloid-Z., 1927, 43, 52).—A reply to Kolthoff (cf. preceding abstract). Kolthoff's explanation is considered to be identical with the author's. L. L. BIRCUMSHAW.

Solubility and surface tension. J. TRAUBE, I. SCHÖNING, and L. J. WEBER (Ber., 1927, 60, [*B*], 1808—1814).—Measurements are recorded of the solubility of aniline, paracetaldehyde, amylene, and ethyl acetate in sodium salicylate solution, of *iso*amyl, *iso*butyl, and octyl alcohols, ethyl acetate, aniline, paracetaldehyde, heptoic acid, amyl acetate, and nitrobenzene in sodium benzoate solution, of chloroform in sodium acetate, of *iso*amyl alcohol in sodium benzenesulphonate, hippurate, naphthionate, *p*-hydroxybenzoate, butyrate, tartrate, succinate, citrate, and acetate, of aniline and ethyl acetate in sodium butyrate, and of *iso*amyl alcohol and paracetaldehyde in aniline hydrochloride solution. In general, greater increase of the solubility of the non-electrolyte is observed as the diminution of the surface tension of water by the salt employed increases. Examination of the systems sodium cinnamate–water–*iso*amyl alcohol and sodium cinnamate–water–*iso*butyl alcohol shows that in each case the effect of the alcohol and salt in causing increases in solubility is reciprocal. H. WREN.

Films responsible for oxidation tints on metals. U. R. EVANS (Nature, 1927, 120, 584).—The separated lead oxide film is transparent, and shows interference colours. Iron oxide films are less transparent; that which gives the first-order yellow tint is perceptibly yellowish-grey. The oxide films also reproduce all the surface irregularities of the metal. The difference in the colours of the separated film and of the film on the metal is considered. A. A. ELDRIDGE.

Collodion membranes. II. Relation between membrane structure and permeability to water. N. BJERRUM and E. MANEGOLD (Kolloid-Z., 1927, 43, 5—14).—It has been found that a given membrane is characterised by the membrane thickness, *d*, the water content per c.c. of membrane, *W*, and the permeability to water in c.c. for 1 sq. cm. of membrane surface in 1 sec. under a pressure of 1 cm. of water, *D*. By the use of these three quantities, formulæ are derived from which the pore radius or fissure width can be calculated for hypothetical membrane structures in which (*a*) the pores or fissures all run perpendicular to the membrane surface; (*b*) the pores or fissures are distributed uniformly among three

directions perpendicular to one another, and run parallel or perpendicular to the surface; and (*c*) the pores or fissures are distributed irregularly throughout the membrane. The derived equations contain, besides a constant, only the quotient dD/W, and are used to calculate the dimensions of the capillaries in collodion membranes from the experimental values of d, D, and W. In the membranes investigated, the calculated pore radius varies from 1 to 90 $\mu\mu$, the number of pores from 2×10^9 to 1×10^{12} per sq. cm., the fissure width from 0·8 to 80 $\mu\mu$, and the fissure length from 1×10^5 to 32×10^5 cm. per sq. cm. Possible explanations, based on the contraction of the membrane with increased drying, are suggested for the fact that the number of capillaries per sq. cm. increases rapidly with decreasing water content. L. L. Bircumshaw.

Density of solutions of sodium in liquid ammonia. C. A. Kraus, E. S. Carney, and W. C. Johnson (J. Amer. Chem. Soc., 1927, 49, 2206—2213).—Measurements at −33·8° for concentrations ranging from 32·6 mols. of ammonia per atom of sodium up to saturation (5·48 mols. of ammonia per atom of sodium) show that the solutions have a density lower than that of either constituent. The volume change per atom of sodium is 40·96 c.c. at saturation; this value passes through a maximum with progressive dilution and then diminishes to a limiting value somewhat less than 40 c.c. The large volume change is attributed to the relatively large volume occupied by the free electrons known to exist in these solutions. S. K. Tweedy.

Refractometric evidence for the existence of undissociated molecules and complex ions in solutions of strong electrolytes. K. Fajans (Trans. Faraday Soc., 1927, 23, 357—375).—From a study of the refractivity of salts in solution and in crystal form, it may be shown that, when ions in solution at infinite dilution unite to form crystals, marked deviations from additivity take place, indicating mutual influences between the ions or between the ions and the solvent. Considering the anions, the refractivity of which is lowered by neighbouring cations, if ΔR is the diminution in the refractivity of a given anion in the alkali halide lattice, r the distance between oppositely-charged ions, and k_A a constant, then $\Delta R\times r^4=k_A$. For the iodine, bromine, and chlorine ions the constant k is approximately proportional to the square of the respective refractivities. From the available data it may be shown that the refractivities of salts and hydrogen chloride undergo, with increasing concentration, changes analogous to those which accompany the association of ions into crystals or molecules. These changes are attributable to the polarising action of the ions on each other, and from their magnitude they must be attributed to oppositely charged ions in direct contact with each other, *i.e.*, undissociated molecules. It follows from the refractivity data that in solution the least distance possible between chlorine and sodium ions is greater than between chlorine and lithium. Since, therefore, the characteristic parameter introduced into the formulæ of Debye and Huckel has a greater value for lithium than for sodium, this parameter does not indicate the distance of nearest approach of the ions as required by the theory. From a comparison of the partial vapour pressures of hydrogen chloride and hydrogen cyanide over their aqueous solutions, it is concluded that, up to concentrations of about 5 g.-mol. of hydrogen chloride per 1000 g. of water, the decrease in refractivity with increasing concentration is due only to a very slight extent to the formation of undissociated hydrogen chloride, possibly being caused by the complex ion H_2Cl^+. At still higher concentrations undissociated hydrogen chloride appears to be formed in increasing quantities. M. S. Burr.

Optical properties of coloured substances which exhibit colour changes in concentrated solutions of neutral salts. F. Vles (Compt. rend., 1927, 185, 644—647).—The observations relate to substances which are not necessarily p_H or r_n indicators, but change colour or are precipitated in the presence of concentrated solutions of neutral salts. The absorption ratio (ϕ) for the two extreme spectral forms has been measured for solutions of sulphonecyanine-5*R* in potassium chloride solutions of various strengths (3·5—0·000001*N*) in which the concentration of the dye was $3\cdot5\times10^{-5}$. Curves in which ϕ is plotted against the logarithm of the salt concentration show clearly the gradual change in colour from rose (saturated to *N*-solutions) to violet. The observations suggest the existence of a potassium salt of the dye, or of some complex substance. J. Grant.

Nature of solutions of cobalt halides. A. Hantzsch (Z. anorg. Chem., 1927, 166, 237—243).—Groh's theory (this vol., 728) that the blue colour of cobalt chloride solutions is due to $CoCl_4''$ ions is in conflict with some of the experimental facts. Thus although above 28° solutions of cobalt chloride in pyridine are blue, conductivity measurements show that even at 85° very few ions are present. The colour change is, however, readily explained by supposing that the red pseudo-salt $Co(C_5H_5N)_4Cl_2$ passes into the blue pseudo-salt $Co(C_5H_5N)_2Cl_2$ on heating (cf. this vol., 327). Even in solutions of cobalt chloride in acetone or ethyl alcohol, where Groh's data show that some blue true salt is present, it seems probable that it is in equilibrium with a much larger amount of the blue pseudo-salt. It is suggested that the violet dihydrate of cobalt chloride passes in solutions into a blue form, which is unstable in the solid state. This would answer Benrath's objection to the theory that the blue colour produced by the addition of certain chlorides to pink solutions of cobalt chloride is due to the formation of lower hydrates (this vol., 829). R. Cuthill.

Stability of suspensions of coarsely-dispersed particles in solutions. II. Determination of colloids with the aid of the rate of clarification. H. Werner (Ber., 1927, 60, [*B*], 1920—1933; cf. this vol., 620).—Starch in concentration of less than 0·0005% and other colloids may be determined by the addition of a suspension of *Bolus alba* in 5*M*-sodium chloride solution and observation of the rate of sedimentation under standard conditions. H. Wren.

Lability in ferric oxide hydrosols. C. H. Sorum (Science, 1927, 65, 498—499).—A ferric oxide sol prepared by hydrolysis of ferric chloride at 100°, and containing 3·5788 g. of iron per litre, was partly coagulated by shaking, stirring, or addition of mechanically coagulated ferric oxide. After removal of the coagulum, the supernatant sol, which contained 3·2 g. of iron per litre, was completely stable towards agitation and inoculation. Dilution decreased the coagulation until a limiting concentration was reached below which coagulation did not occur.

A. A. Eldridge.

"Photo-sols." I. S. S. Bhatnagar, N. A. Yajnik, and V. D. Zadoo (J. Indian Chem. Soc., 1927, 4, 209—219).—The reactions of gold and silver sols with arsenic and antimony trisulphide sols are shown to be photo-sensitive and therefore similar to the reaction between silver and sulphur sols (Freundlich and Nathansohn, A., 1921, ii, 536). Excepting cases when silver sol and arsenic or antimony trisulphide sols are mixed in certain proportions, no changes are observed when the mixtures are kept in the dark. Rapid colour change is produced by exposure to sunlight, and the product is found to consist of metallic sulphides, free sulphur, and arsenious or antimonious acids. G. A. C. Gough.

Stability of suspensions. II. Rate of sedimentation of kaolin suspensions containing colloidal silicic acid. W. O. Kermack and W. T. H. Williamson (Proc. Roy. Soc. Edin., 1927, 47, 202—221; cf. A., 1925, ii, 523; B., 1925, 464).—The rates of sedimentation of kaolin suspensions have been examined in presence of salts of the alkali metals. In acid suspensions, the inhibiting action is least in the case of cæsium and greatest in the case of sodium. The influence of small quantities of colloidal silicic acid has also been examined at various hydrogen-ion concentrations and in presence of univalent, bivalent, and tervalent cations. Small quantities of silicic acid appear normally to have a protective action, but under certain conditions produce precipitation of a film of insoluble material over the surface of the particles. An abnormally rapid rate of sedimentation of the particles is then observed, as, for example, in presence of certain salts of the alkali metals or of calcium at $p_H > 7·5$. In presence of calcium phosphate between p_H 4·5 and 9·2 the effect of silicic acid is to prevent formation of a precipitate, and in this case the abnormal sedimentation occurring in the absence of silicic acid tends to disappear.

W. O. Kermack.

Rigidity and other anomalies in colloidal solutions. E. Hatschek (Proc. Roy. Inst., 1927, 25, 245—259).

Protected silver hydrosols. V. Reduction of silver nitrate solution by irradiation with ultra-violet light in the presence of protective colloids. J. Voigt (Kolloid-Z., 1927, 43, 30—35).—Gum arabic has no reducing action on pure silver nitrate solution in absence of light or in diffused daylight, but illumination by ultra-violet light leads to the formation of a silver hydrosol. The greater the concentration of gum arabic the more finely divided is the sol, and sols obtained by illuminating solutions in quartz tubes are less homogeneous than those obtained by illumination in tubes of Jena glass. No sol-formation occurs on exposing pure silver nitrate solution to ultra-violet light unless a protective colloid is present. A series of experiments was made using a protein degradation product as the protective colloid, and the results are compared with those obtained with gum arabic.

L. L. Bircumshaw.

Colloidal mixed solutions of calcium carbonate and calcium phosphate. G. Stella (Kolloid-Z., 1927, 43, 21—26; cf. A., 1926, 1204).—Colloidal mixtures of calcium carbonate and calcium phosphate have been prepared by mixing sodium carbonate, sodium phosphate, and calcium chloride solutions in aqueous gelatin solution at 95°. The ratio of the two salts in the mixture can vary within wide limits, and the highest concentration which either salt can reach depends both on the gelatin concentration and on that of the second calcium salt. The calcium carbonate may not exceed a maximum concentration of 0·005—0·006*M* above half the calcium phosphate concentration. The phosphate may reach a concentration two or three times as great as that which it could possess alone at the same gelatin concentration. The mixed precipitates of the two salts form a gel in water (provided that the carbonate does not exceed half the phosphate), which is readily peptised by gelatin at 80—90°. The excess of calcium carbonate separates slowly from the colloidal solution in a crystalline state, without causing any change in the appearance or stability of the solution. The results support the hypothesis that a complex salt, or a homochemical compound (in von Weimarn's sense), is formed, in which two calcium atoms of the phosphate are bound with one of the carbonate. Peptisation experiments show that the mixed precipitate is more readily peptised, and offers a greater resistance to the modifying action of temperature, than the phosphate alone.

L. L. Bircumshaw.

Investigation of colloidal systems. N. N. Andreev (Kolloid-Z., 1927, 43, 14—17).—A modification of the method used by Lottermoser (*ibid.*, 1914, 15, 145). The scattering of the light which passes through a colloidal solution is measured by means of a potassium photo-element. From observations with colloidal solutions of colophony, suspensions of barium carbonate, and emulsions of *Staphylococcus albus*, it is found that the galvanometer deflexions become relatively smaller with increasing concentration, due to the fact that the light scattered from the lower particles is intercepted by the upper particles. The method has been used to investigate the formation of colloidal sulphur solution and the coagulation of mastic with barium chloride solution. It has the advantage over tyndallometric measurements in that it gives absolute values. Some applications of the method are discussed.

L. L. Bircumshaw.

Theory of peptisation of metallic hydroxides in presence of non-electrolytes. K. C. Sen (Kolloid-Z., 1927, 43, 17—21).—Experiments on the peptisation of cerium, iron, and chromium hydroxides in presence of non-electrolytes (sucrose and glycerol)

show that if an exactly equivalent quantity of alkali is added to the solution, precipitation occurs even in the presence of the protective non-electrolyte. A minimum excess of hydrogen or hydroxyl ions is necessary for peptisation. It is inferred that the protective action of the so-called protective colloids and non-electrolytes is dependent on the presence of easily adsorbable ions in the solution. The protective action of the non-electrolyte appears to be subordinate to that of the ions. It probably acts only on the surface of the colloid particles, diminishing the surface energy, increasing the hydration, and preventing the growth of the particles.

L. L. Bircumshaw.

Peptisation of metallic hydroxides in the presence of sugars. M. R. Mehrotra and K. C. Sen (J. Indian Chem. Soc., 1927, 4, 117—129; cf. A., 1923, ii, 834).—The minimum amount of dextrose or of lævulose necessary to prevent the precipitation of metallic hydroxides when sodium hydroxide (3 mols.) is added to a solution of the metallic chloride and the sugar, is found to increase in the order Cu, Fe, Hg, Ce in both cases. Sucrose and lactose give the orders Cu, Ce, Fe, Hg, and Cu, Fe, Ce, Hg, respectively. At low concentrations there is a direct proportion between the amount of metallic hydroxide peptised and the sugar required, but at higher concentrations a greater proportion of sugar is needed. This, together with the fact that peptisation is a specific effect, indicates that the formation of metallic sucrates is improbable. In the case of mercuric chloride, the effect of a larger excess of alkali is to increase the sugar required, whereas cupric chloride, under the same conditions, requires less sugar. Whilst the peptisation of cupric and ferric hydroxides requires considerable time, the keeping of peptised mercuric hydroxide causes precipitation. G. A. C. Gough.

Peptisation of iron and chromium hydroxides in presence of non-electrolytes and influence of acid and alkali on the peptisation. K. C. Sen (J. Indian Chem. Soc., 1927, 4, 131—135).—Experiments in presence of glycerol show that an excess of alkali is necessary to prevent precipitation; this excess can be reduced by the addition of larger amounts of glycerol to a limit beyond which further addition is ineffectual. The specific protecting powers of non-electrolytes (preceding abstract) are apparent only when the minimum amount of alkali necessary for peptisation is present. G. A. C. Gough.

Sensitisation of cholesterol sols. R. Stern (Biochem. Z., 1927, **187**, 315—323).—Further experiments (cf. A., 1926, 576) on the flocculation of cholesterol sols by acetate, lactate, and tartrate buffers in presence of electrodialysed ox serum confirm the author's view that the coagulation point is dependent on the concentrations of cholesterol, protein, and hydrogen ions (cf. Rona and Deutsch, A., 1926, 792). P. W. Clutterbuck.

Aluminium hydroxide gels of Willstatter Kraut, and co-workers. R. Zsigmondy and D. G. R. Bonnell (Ber., 1927, **60**, [*B*], 1916—1918).—Aluminium hydroxide *C*, regarded as a colloid, is composed of very coarse particles; it is gradually dissolved to aluminium chloride by dilute hydrochloric acid, but is not peptised. The hydroxide *A* readily forms true hydrosols and therefore contains very small primary particles which, when combined in large numbers to secondary particles, form the suspension of the preparation *A*. H. Wren.

Phenomena caused by the low refractive indices of the alkali fluoborates. J. H. de Boer (Proc. K. Akad. Wetensch. Amsterdam, 1927, **30**, 350—354).—The apparent precipitation of potassium fluoborate as a jelly when potassium chloride solution is added to hydrofluoboric acid is due to the low refractive index of the salt. Precipitation of the cæsium salt by the same method yields a perfectly transparent solution, which exhibits brilliant colours owing to the difference of the dispersions of the solid and liquid phases. Cæsium fluoborate has n_D between 1·3563 and 1·3502, in agreement with the theory of the deformation of the electron layers in an ion, which requires the refractive index to be greater than 1·33. The refractive indices of potassium and rubidium fluoborates should be still smaller and experimental values for the latter are about 1·33. The sodium and lithium salts have refractive indices below that of water: for 12% solutions n_D^{20} for sodium fluoborate is 1·3321, and for lithium fluoborate 1·3303. For a 20% solution of the free acid n_D is 1·3284. H. F. Gillbe.

Volumetric chemical observations on forces of aggregation. I. Traube (Ber., 1927, **60**, [*B*], 1815—1816).—The theory that complex substances, such as cellulose and the proteins, should be regarded, not as compounds in the sense of the older structural chemistry, but as built up by aggregation from smaller units, is examined from the volumetric chemical point of view. It appears that the forces of aggregation and valency are identical in their mode of action and differ in that the former are not operative from atom to atom, but act solely in causing a greater or less diminution of the co-volume. H. Wren.

Hydration of univalent ions. E. Schreiner and E. B. Schreiner (Z. anorg. Chem., 1927, **166**, 219—224).—The calculations of hydration numbers previously made (A., 1924, ii, 524) have been revised, using for the activity, a, Bjerrum's formula, $\log a = \log X - kC^{1/3}$, where X is the molar fraction, k the activity constant, and C the concentration in g.-mol./1000 g. of water. R. Cuthill.

Electronic theory of valency. V. Molecular structure of strong and weak electrolytes. (a) Complete ionisation. T. M. Lowry (Trans. Faraday Soc., 1927, **23**, 508—515).—Theoretical. In general the ions of a strong electrolyte are prevented from neutralising their opposite electric charges by the operation of factors which find expression in the "octet" rule. Badly-conducting solutions may, however, be obtained by dissolving a salt in a medium with a low dielectric constant, when abnormal variations of conductivity with dilution are generally observed. The small "degree of dissociation" is probably due, not to the neutralisation of the ionic charges with the formation of a chemical "bond," but rather to the formation of neutral ionic doublets. Many fused salts, *e.g.*, silver chloride, are good con-

ductors, giving values for the "coefficient of ionisation" which may be above 100%, possibly as a result of the formation of multiply-charged ionic aggregates. Other fused salts, *e.g.*, dimethylanilino hydrobromide, are poor conductors, probably because the crystal lattice breaks down into neutral ionic doublets on fusion. The term "hydrolysis" has no significance from the point of view of the theory of complete ionisation, unless the hydrogen or hydroxyl ion of water can be fixed by one of the ions of the salt, with formation of a covalent compound. Subsequently water may be eliminated from this.

M. S. BURR.

Valency. VI. Molecular structure of strong and weak electrolytes. (*b*) Reversible ionisation. T. M. LOWRY (Trans. Faraday Soc., Sept. 1927, advance proof; cf. A., 1926, 454).—A review of weak electrolytes from the point of view of recent theoretical developments. It is shown that where partial and reversible ionisation occurs there is, in all the cases considered, a possibility of the formation of a covalent linking between the ions either directly or by means of some molecular rearrangement. Weak electrolytes of this class are found amongst acids and bases, pseudo-electrolytes, co-ordinated salts, substituted methyl halides, and a few simple metallic salts such as mercuric chloride. G. A. ELLIOTT.

Dissociation constants of α- and β-alanine, and the transference velocities of the cations of the two isomerides. A. BORK (Z. physikal. Chem., 1927, 129, 58—68).—Aqueous solutions of β-alanine possess a very small conductivity, the acid and basic dissociation constants being $9{\cdot}7\times10^{-11}$ and $4{\cdot}6\times10^{-11}$, respectively. Comparison of these figures with the corresponding values for α-alanine indicates that weakening of the acidic properties of the β-amino-acids is not accompanied by a decrease of basic properties, although this occurs in the case of the α-amino-acids. The transference velocity of the cation of α-alanine is 25·7, whilst that of the isomeric cation of β-alanine is 37·5. H. F. GILLBE.

Ionisation of polyhydrion acids. C. MORTON (Trans. Faraday Soc., Sept. 1927, advance proof).—The variation of p_H in the neutralisation of tricarballylic, camphoronic, citric, and acetic acids by sodium hydroxide has been determined in 0·01*M*-solution. The observations were made with a new form of apparatus in which the potentiometer is connected in the grid circuit of a valve-amplifier with a galvanometer in the plate circuit. A method of differential titration utilising this device is described by means of which very accurate end-point determinations may be made. The classical mass-action equations for the dissociation of weak electrolytes have been modified by the introduction of activity coefficients derived from the Debye–Hückel theory, and in this way formulæ have been obtained which permit of the calculation of the true dissociation constants of polyhydrion acids for which the various stages of dissociation overlap. The theoretical equations are in accord with previous data for acetic, phthalic, and phosphoric acids, and yield the following values for the dissociation constants of the acids examined: tricarballylic acid, $3{\cdot}25\times10^{-4}$, $2{\cdot}65\times10^{-5}$, and $1{\cdot}48\times10^{-6}$; camphoronic acid, $2{\cdot}95\times10^{-4}$, $1{\cdot}05\times10^{-5}$, and $3{\cdot}7\times10^{-8}$; citric acid, $9{\cdot}11\times10^{-4}$, $2{\cdot}69\times10^{-5}$, and $1{\cdot}35\times10^{-6}$; acetic acid, $1{\cdot}77\times10^{-5}$. These results are in general agreement with the known effects of substitution on the strength of acids. The methods used by Enklaar (Z. physikal. Chem., 1912, 80, 620), and by Auerbach and Smolczyk (A., 1925, ii, 118) in computing the dissociation constants of tribasic acids, are criticised.

G. A. ELLIOTT.

Corrections for determination of ionic concentrations in very dilute hydroxide solutions. E. LAUE (Z. anorg. Chem., 1927, 165, 305—324).—The influence of dissolved carbon dioxide on the conductivity of dilute solutions of hydroxides not in equilibrium with the solid has been calculated by application of the mass law. In agreement with Remy's results (A., 1925, ii, 299), it is found that the conductivity is considerably reduced. With sparingly soluble hydroxides, however, where the solid hydroxide is present in equilibrium with the solution, it is calculated that the observed conductivity is very slightly too high. In this instance, Remy's calculations are defective, and the solubility corrections based on them are therefore inaccurate. The concentration of the hydroxide cation is considerably increased by the carbonic acid, however, and this must be taken into account in methods of measuring the solubility dependent on a determination of the cation. The effect of small concentrations of a second hydroxide on the solubility of the hydroxide under consideration may be computed by the application of simple mass action principles, but in calculating the effect of neutral salts the interionic forces cannot be neglected, and it is necessary to utilise the activity theory. All the corrections calculated in this way for the influence of carbon dioxide and electrolytes on the solubility of silver hydroxide prove to be in excellent agreement with experimental data. R. CUTHILL.

Amphoteric nature of silver hydroxide. E. LAUE (Z. anorg. Chem., 1927, 165, 325—363).—Kossel's theory of the behaviour of the hydroxides of the metals of the second short series of the periodic system (A., 1916, ii, 243) has been extended to the whole system. From these considerations, it appears probable that silver hydroxide is feebly amphoteric. The mean value of the solubility in water at 25° determined by the conductivity, equilibrium, and usual analytical methods and corrected for the influence of carbon dioxide dissolved in the water (cf. preceding abstract) is $1{\cdot}36\times10^{-4}$ g.-equiv./litre. By conductivity measurements, the solubility at 18° is found to be $1{\cdot}14\times10^{-4}$ and at 20° $1{\cdot}20\times10^{-4}$ g.-equiv./litre. The fact that these values are in general lower than those found in the literature is to be ascribed to the considerable correction for the concentration of the cation necessitated by the dissolved carbon dioxide. From measurements of the solubility of the hydroxide in sodium hydroxide, the activity product is calculated to be $1{\cdot}85\times10^{-8}$. In the more concentrated solutions, the solubility is greater than in pure water, which is due to the hydroxide functioning as an acid, the activity product

of this argentic acid being 2×10^{-18}. The solubility both in solutions of sodium hydroxide and in solutions of potassium nitrate is in good agreement with the requirements of Bjerrum's theory. R. CUTHILL.

Physical significance of the second fundamental law of thermodynamics. J. E. VERSCHAFFELT (Bull. Acad. roy. Belg., 1927, [v], **13**, 180—184).—If Q_t and Q_0 are the thermal effects at temperatures t and 0, respectively, associated with an isothermal, reversible transformation between the same adiabatics, then $Q_t/Q_0=f(t)$, where $f(t)$ is a universal function. The thermodynamic scale of temperature is not *a priori* an absolute scale. J. S. CARTER.

Computation of the free energy and fugacity in gaseous mixtures of ethylene and argon. G. E. GIBSON and B. SOSNICK (J. Amer. Chem. Soc., 1927, **49**, 2172—2179).—The fugacities are calculated from the experimental results of Masson and Dolley (A., 1923, ii, 462). Lewis and Randall's fugacity rule ("Thermodynamics," p. 197) holds fairly well at low pressures, but at 50 atm. the deviation may attain 20%, and at 100 atm., 100%. S. K. TWEEDY.

Allotropy and internal equilibrium. A. SMITS (Z. physikal. Chem., 1927, **129**, 33—57).—A discussion of intensively-dried substances from the point of view of allotropy, together with new data on the vapour pressure of intensively-dried hexane, carbon disulphide, ethyl bromide, bromine, and nitrogen peroxide. H. F. GILLBE.

Agreement with experiment of the dilution formula deduced from the Debye–Huckel theory. A. FERGUSON and I. VOGEL (Trans. Faraday Soc., 1927, **23**, 404—408).—The value of n in the dilution equation of the general form $\Lambda=\Lambda_0-BC^n$ has been deduced graphically for a large number of electrolytes, from published conductivity data. It is found that n varies in a perfectly regular manner between 0·38 and 0·6, or possibly 1·0, for electrolytes in a related group, and cannot be equal to 0·5 as required by the Debye–Huckel theory. So far as can be seen from the data available, B varies irregularly with temperature, whilst n decreases with rise of temperature, except for potassium bromide and sodium acetate. M. S. BURR.

Activity of electrolytes. J. N. BRONSTED (Trans. Faraday Soc., 1927, **23**, 416—432).—A discussion of the activity of electrolytes, taking into consideration the following points: the thermodynamic laws of salt solutions, the principle of the specific interaction of ions as an explanation of the individual behaviour of salts, the theoretical calculation of activity coefficients, especially with reference to the Debye–Hückel theory, the application of the activity conception to the behaviour of weak electrolytes in the presence of strong electrolytes, or when the weak electrolytes themselves are ions, and, finally, the problems of concentrated solutions and of non-aqueous solutions. M. S. BURR.

Significance of the activity coefficient. M. RANDALL (Trans. Faraday Soc., 1927, **23**, 498—502).—A comparison between the thermodynamic and mechanistic treatments of the theory of solutions. If the composition of the solution be expressed in terms of the mol. wt. of arbitrarily chosen molecular species, then the activity coefficient gives a simple numerical statement of the deviation of this solution from the law of perfect solution. The laws based on the various mechanistic hypotheses all tend to approach the law of perfect solution as a limit. The activity concept makes it possible to bring the various colligative properties of a solution into agreement, and thus is a test of the adequacy of any mechanism which may be proposed. M. S. BURR.

Calculation of activity coefficients. M. RANDALL (Trans. Faraday Soc., 1927, **23**, 502—507).—The methods in use for calculating the activity coefficient of the solute from that of the solvent are mentioned, and it is shown how the same curve is applicable to all the different methods. The results thus obtained may be correlated with directly-measured values of the activity of the solute, so that the curves obtained by plotting log γ plus a constant against the square root of the ionic strength may be superimposed and the best average values selected. A method is suggested for interpolating the activity coefficients of strong electrolytes by plotting log $\gamma/\mu^{\frac{1}{2}}$ against $\mu^{\frac{1}{2}}$, where γ is the activity coefficient and μ the ionic strength. The graph thus obtained is approximately a straight line. M. S. BURR.

Use of amalgam electrodes for determining activities in methyl alcohol. J. H. WOLFENDEN, C. P. WRIGHT, N. L. R. KANE, and P. S. BUCKLEY (Trans. Faraday Soc., 1927, **23**, 491—498).—Attempts have been made to determine the *E.M.F.* of the cell $NaHg_x|NaCl$ in MeOH|AgCl,Ag for dilute solutions below 0·16*M*. A streaming amalgam electrode was used, but the *E.M.F.* was found to depend on the rate of flow of the amalgam, apparently without limit and irrespective of the concentration of the solution. It was also found that, at concentrations of about 0·005*M* and lower, an unknown factor intervenes to make the *E.M.F.* 20—40 millivolts lower than corresponds with the ionic activity calculated from Debye and Hückel's equation. Measurements have also been made for three pairs of solutions with the liquid junction concentration cell $Ag,AgCl|NaCl(c_1)|NaCl(c_2)|AgCl,Ag$. When these are combined with the values obtained with the cell without liquid junction, it is again seen that the latter cannot be correct, since the values for the transport number thus obtained are not in agreement with the known mobilities of the two ions. M. S. BURR.

Activity of zinc chloride in concentrated solution. F. FOXTON and W. J. SHUTT (Trans. Faraday Soc., 1927, **23**, 480—488).—The solutions studied were, in most cases, so concentrated as to approach the conditions of molten salts. Cells without liquid junction, $Zn|ZnCl_2|Cl_2,Pt$, and cells with liquid junction, $Zn|ZnCl_2(m_1)|ZnCl_2(m_2)|Zn$ and $Pt,Cl_2|ZnCl_2(m_1)|ZnCl_2(m_2)|Cl_2,Pt$, were examined. The temperature coefficient for the first cell, in a 5*M*-zinc chloride solution, is 0·0007128 volt/degree between 60° and 80°. The heat of formation of zinc chloride in 5*M*-solution, deduced from this, is in good agreement with Thomsen's and Berthelot's values. To determine the change in activity coefficient with temperature, it

was assumed that barium and zinc chlorides, at molar concentration, have the same activity coefficient. The curves obtained by plotting activity coefficient against the square root of the concentration show a diminution in the rate of increase at the highest concentrations, *i.e.*, above about $20M$. This may be due to some type of polymerisation. The zinc concentration cells appear to behave normally, but the chlorine cells are abnormal at comparatively low concentrations, since the chlorine electrode in the more concentrated solution is positive with respect to the other. This is ascribed to the formation of complex anions in concentrated solution.

M. S. BURR.

Activity coefficients of protein ions. G. S. ADAIR (Trans. Faraday Soc., 1927, 23, 536—537).—A comparison is made between the activity coefficients of the hæmoglobin ion in solution at the isoelectric point p_H 6·8, when the valency is zero, and in solutions of p_H 7·8, when the ion has a negative valency of 8·5. In both cases the activity coefficient increases with increasing concentration, contrary to the requirements of the Debye–Hückel formula, but the first coefficient increases more rapidly than the second.

M. S. BURR.

Activity of hydrogen ion in mixed solvents. H. MILLET (Trans. Faraday Soc., 1927, 23, 515—522).—Hydrogen-ion activities in ethyl alcohol–water mixtures containing 0·5N-HCl at 25° and 30°, alone and in the presence of sucrose, have been determined by *E.M.F.* measurements, using the ordinary hydrogen electrode. The values obtained pass through a minimum in a mixture containing 30% g.-mol. of alcohol, approaching a composition corresponding with $EtOH,3H_2O$. The hydrogen-ion activity coefficients α for hydrochloric acid in alcohol–water mixtures are connected with the values of the corresponding equivalent conductivities λ_v, and the dielectric constants D of the media, by the relationship $k=\alpha D^2/\lambda_v$, where k is a constant, but the formula has only a limited application. The hydrogen-ion activity of picric acid in alcohol, measured by the quinhydrone electrode, is found to diminish rapidly on the addition of small amounts of water. There is also a corresponding fall in hydrogen-ion mobilities. Calculated values of the hydrogen-ion activities, made on the assumption that hydration of the hydrogen has taken place, agree with the observed values.

M. S. BURR.

Some anomalies in the theory of solution of strong electrolytes and their explanation. N. BJERRUM (Trans. Faraday Soc., 1927, 23, 445—454).—Certain phenomena in dilute solutions of electrolytes do not at first sight appear to be explicable by the Debye–Hückel theory, viz., the variation in the heats of dilution of solutions of strong electrolytes, the values for the partition coefficients of ions between different solvents, the small Soret effect of many electrolytes, the amount of contraction on dissolution of a salt in water, and the negative heat capacity of ions in aqueous solution. All these, however, may be explained quantitatively on the assumption that the effective dielectric constant of the solution decreases in the immediate neighbourhood of the ions.

M. S. BURR.

Mixed solutions of electrolytes and non-electrolytes. G. SCATCHARD (Trans. Faraday Soc., 1927, 23, 454—462).—If the properties of mixed solutions of electrolytes and non-electrolytes are deduced on the assumption that the ions consist of spheres in a continuous medium, they agree more closely than might be expected with the observed properties. The use of the same model may, therefore, be justifiable in the study of other phenomena.

M. S. BURR.

Strong electrolytes in relation to statistical theory, in particular the phase integral of Gibbs. R. H. FOWLER (Trans. Faraday Soc., 1927, 23, 434—443).—Mathematical. The theory of Debye and Hückel is developed from the fundamental principles of statistical mechanics, using the method of Gibbs (cf. Kramers, this vol., 626).

M. S. BURR.

Interionic attraction theory of Debye and Hückel. D. L. CHAPMAN (Trans. Faraday Soc., 1927, 23, 443—445).—The approximation method adopted in the development of the Debye–Hückel equation does not appear to be justified in the case of small ions.

M. S. BURR.

Thermodynamic properties of a few concentrated salt solutions. H. S. HARNED (Trans. Faraday Soc., 1927, 23, 462—470).—By a study of *E.M.F.* data for cells of the type $Ag|AgX|MX(m_2)$, $HX(m_1)|H_2|HX(m_0)|AgX|Ag$ and $H_2|MOH(m_0)$, $MX(m)|M_xHg|MOH(m_0)|H_2$, the thermodynamic properties of strong acids in homoanionic salt solutions are contrasted with those of strong bases in homocationic salt solutions. Methods for determining the ionic activity coefficient product and dissociation of water in salt solutions are described. Consideration is also given to the derivation of individual thermodynamic activities for the ions of some simple electrolytes and for hydrogen and hydroxyl ions in pure aqueous halide solutions, or in acid–halide and hydroxide–halide solutions. For a given concentration of halide solution, the hydrogen-ion activity coefficient is greatest, and that of the hydroxyl ion least, when the electrical field intensity has its highest value. The behaviour of the hydroxyl ion is, therefore, contrary to that expected on the basis of an interionic attraction theory. This is attributed to the highly unsymmetrical structure of the hydroxyl ion and hence its ready deformability in an electric field, accompanied by a lowering of the activity coefficient. The unsymmetrical formate ion acts similarly to the hydroxyl ion (this vol., 206).

M. S. BURR.

Computation of partial molal quantities of binary solutions. B. SOSNICK (J. Amer. Chem. Soc., 1927, 49, 2255—2257).—An equation is derived which enables partial molar quantities to be obtained from directly-measured molal quantities. A correction term is required which is small for nearly perfect solutions.

S. K. TWEEDY.

Relation of temperature to hydrogen-ion concentration of buffer solutions. A. G. OLSEN (Science, 1927, 65, 477—478).—Published measurements demonstrate the importance of proper selection of the buffer solution where the reactions occur at

temperatures other than that at which the acidity is measured. A. A. ELDRIDGE.

Application of the hydrogen electrode to organic bases: piperidine and its use as an alkaline buffer. E. B. R. PRIDEAUX and F. L. GILBERT (J.C.S., 1927, 2164—2168).—The neutralisation of piperidine by hydrochloric acid can be accurately followed by the hydrogen electrode, and the dissociation constant obtained by this method is 1×10^{-3} at 18°. The constant slowly decreases during the neutralisation, but since the addition of sodium chloride has no appreciable influence on the potential, the decrease cannot be attributed to the formation of the salt. The alkalinities of partly neutralised solutions calculated from the constant were checked by colorimetric titration, and found to agree. It follows that such solutions can be used as alkaline buffers. F. S. HAWKINS.

Buffer action. VI. Phase buffers. K. KLINKE (Helv. Chim. Acta, 1927, **10**, 627—642).—The systems considered are distinguished by the presence of weak acids and by the limited solubility of at least one of the substances concerned. Equations representing the change in the hydrogen-ion concentration on the addition of a completely dissociated acid to solutions of salts of sparingly soluble buffer acids and suspensions of sparingly soluble salts of soluble and sparingly soluble buffer acids are derived. Where possible illustrative titration curves are given. J. S. CARTER.

Mechanism of titrations with adsorbed indicators. J. W. HODAKOV (Z. physikal. Chem., 1927, **129**, 128).—The work of Fajans and Wolff (A., 1924, ii, 776) and of Hassel (A., 1924, ii, 738) renders the final conclusion of the author's previous communication invalid (this vol., 743). H. F. GILLBE.

Titration potential curves for precipitation reactions. E. LANGE and E. SCHWARTZ (Z. physikal. Chem., 1927, **129**, 111—127).—The maximum potential change during a titration in which a sparingly soluble uni-univalent precipitate is formed is given by $\Delta E=RT/nF\times p/2v\sqrt{L}$, where $\sqrt{L}$ is the solubility of the precipitate, v the volume of the solution titrated, and p the volume of each successive small quantity of solution added. The greatest slope of the potential curve is at a distance $P-\sqrt{2}\times v\sqrt{L}$ from the end-point, P being the total volume of solution added; the accuracy of determination of the end-point can thus be calculated. The influence of neutral salts on the sharpness of the end-point is in accord with the Debye–Hückel theory. Flattening of the potential curve due to the adsorption of ions is discussed, together with the influence of temperature on the potential in the neighbourhood of the end-point. H. F. GILLBE.

Critical state. I. Critical state of water and of aqueous solutions. E. SCHROER (Z. physikal. Chem., 1927, **129**, 79—110).—The most probable value of the critical temperature of water, determined from the temperature–density diagram, is 374·20°± 0·20°. The densities of the liquid and vapour phases do not become identical until the temperature is about 0·5° above the critical temperature. Solutions of the alkali halides exhibit no linear relation between the concentration and elevation of the critical temperature; neither are the elevations produced by different salts at the same equivalent concentrations equal. Experiments with coloured salts prove that at the critical temperature very little salt enters the vapour phase unless the contents of the vessel be stirred, in which case the vapour becomes saturated with salt; the temperature at which the meniscus disappears, however, remains unaltered. H. F. GILLBE.

Ebullioscopic paradox. A. BERTHOUD, E. BRINER, and A. SCHIDLOF (Helv. Chim. Acta, 1927, **10**, 585—588).—The fact utilised in the Landsberger process of mol. wt. determination that vapour of solvent at its b. p. is able to raise a solution to a higher temperature is not at first sight in accordance with the second law of thermodynamics and the suggestion that the necessary heat is supplied by the latent heat given out on condensation is incomplete. Assuming that the external compensating work permitting the heat transfer is the osmotic work caused by the dilution of the solution by the condensed solvent, the authors re-obtain the classical equation of van 't Hoff for the elevation of the b. p.

On passing water vapour at 100° into a concentrated solution of ammonium nitrate contained in a Dewar flask the temperature of the solution is rapidly raised and a b. p. of the order of 120° attained. J. S. CARTER.

Occurrence of points of inflexion in the concentration–vapour pressure curves of aqueous solutions of certain electrolytes. A. J. ALLMAND (Trans. Faraday Soc., 1927, 23, 477—480).—The concentrations at which the curves connecting lowering of vapour pressure with concentration, for solutions of sodium, potassium, and lithium chlorides, show minima, and the vapour pressure–concentration curves show points of inflexion, have been calculated by Harned's equation (A., 1920, ii, 664). The values are not in agreement with those found experimentally by various investigators. M. S. BURR.

Intermetallic compounds. VI. Reaction between solid magnesium and liquid tin. W. HUME-ROTHERY (J. Inst. Metals, Sept., 1927, advance copy, 5 pp.; cf. A., 1926, 356).—The reaction between solid magnesium and liquid tin has been investigated between 250° and 350° in order to see whether reactions of the type primary solid X+liquid⟶secondary solid Y can proceed when the solid phases concerned do not form solid solutions. According to the equilibrium diagram, when a rod of magnesium is suspended in a limited amount of molten tin, the magnesium should dissolve until the liquid has the equilibrium composition, after which a slow reaction of the type solid magnesium+liquid ⟶ magnesium stannide (Mg_2Sn or Mg_4Sn_2) should take place. Actually when sufficient magnesium has dissolved to give the equilibrium composition, all further direct action is stopped by a thin film of magnesium stannide which shows no thickening even after 3 weeks at the above temperatures. A few large crystals of magnesium stannide are, however, sometimes formed by a slow reaction, which is probably analogous to crystal

growth due to surface energy effects, since the thin surface film has a high surface energy and so tends to form a more compact mass, but since dissolution at any point exposes more magnesium to the liquid, the action proceeds slowly in spite of the absence of solid solutions. W. HUME-ROTHERY.

Method of measuring variations of electrical resistance for the determination of the thermal equilibrium diagram of an intermetallic system. F. H. JEFFERY (Trans. Faraday Soc., 1927, **23**, 563—570).—Two continuous methods are described for measuring the change of electrical resistance of alloys with change in temperature, as determined by a chromel–alumel couple. The first is a null method, using Callendar records, and the second involves a "back *E.M.F.*" method of measuring temperature and the measurement of variations of resistance by means of the current through an Ayrton–Mather galvanometer. The accuracy of the second method has been tested by application to copper–tin alloys containing from 40 to 98 atoms per cent. of tin. The results are in almost complete agreement with those of Heycock and Neville, but deviate from those of Isihara (J. Inst. Metals, 1924, **1**, 315) and of Haughton (*ibid.*, 321). The higher transition point of tin, as determined by this method, is 162°. This electrical resistance method, with slow cooling, is very sensitive to the formation of a new phase, but for accurate work there is an upper limit to the rate of cooling. This, however, is not necessarily the same for every alloy. Preliminary experiments to fix the solidus, when solid solutions are formed, gave results in agreement with those of micrographic analysis.
M. S. BURR.

System aluminium–thorium. A. LEBER (Z. anorg. Chem., 1927, **166**, 16—26).—The equilibrium diagram for concentrations up to 56% of thorium has been obtained. In addition to the compound Al_3Th (Honigschmid, A., 1906, ii, 173) it would seem that a compound richer in thorium is formed, or that mixed crystals separate from the more concentrated solutions.
R. CUTHILL.

System phenol–water. E. R. JONES (J. Physical Chem., 1927, **31**, 1316—1321).—The system phenol–water at temperatures below 13° has been studied, and the phase diagram established. Two eutectic points, phenol hydrate, solution, ice, and solid phenol, solution, and ice, respectively, have been observed at respective temperatures and concentrations of −0·843° and 4·607 g. phenol/100 g. solution, and −1·174° and 6·839 g. phenol/100 g. solution. An unstable invariant point (ice and two liquid phases) has also been observed at −1·252°. Solubility measurements are given, and the f. p. of pure phenol is found to be 40·71°. L. S. THEOBALD.

Gold–palladium–nickel alloys. W. FRAENKEL and A. STERN (Z. anorg. Chem., 1927, **166**, 161—169; cf. A., 1926, 344).—The solidus curve for alloys of gold and nickel cannot be determined from cooling curves in the usual way, since with the normal rate of cooling the mixed crystals do not reach equilibrium with the liquid. It was therefore necessary to trace the curve by observation of the heating curves of alloys rendered homogeneous by annealing, and in the course of these experiments the existence of a miscibility gap in the solid state was revealed. The solidus and liquidus curves for the system palladium–nickel pass through a minimum at a point corresponding with 60% of palladium, and here also there is a miscibility gap in the solid state. Determination of the freezing surface for the system gold–palladium–nickel shows that the minima exhibited by the binary systems gold–nickel and nickel–palladium become one in the ternary system. R. CUTHILL.

Systems sodium chloride–lead chloride–water and lithium chloride–lead chloride–water. G. E. R. DEACON (J.C.S., 1927, 2063—2065).—The equilibrium relations at 25° afford no evidence of double compounds. F. S. HAWKINS.

Electrometric study of the system potassium chloride–lead chloride–water at 25°. A. J. ALLMAND and L. J. BURRAGE (Trans. Faraday Soc., 1927, 23, 470—477).—In the above system a detailed study has been made of the activity of the lead chloride by measurements on the cell Pb(amalgamated)|solution, AgCl(solid)|Ag. If N_1, N_2, and N_3 are the molar fractions of lead chloride, potassium chloride, and water, respectively, then continuous addition of potassium chloride to a solution of constant N_1/N_2 ratio causes first an increase in the activity of lead chloride and then a decrease. By making certain assumptions, based on the published data for the vapour pressure of potassium chloride solutions, it is shown that the addition of lead chloride to a solution of constant N_2/N_3 ratio causes a decrease of the activity of potassium chloride if N_2/N_3 is small. This becomes less pronounced, and is finally converted into an increase, as N_2/N_3 becomes larger, but the increase also becomes less marked as saturation with potassium chloride is approached.
M. S. BURR.

Systems boron trioxide–sulphur trioxide–water and boron trioxide–phosphorus pentoxide–water. M. LEVI and L. F. GILBERT (J.C.S., 1927, 2117—2124).—The equilibrium relations at 25° and 45° show the formation of $B_2O_3,SO_3,4H_2O$ and $3B_2O_3,SO_3,3H_2O$; this result is confirmed by direct analysis. Difficulty was experienced owing to the supersaturation and high viscosity of the liquid phase. The data for the second system at 25° indicate that orthoboric acid and boron phosphate (BPO_4) occur as solid phases. Measurements of the viscosity of solutions of orthoboric acid in sulphuric acid are recorded. F. S. HAWKINS.

Equilibrium between two liquid phases. IV. System *o*-toluidine–lactic acid–water. M. ANGELESCU (Bul. Soc. Chim. Romania, 1927, 9, 19—25).—The isotherms for 20° and 30° and the partition coefficient at 30° have been determined. The miscibility curves for given concentrations of lactic acid indicate the existence of a lower critical solution temperature, but chemical action between the components occurs before the upper critical solution temperature can be realised. F. S. HAWKINS.

Equilibria in the reduction, oxidation, and carburation of iron. III. R. SCHENCK and T.

DINGMANN [with J. BOKMANN, W. EBERT, W. KESTING, G. LEPETIT, J. MULLER, and W. PRATJE] (Z. anorg. Chem., 1927, **166**, 113—154; cf. this vol., 939).—The equilibria $Fe_3O_4+CO \rightleftharpoons 3FeO+CO_2$ and $FeO+CO \rightleftharpoons Fe+CO_2$ have been examined between 600° and 1100° by gradually removing the oxygen from ferric oxide by means of carbon monoxide at constant temperature, the composition of the gas phase being ascertained at each stage when equilibrium had been established. The experimental conditions were such that carbide formation was prevented. At a given temperature, with decrease in the amount of oxygen in the solid phase the composition of the gas phase first remains constant, then the carbon dioxide concentration falls rapidly for a time, after which it ultimately becomes steady again, and decreases further only when the solid phase contains less than about 0·5 atom of oxygen per 3 atoms of iron. The first steady state corresponds with the coexistence in equilibrium of ferrosoferric oxide and a solid solution in this oxide of ferrous oxide. During the second period of constancy, the solid phases are solutions of ferrous oxide in metallic iron ("oxoferrite") and of ferrosoferric oxide in ferrous oxide. The two solid solutions of ferrosoferric and ferrous oxides are to be regarded as the extreme portions of a continuous series of mixed crystals of the two oxides, for which the name "wüstite" is proposed. The data obtained permit of the construction of the diagram of state for the system iron–oxygen, which shows that at 560° wüstite, ferrosoferric oxide, and oxoferrite coexist in equilibrium, but below this temperature the first of these breaks up into the other two. At none of the experimental temperatures does ferrous oxide in the pure state appear as a solid phase. All substances which are able to form compounds or solid or liquid solutions with the oxides of iron influence the reduction in the sense that a larger proportion of carbon monoxide must be present in the gaseous phase to effect reduction than when the oxides of iron alone are present, *i.e.*, more carbon must be used in the furnace. The effect of magnesium oxide has been examined in some detail. With a mixture of the composition $Fe_2O_3+11MgO$ the ferric oxide is reduced directly to the ferrous state without passing through ferrosoferric oxide and wüstite, and solid solutions of ferrous oxide and magnesium oxide exist in equilibrium with oxoferrite in the stage corresponding with the second period of constancy of the composition of the gas phase when no foreign substance is present. This mixture of oxides must be regarded as a mixture of a magnesium ferrite, MgO,Fe_2O_3, with an excess of magnesium oxide. If, on the other hand, the ferric oxide is in excess, as in the mixture $2Fe_2O_3+MgO$, ferrosoferric oxide is present along with the magnesium ferrite in the first part of the reduction. R. CUTHILL.

Equilibrium in systems the phases of which are separated by a semipermeable membrane. XX. F. A. H. SCHREINEMAKERS (Proc. K. Akad. Wetensch. Amsterdam, 1927, **30**, 401—410).—A mathematical discussion of the influence of pressure on the osmotic relationships of a system consisting of an aqueous solution separated from the vapour phase by a semipermeable membrane. H. F. GILLBE.

Precipitation laws. P. P. VON WEIMARN (Kolloid-Z., 1927, **43**, 26—30).—The author's three precipitation laws are summarised and discussed. The view is held that the laws are supported by the recent investigations of Odén (cf. A., 1926, 678). L. L. BIRCUMSHAW.

Equation of state of solid substances. IV. Heats and pressures of evaporation, sublimation, and melting in the neighbourhood of absolute zero, and Nernst's so-called heat theorem. J. J. VAN LAAR (Proc. K. Akad. Wetensch. Amsterdam, 1927, **30**, 383—400).—Polemical. The Nernst theory is invalid for all cases except that of the equilibria between two solid phases at very low temperatures. H. F. GILLBE.

Source of error in conductivity measurements. F. A. SMITH (J. Amer. Chem. Soc., 1927, **49**, 2167—2171).—Conductivity values determined by the use of cells with differently-disposed electrodes agree only for that range of conductivity which corresponds with that of the potassium chloride solution used to determine the cell constants (cf. Washburn, A., 1917, ii, 10). S. K. TWEEDY.

Conductivity of strong electrolytes in dilute solutions. P. DEBYE (Trans. Faraday Soc., 1927, **23**, 334—340).—Theoretical. The interionic attraction theory offers an adequate explanation of Kohlrausch's square-root law, provided two factors are taken into account. The first is the variation in dissymmetry of the charge density in the ionic atmosphere, as the ion moves under the influence of an electric field, in solutions of different concentration. It may be shown that, as a result of the finite time of relaxation responsible for this dissymmetry, the ion is acted on by a force which tends to decrease its velocity, and that this apparent frictional force increases with increasing velocity. The second factor, which also tends to increase the frictional force on the ion, is a cataphoretic effect, due to the movement of the ion in a solvent containing ions. M. S. BURR.

Ionisation of some typical strong electrolytes. D. A. MACINNES and I. A. COWPERTHWAITE (Trans. Faraday Soc., 1927, **23**, 400—404).—Transference and conductance measurements have been made on nitrates and chlorides in 0·1*N* solutions, and the results indicate that, if the alkali chlorides and hydrochloric acid are completely dissociated, then nitric acid and ammonium nitrate are also of this class. Sodium, potassium, and silver nitrates, however, must be partly associated. M. S. BURR.

Revision of the conductivity theory. L. ONSAGER (Trans. Faraday Soc., 1927, **23**, 341—349).—The Debye–Hückel theory of the conductivity of strong electrolytes may be modified by taking into consideration the Brownian movement of the ions. A knowledge of the ionic radius then becomes unnecessary and all arbitrary constants are eliminated from the limiting formula. When Λ is plotted against $\sqrt{n\mu}$, where n is the sum of the valencies

of the two ions and μ the concentration, deviations at higher concentrations from the limiting slope at zero concentration probably indicate association. M. S. BURR.

Mobilities of the elementary ions in methyl alcohol. H. HARTLEY and H. R. RAIKES (Trans. Faraday Soc., 1927, 23, 393—396).—The mobilities of all the univalent and most of the bivalent ions in methyl alcohol at infinite dilution are tabulated and compared with those in water at 25°. The general relationships are the same in both solvents, although the relative mobility of the ions in the two solvents is not constant. For the bivalent ions the value is approximately unity, as is the case for lithium. Applying Stokes' law, the ionic radii in water and methyl alcohol are compared with one another, and also with the effective ionic radii in the crystal lattice as determined by other investigators. The radii of all ions in methyl alcohol are greater than in water. The fact that the radii in water of several of the alkali and halide ions appear to be smaller than their effective radii in the lattice throws doubt on the absolute values of the ionic radii obtained by these means. M. S. BURR.

Ionic mobilities in non-aqueous solvents. H. ULICH (Trans. Faraday Soc., 1927, 23, 388—393).—According to Walden the product of the mobility l of a large ion, which may be regarded as not solvated because of its size, and the viscosity η is a constant and independent of the solvent. This is shown to be true for a number of solvents, including water, in the case of certain large organic ions such as the tetramethyl- and tetraethyl-ammonium ions and the picrate ions. On the assumption that Stokes' law holds, and that solvation is indicated when the product $l\eta$ is not constant, the number of molecules of solvent per ion has been calculated for the alkali and halide ions in different solvents and the results are tabulated. M. S. BURR.

Debye-Hückel theory. H. HARTLEY and R. P. BELL (Trans. Faraday Soc., 1927, 23, 396—400).—Examination of a large number of conductivity data in organic solvents shows that, in general, the Kohlrausch square-root relation is confirmed in dilute solution. This is in accordance with the Debye–Hückel theory. A further test of the latter may be applied by calculating b, the harmonic mean of the ionic radii, from the Debye–Hückel equation, and comparing it with the value calculated on the assumption that, at infinite dilution, the motion of the ions obeys Stokes' law. Divergences between the two values for solvents with dielectric constants less than 20 are rather large, but the approximate agreement among the remainder is regarded as evidence of the essential correctness of the Debye–Hückel theory. The results also show that conformity to the square-root law is no guarantee that the conductivity–concentration curve will be in accordance with Debye's equation. This may arise from incomplete ionisation. M. S. BURR.

Conductivity of acids and salts in liquid ammonia. F. A. SMITH (J. Amer. Chem. Soc., 1927, 49, 2162—2167).—Solutions of amides, imides, etc., and of their monoalkali derivatives were examined at −33·5° (cf. this vol., 1023). Values of Λ_∞ are calculated by Kraus and Bray's method. Except in the case of succinimide, the salt is always a better conductor than the corresponding acid, although the difference is small for the "strong" acids which probably form ammonium salts. Mercury succinimide has a very low conductivity. The conductivity of ammono-carbonic acids and of their alkali salts increases with de-ammonation of the acid and decreases with polymerisation. Sulphur nitride behaves as a typical binary electrolyte; this compound is the mixed "anammonide" of ammonosulphurous and ammonothiosulphuric acids, and it probably dissociates in ammonia solution into the two anammonous radicals which on ammonation would give these acids. S. K. TWEEDY.

Electrolytic transference of water, true transference numbers, ionic mobilities, and water sheaths of the ions. H. REMY (Trans. Faraday Soc., 1927, 23, 381—388).—True transference numbers have been calculated from the available data for the electrolytic transference of water in normal aqueous solutions of inorganic electrolytes. A comparison of solutions of homologous types shows that the product of the true mobility of an ion and the viscosity of the solution varies much less from solution to solution than the product of the apparent mobility and the viscosity. This applies similarly to the quotient of the mobility and the coefficient of conductivity. On the assumption that large organic ions do not carry water sheaths (cf. von Hevesy, A., 1916, ii, 594; Lorenz, *ibid.*, 312), values have been deduced for the amount of water carried by chlorine and bromine ions in normal solutions of aniline and *p*-toluidine hydrochloride and hydrobromide. Hence the absolute values for the number of water molecules carried by hydrogen, alkali, and alkaline-earth metals, iodine, and also some small organic ions have been determined and the results tabulated. M. S. BURR.

Electrolytic conduction of potassium through glass. V. ZWORYKIN (Physical Rev., 1926, [ii], 27, 813).—Burt's experiments on the introduction of sodium into a thermionic vacuum tube by electrolysis have been extended to potassium. When a soda-potash glass is immersed in potassium nitrate, the metal introduced is primarily sodium; the glass is enriched in potassium and becomes brittle. With potash glass, potassium passes into the tube without corroding or embrittling the glass. A. A. ELDRIDGE.

Ionic mobilities in mixed crystals and their relationship to those in the pure salts. C. TUBANDT, H. REINHOLD, and W. JOST (Z. physikal. Chem., 1927, 129, 69—78).—A quantitative method of expressing the degree of interlocking between the various components in a mixed crystal has been derived by comparing the ionic mobilities of the pure salts with those of the mixed crystals, as calculated from measurements of conductivity and of transport number. From the relationship between the mobilities it is possible to determine the extent to which the diffusion coefficients obtained from diffusion measurements represent the true diffusion coefficients of the pure components. H. F. GILLBE.

Effect of temperature on diffusion potentials. E. B. R. PRIDEAUX (Trans. Faraday Soc., Sept., 1927, advance proof).—From the ionic mobilities of a series of univalent electrolytes, it is shown that the temperature coefficients of the diffusion potentials are small and possibly zero; this is attributed to the tendency towards equalisation of the mobilities of anion and cation as the temperature is raised. Measurements of the diffusion potentials at 18° and 25° and over the concentration range from 0·1 to 0·01*N*, using a flowing junction, are in agreement with this view. For univalent electrolytes of varying character the observed change in diffusion potential is less than 0·5 millivolt. For acetic acid, the increase in the diffusion potential with the temperature is larger, amounting to 0·7 millivolt between 18° and 25°. G. A. ELLIOTT.

Cells of the standard-cell type with low *E.M.F.* W. C. VOSBURGH (J. Amer. Chem. Soc., 1927, **49**, 2222—2229).—The *E.M.F.* of the cells (Cd+Pb)Hg|$CdCl_2$,2·5H_2O (sat. soln.)|$CdCl_2$,2·5H_2O+$PbCl_2$ (sat. soln.)|Hg(Pb) and (Cd+Pb)Hg|CdI_2 (sat. soln.)|CdI_2+PbI_2 (sat. soln.)|Hg(Pb) were measured at 5° intervals between 15° and 40° over a period of several months. The former cell is the more reproducible, but exhibits a transition point at 26·2°. The *E.M.F.* of the corresponding cells containing pure cadmium amalgam are given by E=0·13759—0·000193(t—25)—0·0000012(t—25)^2 and E=0·0996+0·000235(t—25)—0·0000002(t—25)^2, respectively. The former equation gives values in slight disagreement with those of Obata (Proc. Phys. Math. Soc. Japan, 1921, [iii], **3**, 64, 136) and of Taylor and Perrott (A., 1921, ii, 303). The *E.M.F.* of the corresponding cells with pure metal electrodes are given by E=0·1824—0·000453(t—25)—0·0000012(t—25)^2 and E=0·1444—0·000025(t—25)+0·0000002(t—25)^2, whence for the reaction Cd+$PbCl_2$+2·5H_2O (in sat. soln.)=$CdCl_2$,2·5H_2O+Pb, ΔF=—8417 g.-cal., ΔS=—20·9 g.-cal./degree, and ΔH=—14,650 g.-cal. at 25°, and for the reaction Cd+PbI_2=CdI_2+Pb, ΔF=—6664 g.-cal., ΔS=—1·15 g.-cal./degree, and ΔH=—7008 g.-cal. These values agree with the thermochemical data. None of these cells is suitable as a standard cell; their temperature coefficients are large and the iodide cells exhibit persistent hysteresis. S. K. TWEEDY.

Electrical action due to the atomisation of a solution of a univalent electrolyte. A. BUHL (Ann. Physik, 1927, [iv], **83**, 1207—1224).—The effects produced by the air spraying of solutions of electrolytes and the charged particles resulting thereby have been investigated. The number of charged particles depends on the concentration of the solution and the velocity of the air stream. The results are discussed in terms of Lenard's conception of the structure of the surface layers of liquids. W. E. DOWNEY.

Dissolution velocity and the electrolytic solution pressure of lead and of bismuth. J. GRÓH (Z. physikal. Chem., 1927, **128**, 449—458).—The rate of exchange of lead between lead amalgams and aqueous solutions of lead nitrate has been measured by an electroscopic method. The rate of dissolution of lead from the amalgam increases with increase of the concentration of the lead nitrate solution: change of concentration from 0·01 to 0·1*M* increases the velocity about one hundredfold, but at higher concentrations the rate of increase diminishes. A method is described for measuring the velocity when the time of contact between the amalgam and the solution is a minimum. The mean velocity at 18°, calculated for a saturated amalgam, is 0·0051 g./cm.^{2}/sec. Qualitative observations with bismuth indicate that the velocity is greater than $1{\cdot}5\times10^{-5}$. H. F. GILLBE.

Electrochemical studies of titanium. E. D. BOTTS and F. C. KRAUSKOPF (J. Physical Chem., 1927, **31**, 1404—1419).—The preparation of titanium, its single potential, and its power of replacing other metals from salt solutions have been studied. The method of Nilson and Pettersson, as modified by Hunter (A., 1910, ii, 302), yielded crystalline titanium of 99·6—99·9% purity in pieces varying in size up to 5 g. The optimum conditions are described, and sodium is shown to be preferable to potassium, or to a mixture of both, as the reducing agent. Single potential measurements of titanium in 0·25*M* solutions of the trichloride and of the corresponding sulphate gave average values of 0·23 and 0·18 volt, respectively. The presence of hydrofluoric acid in the titanous solution increased the single potential by 0·22 volt, but additions of hydrochloric and sulphuric acids to the corresponding salt solution lowered it. Alkali salts having an ion in common with the titanium salt caused a slight increase. Replacement experiments do not agree with these measurements except in solutions of the fluorides, copper, silver, lead, and cadmium, but not cobalt, nickel, zinc, or iron, being replaced by titanium only from a solution of the respective fluoride. L. S. THEOBALD.

Helmholtz double layer related to ions and charged particles. E. F. BURTON (Fourth Colloid Symposium Monograph, 1926, 132—144).—There appears to be mutual action of charged particles, and interaction of colloid particles and ions in solution; this opposes the view that within molecular distance of the surface there exists an electrically equivalent layer of opposite charge. Gouy's equations indicate that the thickness of the outer Helmholtz double layer decreases as the concentration of the electrolyte increases, the decrease for electrolytes of the same molar concentration being the greater the higher is the valency of the ions; if the ions have the same valency their concentrations remain proportional, but if they differ in valency their concentrations in the neighbourhood of the surface differ. CHEMICAL ABSTRACTS.

Thermodynamic *P.D.* at the boundary between two liquid phases. V. S. VOSNESSENSKI and K. ASTACHOV (Z. physikal. Chem., 1927, **128**, 362—368).—A method is described for measuring the *P.D.* at the interface between two liquid phases in which various electrolytes are dissolved. If the partition coefficient of the electrolyte be constant, the *P.D.* is constant at moderate concentrations. At concentrations above about 0·5*N* the *P.D.* remains constant, even although the partition coefficient undergoes

change. The partition of the cations sodium, potassium, and hydrogen is in the same order as that of their degree of hydration, and a similar relation probably obtains for the commoner anions.

H. F. GILLBE.

Experimental investigation of the theory of local currents. M. CENTNERSZWER and M. STRAUMANIS (Z. physikal. Chem., 1927, **128**, 369—393).—Simultaneous measurements have been made of the electrode potential, current strength, and internal resistance of typical polarisable cells. The logarithm of the current strength at constant anode potential decreases in direct proportion to the time, a conclusion which follows from Boguski's law. With the cell short-circuited, rise of temperature produces a logarithmic increase of the current strength. On anodic dissolution of a metal in acid its potential increases; increase of external resistance causes the anode to become more negative, whilst increase of internal resistance has the reverse influence. With increase of current strength the potential of the anode increases up to a limiting value dependent on the electrolyte. The velocity of dissolution of an anode in different acids or in the same acid at different concentrations increases as the equivalent conductivity of the solution increases and is the greater the smaller the overvoltage at the cathode. The properties of tin, cadmium, and iron anodes are very similar to those of zinc. H. F. GILLBE.

Passivation of metals by anodic polarisation. G. GRUBE (Z. Elektrochem., 1927, **33**, 389—399).—Theories of passivity are briefly reviewed and recent work, mainly by the author and his collaborators, on the anodic passivation of metals in alkaline solutions is discussed (cf. A., 1921, ii, 49; 1922, ii, 570; 1923, ii, 118; 1926, 362, 687; B., 1923, 233). At low current densities iron, cobalt, manganese, and lead dissolve anodically in bivalent form in solutions of sodium or potassium hydroxides, but with increasing current density the polarisation eventually increases sufficiently to permit oxidation of the bivalent ions to the tervalent or quadrivalent stages. Relatively insoluble intermediate oxides, such as Fe_3O_4, Co_3O_4, and Mn_3O_4, can then be deposited as a film on the anode. Passivity then ensues, the polarisation increasing rapidly and higher oxides being formed, which may decompose, giving oxygen evolution, or, at least in part, dissolve in the electrolyte as in the formation of ferrates and manganates. The behaviour of chromium is similar, but passivation occurs at an exceptionally low current density. Anodic passivity in acid solutions, however, does not seem to be of this mechanical type. An anomaly in the behaviour of chromium in acid solutions is discussed. H. J. T. ELLINGHAM.

Corrosion of metals as an electrochemical problem. A. THIEL [with J. ECKELL] (Z. Elektrochem., 1927, **33**, 370—386).—One side of a disc of specially purified zinc was exposed to 0·5*N*-hydrochloric acid, which was vigorously stirred, and, when the rate of dissolution of the metal had become practically constant, the disc was connected through an external variable resistance with a plate of a nobler metal (platinum, copper, lead, tantalum, or silver) dipping into the same solution. The current passing through the system, of which the zinc forms the anode, was measured under various conditions, and changes in the rate of dissolution of the zinc could be followed from measurements of the rate of hydrogen evolution from the complete cell. In accordance with the "local element" theory of corrosion, it was found that with given external resistance lower currents were obtained when cathode metals of higher hydrogen overvoltage were used. Also the single potentials of the various cathode metals combined with the zinc are of the order of magnitude to be expected from known overvoltage data. If v_0 is the rate of dissolution of the zinc before connexion with the other metal and v the velocity when so connected, then if v_e is the rate of "enforced" dissolution which corresponds with the current passing under the latter conditions, it is found that $v_0+v_e=v+\Delta$, where Δ is a positive quantity named the "difference effect." Provided that v_0 exceeds a certain critical value, $\Delta=kI$, where I is the current and k is a constant independent of the nature of the cathode metal. For low values of v_0, however which can be obtained by using a polished zinc surface, k is no longer constant, but falls towards zero as v_0 is diminished. Experiments with aluminium in *N*-sodium hydroxide solution yielded similar results, but the value of k is notably greater in this case. A negative value of Δ for aluminium in dilute hydrochloric acid is being further investigated. The results described give strong support to the local element theory of corrosion of metals, but it is pointed out that, when conditions are such that hydrogen evolution from the surface of the dissolving metal is very rapid, the rate of diffusion of hydrogen ions towards that surface can become a determining factor, so that eventually the phenomenon passes over into that described by Nernst and Brunner (1904) for the dissolution of other solid substances in acids. The difference effect is attributed to the retardation of diffusion of hydrogen ions towards the metal surface caused by accumulation of salts of the dissolving metal in that region. Provided that v_0 is high enough for diffusion to be the ruling factor, Δ may be expected to be proportional to I which determines v_e and hence the extent of this accumulation of metallic salt. Measurements of the single potential of zinc when combined with a platinum cathode in 0·5*N*-hydrochloric acid show an increasing ennoblement as the current increases, which corresponds with an increasing concentration of zinc ions at the metal surface. Wide variations in the values of v_0 observed with discs of zinc cut from the same rod are found to be accompanied by corresponding variations in the microscopic appearance of the metal after corrosion. An exceptionally pure sample of zinc showed no corrosion during 2 hrs. in 0·5*N*-hydrochloric acid, but scratching with a diamond led to formation of hydrogen bubbles along the crevice, a result which is attributed to decreased hydrogen overvoltage at an irregular surface. Palmaer's view (B., 1926, 589) that the increased rate of dissolution of iron containing graphite can be attributed to a low overvoltage of the latter is disputed and conclusions of Centnerszwer and Zablocki (A., 1926, 1010)

as to the mechanism of the dissolution of aluminium in acids are criticised. H. J. T. ELLINGHAM.

Photo-voltaic cells. C. W. TUCKER (J. Physical Chem., 1927, **31**, 1357—1380; cf. Case, B., 1917, 1102; Garrison, A., 1923, ii, 728; 1924, ii, 339, 401).—The cuprous oxide and silver halide photo-voltaic systems have been studied in cells of the type—illuminated metal|oxide or halide-solution-oxide or halide|metal. Illuminated electrodes of cuprous oxide deposited in the meshes of platinum gauze gave small but definite photo-voltages. In reducing solutions, photochemical reduction of cuprous oxide tends to occur, and oxidation in oxidising solutions. Substitution of copper for platinum has a specific influence on the behaviour of the copper–cuprous oxide electrode, and cells with copper in the form of gauze show the so-called "Minchin effect," *i.e.*, the illuminated electrode is at first anodic, changing to cathodic on continued illumination. The initial anodic effect is more permanent with an oxidising than with a reducing solution in the cell. Removal of the light results in an increase in cathodic tendency and the *P.D.* between the two cell electrodes slowly returns to zero. When the gauze is replaced by sheet copper, the anodic effect is magnified as the local cell formation is decreased, but the voltage maximum indicates that local cell action is still appreciable and that sign reversal of the electrodes would still occur with continued illumination. The anodic effect is now greatest in reducing solutions. The general form of time–voltage curve is independent of the solution used. The behaviour of platinum|silver halide electrodes closely resembles that of the copper|cuprous oxide electrodes, and the photo-voltage with silver chloride is, in general, greater than that with the bromide, which, in turn, is greater than that with the iodide. The silver|silver halide electrodes have also been examined. The above results are explained in terms of local cell formation, which will be at a minimum on the illuminated surface when the photosensitive substance on this surface is present as a uniform layer; in these circumstances the exposed electrode is the anode. On the other hand, when the layer is non-uniform, local cells are set up in the illuminated electrode, which becomes the cathode on continued illumination. When the local cells are completely reversible, the behaviour of the electrode is determined by the oxidising or reducing nature of the cell solution; it is a cathode in the former and in a neutral solution, and an anode in a reducing solution.

The work of previous investigators is summarised and discussed. L. S. THEOBALD.

Velocity of coupled reactions. J. A. CHRISTIANSEN (Z. physikal. Chem., 1927, **128**, 430—438).—The method of instantaneous velocities is shown to be applicable to the kinetics of reaction. For the velocity of a series of consecutive reactions, without side reactions, an expression has been derived which is in agreement with thermodynamic considerations if with Bronsted the assumption be made that the probability of reaction is proportional to the product of the activity coefficients of the reactants and a divisor f_x which is common to the two opposing reactions. For a special case of consecutive reactions accompanied by side reactions an expression for the velocity has been deduced, and is discussed in its application to the reactions between hydrogen peroxide and the bromine ion and molecule.

H. F. GILLBE.

Thermal decomposition of hydrogen peroxide vapour. L. W. ELDER, jun., and E. K. RIDEAL (Trans. Faraday Soc., 1927, **23**, 545—552; cf. Hinshelwood and Prichard, J.C.S., 1923, **123**, 2726).—An apparatus for the measurement of the rate of decomposition of hydrogen peroxide vapour at constant volume is described. By comparison of the vapour pressure of the original mixture, obtained from a hydrogen peroxide preparation of approximately 60%, with that of the resulting water vapour, it has been shown that hydrogen peroxide vapour, under about 85 mm. pressure at 85°, consists of simple unhydrated molecules. The decomposition bulb was made of quartz, since glass gives no reproducible results. The thermal decomposition at 85° is a reaction of zero order, inhibited by molecular oxygen, which brings the reaction to an end when only about 20% of the hydrogen peroxide is decomposed. The inhibiting reaction is stronger still at 95°. On a platinum surface the reaction is apparently unimolecular, and is probably determined by the rate of diffusion through an adsorbed or dissolved layer of oxygen. The reaction on a mercury surface consists of a preliminary direct oxidation of mercury to mercurous oxide, followed by oxidation of the latter to mercuric oxide, with simultaneous liberation of an equivalent amount of atomic oxygen which oxidises a further quantity of hydrogen peroxide. The mercuric oxide is not reduced by hydrogen peroxide vapour. A method is described for the preparation of pure concentrated hydrogen peroxide from "Hyperol."

M. S. BURR.

Thermal decomposition of hydrogen peroxide. F. O. RICE and O. M. REIFF (J. Physical Chem., 1927, **31**, 1352—1356).—The decomposition of pure aqueous solutions of hydrogen peroxide, prepared by the method of Kilpatrick, Reiff, and Rice (this vol., 120), and of commercial solutions at 80·2° has been studied. The rate of decomposition of the former, freed from suspended matter and heated in vessels with smooth walls, is very slow. Pure, aqueous solutions, free from inhibitors but not from dust, give a linear decomposition curve; addition of chlorides, alkalis, and inhibitors gives curves which are often unimolecular in type. Merck's perhydrol, and pure solutions to which were added inhibitors such as barbituric or uric acid, or benzamide, show an initial induction period on the decomposition curves. The catalysis of hydrogen peroxide by the iodine–iodic acid couple (Bray, A., 1921, ii, 629) appears to be a heterogeneous reaction occurring on the surface of dust particles. The ordinary decomposition of hydrogen peroxide also takes place on these surfaces and on the walls of the vessel, and an inhibitor evidently acts by poisoning the surface.

L. S. THEOBALD.

Thermal dissociation of carbonyl chloride. H. INGLESON (J.C.S., 1927, 2244—2254).—The thermal dissociation of carbonyl chloride has been

investigated between 357° and 480° in quartz vessels. Trustworthy results could not be obtained in glass, as it is attacked by the chlorine produced. The heat of reaction at constant volume is 25,500 g.-cal. at a mean temperature of 416°. A linear relation is found between the reciprocal of the absolute temperature and the logarithm of the reaction velocity constant. Christiansen's view that the decomposition is accelerated by the products (A., 1923, ii, 62) is supported qualitatively (cf. Atkinson, Heycock, and Pope, J.C.S., 1920, **117**, 1410). C. W. GIBBY.

Oxygen required for the propagation of hydrogen, carbon monoxide, and methane flames. G. W. JONES and G. ST. J. PERROTT (Ind. Eng. Chem., 1927, **19**, 985—989).—The minimum proportion of oxygen necessary to propagate the flames of methane, hydrogen, and carbon monoxide in admixture with varying proportions of nitrogen was determined. With less than 12% of oxygen no methane–nitrogen mixture was combustible, but for sufficiently high proportions of hydrogen and carbon monoxide (4% and 14%, respectively) the minimum oxygen concentration is 5—6%. The presence of carbon dioxide raises the oxygen concentration necessary. Helium has a similar effect on the combustion of hydrogen. C. IRWIN.

Inflammation of mixtures of the paraffins and air in a closed spherical vessel. G. B. MAXWELL and R. V. WHEELER (J.C.S., 1927, 2069—2080).—The pressures in mixtures of air with the first five members of the paraffin series developed on ignition centrally in a spherical bulb have been measured, and are compared with the calculated values. Discrepancies are probably due to errors in specific heat and equilibrium data. The mean temperature of the explosion is the main factor in determining the mean rate of development of pressure. C. W. GIBBY.

Influence of hydrogen on two homogeneous reactions. C. N. HINSHELWOOD and P. J. ASKEY (Proc. Roy. Soc., 1927, A, **116**, 163—170; cf. this vol., 26, 212).—If a molecule in a gaseous reaction is activated by collision, transformation may follow immediately, or it may be delayed until the molecule passes through a suitable internal phase. If the transformation is immediate, the reaction is kinetically bimolecular, but if there is a time lag, then, as Lindemann has indicated (Trans. Faraday Soc., 1922, **17**, 599), the reaction appears to be unimolecular. The time lag after activation is considered to be most probable when the structure is complex and the energy distributed among a number of degrees of freedom, whilst its absence is to be expected when the mechanism of activation is very simple. The reactions involved in the decomposition of propaldehyde and dimethyl and diethyl ether are unimolecular at higher pressures, but betray their dependence on molecular collisions by decreasing in rate when the pressure of the reacting gas is reduced below a certain limit. In the case of the two ethers, it has been found (*loc. cit.*) that the rate of decomposition maintains its unimolecular character at low pressures if sufficient hydrogen is present, and it is now shown that the decomposition of propaldehyde is similar, but that the bimolecular decomposition of acetaldehyde is influenced less, and in a different way, by hydrogen. These results are consistent with the assumption that the activation of acetaldehyde involves only a few degrees of freedom, whilst that of propaldehyde is a more complex process, and that in the propaldehyde process a time lag exists between activation and transformation.

L. L. BIRCUMSHAW.

Esterification in mixed solvents. B. W. BHIDE and H. E. WATSON (J.C.S., 1927, 2101—2107).—The velocities of esterification of suberic and *n*-butyric acids in mixtures of *iso*amyl alcohol with benzene or petroleum have been measured in the presence of hydrochloric acid as catalyst. The velocity coefficients given by the formula of Goldschmidt and Udby (A., 1907, ii, 852), $kt=(r-a)\log a/(a-x)-x$, are satisfactory and increase on dilution of the alcohol in an approximately hyperbolic relation with the composition of the solution. Conductivity and viscosity measurements show that ionisation of the catalyst has no influence on the velocity, and it is suggested that the latter depends on the molecular ratio of catalyst to alcohol. C. W. GIBBY.

Coefficient of hydrolysis of ethyl acetate by sodium hydroxide. (MISS) E. M. TERRY and J. STIEGLITZ (J. Amer. Chem. Soc., 1927, **49**, 2216—2222).—The experiments were carried out in approximately 0·01*N*-sodium hydroxide solution, the apparatus being an improvement of that described by Reicher (A., 1885, 1034). The coefficient is 6·76 (±0·75%) at 25° (concentrations in mol./litre) and increases 0·045 per 0·1°. Improved experimental technique is described in detail. S. K. TWEEDY.

Hydrolysis of ethyl acetate. W. T. GOOCH (J. Amer. Chem. Soc., 1927, **49**, 2257).—Intensity variations of diffused daylight do not influence the rate of hydrolysis of ethyl acetate in aqueous sodium hydroxide at 25°. S. K. TWEEDY.

Kinetics of the hydrolysis of glyoxal tetra-acetate. A. SKRABAL and E. GITSCHTHALER (Z. physikal. Chem., 1927, **128**, 459—471).—The hydrolysis constants of the hydrolysis of glyoxal tetra-acetate in neutral, acid, and alkaline solution are for the first stage 0·000138, 0·01640, and 2740, and for the second stage 0·000069, 0·00820, and 1370, respectively. The relationship between the constitution of a number of esters of acetic acid and their rates of hydrolysis is discussed. H. F. GILLBE.

Kinetics of oxime formation. A. OLANDER (Z. physikal. Chem., 1927, **129**, 1—32).—The quantity of iodine reduced in the iodometric determination of hydroxylamine is not directly proportional to the amount of the latter. The relation between them has been ascertained for quantities of hydroxylamine up to 5·5 mg. The dissociation constant of hydroxylamine at 20° is $1\cdot07\times10^{-8}$, and that of dibromocresolsulphonephthalein in presence of 0·1*M*-phosphate is $7\cdot4\times10^{-7}$. Free hydroxylamine reacts slowly with acetone, but the hydroxylammonium ion reacts comparatively quickly and reversibly; for the reaction between the ion and acetone the bimolecular velocity coefficient is 84. The additive reaction product decomposes reversibly with the formation of acet-

oxime and water; the unimolecular velocity constant of the reverse reaction is 0·07. The optimum p_H, at 20° and 0·003M solution, is 4·5 for the formation of the oxime and 2·3 for its decomposition; the forward reaction is complete only at $p_H>7$. The velocity and degree of completeness of the reaction have been determined in 0·003M solution in presence of acid at various concentrations. H. F. GILLBE.

Reactions in the solid state at high temperatures. II. Reaction velocity of exothermic changes. W. JANDER (Z. anorg. Chem., 1927, **166**, 31—52).—Extension of the theory that reactions in binary mixtures of solids are governed by the ordinary laws of diffusion (this vol., 736) to solids between which an exothermic reaction occurs shows that the percentage reaction, x, is related to the time, t, by the formula $1-[(100-x)/100]^{1/3}=2\cdot3\{\log t+\log b'-2\log[1-\sqrt[3]{(100-x)/100}]\}/c$. Here b' measures the diffusivity at the start of the reaction, and c is a function of x and the temperature, T. This equation is in good agreement with the experimental results for mixtures of barium carbonate and tungstic anhydride and of silver sulphate and lead monoxide. Both b' and the velocity coefficient at the final stage of the reaction are related to the temperature by an exponential expression. R. CUTHILL.

Application of Tammann's method of thermal analysis to reactions between solid phases. J. GUILLISSEN (Bull. Acad. roy. Belg., 1927, [v], **13**, 233—238).—The application of Tammann's method (A., 1926, 921), *i.e.*, comparison of temperature–time curves of the initial reaction mixture and of the reaction product, to the study of the formation of certain ferrites not yielding a trustworthy indication of the temperature of commencement of reaction, an attempt has been made to increase the sensitivity of the method by using a Le Chatelier–Saladin differential galvanometer and constructing a temperature–temperature difference curve.

The reaction between barium carbonate and ferric oxide commences at about 800°. An equimolar mixture, when heated for 3 hrs. at 830° in a slow current of air, undergoes a change in weight corresponding with the formation of 87·5% of barium ferrite. The direct addition of barium oxide to ferric oxide occurs at about 300°. Owing to secondary disturbances no definite indication of the temperature of reaction between calcium carbonate and ferric oxide could be obtained. The reaction certainly occurs at relatively low temperatures.

J. S. CARTER.

Temperature of formation of zinc ferrite from the solid constituents. J. GUILLISSEN and RICHARD (Bull. Acad. roy. Belg., 1927, [v], **13**, 238—240; cf. preceding abstract).—Interaction between zinc and ferric oxides commences at 620—650°. On account of the stability of zinc ferrite towards dilute acids the importance of considering its probable formation during the roasting of zinc blendes preparatory to an electrolytic process is emphasised. After being heated at 890° a mixture containing 34% of zinc oxide yielded only 8% of zinc oxide to an ammoniacal solution of ammonium chloride.

J. S. CARTER.

Influence of diffusion of oxygen on the rate of combustion of solid carbon. J. T. WARD and J. B. HAMBLEN (Ind. Eng. Chem., 1927, **19**, 1025—1027).—A carbon block was burned in air and by very slow sampling the gas was drawn off from the carbon side of the gas film by a quartz capillary sealed into the end of the block. The analyses showed an average ratio of 28·07 mols. of oxygen to 100 mols. of nitrogen, carbon dioxide and carbon monoxide being returned as oxygen, as against an air ratio of 26·58. This is in accordance with the theory that the rate of the reaction $C+O_2=CO_2$ is limited by the rate of diffusion of oxygen through the gas film surrounding each particle of carbon. C. IRWIN.

Corrosion of non-ferrous metals and alloys. T. S. FULLER (Proc. Amer. Soc. Testing Materials, [advance copy], 1927, No. 19, 1—18).—Modified procedures are given for the total immersion and alternate immersion tests. The spray test and the electrolytic test do not appear to be generally applicable.

CHEMICAL ABSTRACTS.

Corrosion fatigue of non-ferrous metals. D. J. MCADAM, jun. (Proc. Amer. Soc. Testing Materials, [advance copy], 1927, No. 36, 1—26).—An examination of 18 non-ferrous metals and alloys with fresh and salt water. For nickel and Monel metal, the fully annealed and strain-hardened metal have the same "corrosion-fatigue limits," but this is not the case for copper–nickel alloys. The corrosion-fatigue limits of these alloys may depend chiefly on their electrode potentials. The stress-cycle curves for aluminium and for aluminium–manganese alloys give a corrosion-fatigue limit far below the endurance limit in air. Each metal and alloy appears to have an intrinsic corrosion-fatigue limit depending chiefly on the corrosion agent and the corrosion resistance of the metal. Possibly this limit depends on the ease of removal of atoms from the space lattice under the combined influence of electrolytic solution pressure and cyclic strain of the lattice.

CHEMICAL ABSTRACTS.

Passivity of iron mirrors. H. FREUNDLICH, G. PATSCHEKE, and H. ZOCHER (Z. physikal. Chem., 1927, **128**, 321—344).—The physical and chemical properties of iron mirrors on glass, produced by the thermal decomposition of iron pentacarbonyl, have been studied in their relationship to the problem of passivity. The mirrors are rendered passive by treatment with concentrated nitric acid, and are then in the same condition as ordinary passive iron. Mirrors maintained out of contact with air are considerably more active than those to which air has access, being readily dissolved by nitric acid; this activity is unaffected by carbon dioxide, nitrogen, or water. The passivity produced by contact with the atmosphere cannot be destroyed by placing the mirror in a vacuum, although in certain cases heating the mirror in a vacuum restores its activity. Similar conditions obtain for mirrors rendered passive by acids. Considerations of "vacuum activity" and "air passivity," together with observations of the brown film of insoluble matter which remains when an iron mirror is dissolved in acid, lead to a simple oxidation theory of the passive state. H. F. GILLBE.

Catalysis in homogeneous gas reactions. A. VON KISS (Chem. Weekblad, 1927, **24**, 466—471).—The modern theories of the relations between kinetic and internal energies of molecules and frequencies of molecular collisions and reaction velocities are considered in the discussion of the mechanism of catalysed reactions. If an unalterable energy of activation be postulated, it becomes impossible to understand the action of a "physical" catalyst, *i.e.*, of one which takes no part in the reaction; the effect of a chemical catalyst, on the other hand, is readily explained by the theory. S. I. LEVY.

Acid and salt effects in catalysed reactions. X. Hydrolysis of ethyl acetate with acetic acid as catalyst. H. M. DAWSON and W. LOWSON (J.C.S., 1927, 2107—2114).—If the effect of the reverse reaction is neglected in the calculation of the true velocity coefficient for ester hydrolysis, correct values are obtained only at low concentrations of the ester.

The rate of hydrolysis of ethyl acetate in the presence of acetic acid has been measured and the velocity at various stages compared with the theoretical values. The catalytic coefficient for the hydrogen ion is calculated to be $1{\cdot}14\times10^{-4}$ at 25°.

C. W. GIBBY.

Significance of iso-catalytic data and the so-called protion theory of chemical reactivity. H. M. DAWSON (J. Physical Chem., 1927, **31**, 1400—1403).—A reply to Bergstein and Kilpatrick (this vol., 214) and a criticism of their conclusions on the catalytic minimum point. The interpretation of observations on the reaction between acetone and iodine is also discussed (cf. Dawson, this vol., 320) and the factors determining minimum reaction velocity are considered in relation to the catalytic catenary. Further, it is shown that Rice's protion theory is at variance with established facts.

L. S. THEOBALD.

Catalytic properties of mineral waters. II. The benzidine reaction of the Wiesbaden hot spring. L. FRESENIUS and H. LEDERER (Z. anorg. Chem., 1927, **166**, 99—109; cf. this vol., 320).—Artificially prepared solutions containing no iron, but otherwise similar in composition to the water of the Wiesbaden hot spring, do not give the benzidine reaction unless ferrous hydrogen carbonate is added, or unless manganese is present and the water is made alkaline, in which case part of the manganese passes into a higher state of oxidation. Since the natural water is acid in reaction, its activity must therefore depend on the presence of iron. It is found, further, that the gradual loss of the ability to give the benzidine reaction which occurs on keeping the natural water runs parallel with an increase in the amount of ferric iron present, and a decrease to zero of that of the ferrous iron, and that the rate at which the activity is lost depends on the rate at which the dissolved carbon dioxide escapes. The disappearance of the activity must consequently be attributed to the oxidation of ferrous hydrogen carbonate with subsequent precipitation of the product. If there is present an acid which is able to form some ferric ions before settling out is complete, *e.g.*, hydrochloric acid when benzidine hydrochloride is used for the test, a positive reaction may be obtained in absence of any ferrous salt, unless there is also present some acid, such as tartaric acid, which forms a very stable complex with the ferric ion. Light exerts no appreciable effect on the loss of activity of the water, except in so far as it influences the rate at which carbon dioxide escapes. The present results thus confirm those of Simon and Kotschau (this vol., 843).

R. CUTHILL.

Activity of hydrogen. C. F. HOLMBOE (Z. komp. fluss. Gase, 1927, **26**, 17—19).—Hydrogen prepared from steam and iron is less efficient in catalytic hydrogenation than electrolytic hydrogen; possibly the latter is "activated." CHEMICAL ABSTRACTS.

Active nitrogen. III. Active nitrogen and the metals. E. J. B. WILLEY (J.C.S., 1927, 2188—2196).—The relative catalytic efficiencies of various metals for the destruction of active nitrogen have been determined by measuring the rise in temperature produced when the gas is passed over filaments of the metals. With platinum, iron, silver, zinc, tungsten, and molybdenum a linear relation was found between the rise in temperature and the rate of flow, but in the case of copper the rise in temperature was much greater. The decay process is bimolecular with respect to the active nitrogen, and the energy of active nitrogen is calculated to be 46,000 g.-cal. per g.-mol. It is considered that the mechanism of the process is the alternate formation and decomposition of the nitrides of the metals. C. W. GIBBY.

Catalytic activity of metallised silica gels. V. N. MORRIS and L. H. REYERSON (J. Physical Chem., 1927, **31**, 1332—1337).—The hydrogenation of acetylene using silica gels metallised with platinum, palladium, and copper has been studied by the method employed in the case of ethylene (this vol., 839). Ethylene and ethane are both produced, the palladium–silica gel becoming active at 50°, the platinum gel at 100°, and the copper gel at 200°. Palladium is the better catalyst for the production of ethylene, regardless of the original mixtures used, whilst platinum favours the production of ethane. Further, as the ratio of acetylene to hydrogen increases from 1 : 10 to 3 : 1, the production of ethylene passes through a maximum. It is probable that the combined adsorptions of gel and metal produce a more satisfactory condition for the catalysis of ethylene formation than does the adsorption of either alone. The ready production of ethylene is noteworthy, especially in view of the work of Ross, Culbertson, and Parsons (A., 1921, i, 761). L. S. THEOBALD.

Adsorption of hydrogen and ethylene on a copper catalyst poisoned with carbon monoxide. C. W. GRIFFIN (J. Amer. Chem. Soc., 1927, **49**, 2136—2145).—The above adsorption was investigated at 0° and 20° in the manner previously described (cf. A., 1923, ii, 842, 862). An increase of poison causes progressive decrease of adsorption at higher pressures, and an increase of adsorption at lower pressures, which, however, persists at higher pressures in the case of hydrogen than of ethylene. For either gas the smallest amount of poison causes the greatest increase or decrease of adsorption. The results

possibly indicate that each poison molecule is adsorbed on a very active centre and thereafter takes up hydrogen or ethylene molecules to such an extent that the total adsorption at low pressures is greater than on the unpoisoned catalyst. The poison, however, prevents dissolution of the hydrogen in the copper, so that at higher pressures the adsorption appears to decrease when the catalyst is poisoned. This explanation is not readily deduced in the case of ethylene. The extra sorption at low pressures does not leave the gases activated.

S. K. TWEEDY.

Catalytic combustion of ammonia in presence of alkaline surfaces. L. ANDRUSSOV (Z. anorg. Chem., 1927, **166**, 60—62).—The fact that the presence of alkaline surfaces in the catalytic oxidation of ammonia causes a quantitative yield of nitrites and nitrates, no nitrogen being produced, is readily explained by supposing that the nitroxyl formed as an intermediate stage in the oxidation (cf. B., 1927, 217) combines with the alkali, and is then oxidised to nitrite and nitrate, instead of breaking down with liberation of nitrogen. R. CUTHILL.

Rapid catalytic processes in currents of gases and the oxidation of ammonia. V. L. ANDRUSSOV (Ber., 1927, **60**, [*B*], 2005—2018; cf. B., 1926, 318).—The interaction of ammonia and oxygen when passed through heated platinum capillary tubes of varying length at 1100°±100° has been investigated. Even with very rapid currents of gas only traces of ammonia are present at the end of a sufficiently long capillary. If the capillary is sufficiently shortened, the great bulk of the ammonia is burnt immediately at the end of the capillary to nitrogen. A flame cone is then formed which, under certain conditions, can have a very unstable existence within the capillary. Under favourable conditions the cone is very stable and cannot be destroyed by great increase in the velocity of the gas. If oxygen is deficient, it does not appear. Nitric oxide is comparatively stable in the cone, but possible decomposition to the extent of 10% must be assumed, so that the actual change at the wall of the capillary is certainly 10—20% greater than is indicated by the yield of nitric oxide. The dependence of concentration distribution on the velocity of the gas current is examined in detail. The quantity of undecomposed ammonia increases very little with increasing velocity and considerable quantities of ammonia escape combustion on the explosion zone only with short capillaries. With excess of oxygen (more than 1·5—1·7 mols. O_2 to 1 mol. NH_3) the production of nitric oxide is little influenced by the initial concentration. At very great dilution ($O_2/NH_3>5$) slight diminution of the yield is observed, corresponding with a broadening of the reaction zone, but, in such cases, the mean temperature of the mixture is considerably lowered by the cooling effect of the excess of gas. With mixtures poor in oxygen the production of free nitrogen is still considerable, and undecomposed ammonia is first observed with an initial gas ratio $O_2/NH_3=1·3$. The thermal decomposition achieves increased importance and becomes more comparable with the actual combustion. The co-existence of free hydrogen and oxygen if the initial gases are in the ratio $O_2/NH_3<0·8$ is remarkable. H. WREN.

Decomposition of ammonia on iron catalysts. C. H. KUNSMAN (Science, 1927, **65**, 527—528).—The catalytic activity of iron catalysts (unpromoted iron catalyst, iron catalyst promoted with aluminium and potassium oxides, catalyst poisoned by tin) used in the synthesis of ammonia was investigated by the decomposition of ammonia on specially prepared surfaces. Values of E in Arrhenius' expression $Ae^{-E/RT}$ for the rate of chemical change are 38,000—42,000 g.-cal. per g.-mol. for the various catalysts, although the ratio in catalytic activity was 18·1. It is concluded that the primary effect of promoters on the iron catalysts is to increase the number of atoms on which decomposition takes place; that the effect of heat-treatment and poisoning is to decrease that number; and that poisoning, heat-treatment, or promoter action does not sufficiently alter the quality or nature of the atoms on which the reaction takes place to cause an appreciable change in the heat of activation.

A. A. ELDRIDGE.

Low-temperature oxidation at charcoal surfaces. IV. Active areas for different acids and relative rates of oxidation. W. M. WRIGHT (J.C.S., 1927, 2323—2330; cf. A., 1925, ii, 806; 1926, 582).—The rates of oxidation of formic, oxalic, malonic, and aminoacetic acids on charcoal surfaces, and the effect of poisoning by hexoic acid have been determined. Identical amounts of poison are required to inhibit the oxidation of all the acids, and the effective area is 4—8% of the total area. All except malonic acid are oxidised more rapidly on promoted charcoal prepared from sugar, carbamide, and ferric chloride. The depolarising capacities of the acids were measured, and follow the same order as the velocities of the reactions. C. W. GIBBY.

Chemical effect of electric discharge in ethane. S. C. LIND and G. GLOCKLER (Amer. Electrochem. Soc., Sept., 1927, advance copy, 9 pp.).—Ethane was submitted to a silent discharge in a Siemens ozoniser through which it was circulated continuously by means of an all-glass magnetic pump. Most of the ethane is decomposed in 3 hrs., yielding a gas consisting mainly of hydrogen, methane, and propane with smaller amounts of higher homologues, but as much as 45—55% of the ethane is converted into a very viscous, reddish-yellow oil, d 0·862, n^{20} 1·490. This oil has the composition C 85·48%, H 13·09%, and its apparent mol. wt. from f.-p. depression of benzene is 467. It readily forms substitution products with bromine. The production of 5 g. of oil requires about 10 kw.-hrs. The action of the silent discharge on ethane is compared with that caused by α-particles from radon (cf. A., 1926, 1077).

H. J. T. ELLINGHAM.

Nature of the activating radiation in photochemical action. W. TAYLOR and A. ELLIOT (Trans. Faraday Soc., 1927, **23**, 583—592; cf. this vol., . 216).—Actinic extinction curves have been obtained by allowing light filtered through various concentrations of chlorine to activate a mixture of hydrogen and chlorine. The results can be accounted for on the assumption that the efficiency is independent

of the frequency throughout the range 3500—5500, and that, for a given frequency, the activation is directly proportional to the light intensity. There is thus no evidence that there are two different types of absorption, "actinic" and "thermal," nor that activation is due to a few superposed bands, rather than to the whole general absorption band. This latter may account for the failure to separate isotopes of chlorine by photochemical methods, since the general absorption is continuous. The chlorine molecule absorbs the same actinic radiation when in the gaseous state as when dissolved in carbon tetrachloride. M. S. BURR.

Action of light on chlorine. G. B. KISTIAKOWSKY (J. Amer. Chem. Soc., 1927, **49**, 2194—2200).—Intensive drying of chlorine has no appreciable influence on the structure of its absorption spectrum or on the total amount of light energy absorbed. Less than 5% of the latter is re-emitted as fluorescence. It is difficult to reconcile these data with those theories requiring the presence of foreign molecules for the primary photochemical process in chlorine. It is suggested that chlorine is dissociated into atoms on absorption of light energy in the region of continuous absorption independently of its degree of purity; water is assumed to have a catalytic influence on the rate of recombination of the atoms and, therefore, also on the rate of thermal dissociation of chlorine molecules. S. K. TWEEDY.

Function of water vapour in the photosynthesis of hydrogen chloride. B. LEWIS (Nature, 1927, **120**, 473—474).—The Nernst atomic chain provides the most plausible mechanism for the photochemical union of hydrogen and chlorine. The chain cannot be initiated in the absence of water vapour, but there is no evidence that water vapour functions in the chain itself. Two mechanisms for the interaction of moist hydrogen and chlorine in visible light, and of dry hydrogen and chlorine in ultra-violet light are considered. The mechanism of the moist reaction is considered as involving a primary dissociation of the chlorine molecules under the influence of water vapour, followed by an atom chain—that of Nernst or of Thon. The dry reaction is regarded as involving activation of a chlorine molecule and its interaction with hydrogen molecules to form 2 mols. of hydrogen chloride. If water has a rôle in the chain mechanism, no chains should be propagated when a dry mixture of hydrogen and chlorine is exposed to α-radiation. A. A. ELDRIDGE.

Photosynthesis with ammonia. D. BURK (J. Physical Chem., 1927, **31**, 1338—1351).—Possible photochemical reactions between ammonia and various carbon compounds, including carbon dioxide, formic acid, formaldehyde, and dextrose, have been investigated. Sunlight condensed through 30 cm. lenses in combination with coloured inorganic catalysts was used, the exposures being made in very thin glass vessels. Some 500 experiments were made, but the results were generally negative, only one type of reaction being observed. This was the oxidation of ammonia, in the presence of ferric chloride, to nitrates, and in the presence of zinc or mercuric oxide, to nitrites and nitrates. Hydroxylamine and hydrogen peroxide were never produced. The zinc oxide to be effective must be in the solid state, and its previous exposure to sunlight enables the oxidation of aqueous ammonium salts to be accomplished in the absence of light. Photochemical reduction of carbon dioxide was not observed, and no complex nitrogen compounds could be produced from ammonia and carbon compounds. The positive photosynthesis claimed by Moore ("Biochemistry," 1921), by Dhar and Sanyal (A., 1925, ii, 884), and other workers is challenged. L. S. THEOBALD.

Photochemical oxidation of alcohols by the dichromate ion. E. J. BOWEN and C. W. BUNN (J.C.S., 1927, 2353—2358).—The photochemical oxidation of methyl, ethyl, *n*-propyl, and *iso*propyl alcohols by the dichromate ion has been investigated. The quantum efficiency is independent of the light intensity over a range of 1 : 80, of added acid above a certain limit, of dichromate-ion concentration between 0·1*N* and 0·01*N*, and of temperature between 15° and 50°. The reaction rate diminishes regularly with decreasing acid concentration. In acid solution aldehyde is formed without the production of any precipitate. In neutral and alkaline solutions the chromate ion is photochemically insensitive towards alcohols, and in neutral solution a precipitate of uncertain composition is formed. The mechanism of the reaction is discussed. C. W. GIBBY.

Photosynthesis of naturally occurring compounds. I. Action of ultra-violet light on carbonic acid. E. C. C. BALY, J. B. DAVIES, M. R. JOHNSON, and H. SHANASSY (Proc. Roy. Soc., 1927, A, **116**, 197—211).—When carbonic acid in aqueous solution is illuminated with ultra-violet light, a photostationary state is established, involving as one of the components a complex aldehyde. In an attempt to effect the photosynthesis of carbohydrates by the addition of a reducing agent to the carbonic acid solution, it was found that ferrous hydrogen carbonate in aqueous solution is converted by ultra-violet light in absence of oxygen into ferric hydroxide, organic compounds with reducing properties being formed simultaneously. This reaction appears to take place chiefly on the surface of the quartz tubes containing the solution, and also on the iron rods used. Complex organic compounds may be synthesised by the action of ultra-violet light on suspensions of various insoluble powders (aluminium powder, barium sulphate, freshly-precipitated aluminium hydroxide, and the basic carbonates of aluminium, magnesium, and zinc) in water through which a stream of carbon dioxide is maintained. Aluminium hydroxide which has been in contact with water for some hours loses its efficacy, due to the fact that it then has no affinity for carbonic acid. The organic compounds thus produced may be recovered by evaporation of the solution after removal of the insoluble powder, and appear to be of the nature of complex carbohydrates. Photosynthesis of complex organic compounds containing nitrogen takes place in presence of ammonium hydrogen carbonate or a soluble nitrite. Rigid proof is given that the carbon dioxide and other materials used were free from all organic impurity, and negative results were obtained

in control experiments in which powders incapable of adsorbing carbon dioxide were employed.

L. L. Bircumshaw.

Photosynthesis of naturally occurring compounds. II. Photosynthesis of carbohydrates from carbonic acid by means of visible light. E. C. C. Baly, W. E. Stephen, and N. R. Hood (Proc. Roy. Soc., 1927, **A**, **116**, 212—219).—Photosynthesis of organic compounds occurs when carbon dioxide, rigidly free from organic impurities, adsorbed on the surface of a fine coloured powder (nickel or cobalt carbonate) suspended in water, is exposed to visible light. The carbonates must be free from alkali, nitrate, chloride, and sulphate. One of the products of the photosynthesis is a carbohydrate which reduces Benedict's solution, gives well-marked Molisch and Rubner reactions, and forms a solid osazone. The reducing power of the photosynthesised compounds is materially increased by hydrolysis with hydrochloric acid. The total quantity of material photosynthesised by means of a coloured surface in visible light, and also the percentage reducing power, is greater than with a white surface in ultra-violet light (cf. preceding abstract). In this case, the products are not so liable to undergo photochemical decomposition. When moist nickel and cobalt carbonates are exposed to visible light in presence of carbon dioxide, a surface film of nickel and cobalt oxide, respectively, is formed, and it is found that the oxygen set free during the photosynthesis tends to poison the surface. Increased yields of the carbohydrates are obtained with unit quantity of light when the intensity of illumination is decreased, owing to the fact that the poisoned surface slowly recovers under water. When the surface has become completely poisoned the photosynthetic process ceases, and then with intense illumination the carbohydrates previously formed are photochemically decomposed. Complex nitrogen compounds may be photosynthesised by exposing to visible light ammonium hydrogen carbonate solution containing nickel or cobalt carbonate in suspension.

L. L. Bircumshaw.

Photosynthesis of naturally occurring compounds. III. Photosynthesis *in vivo* and *in vitro*. E. C. C. Baly and J. B. Davies (Proc. Roy. Soc., 1927, **A**, **116**, 219—226).—A marked similarity is shown to exist between the laboratory photosynthesis of complex carbohydrates in a single operation from carbonic acid (cf. preceding abstracts) and the natural process of photosynthesis in the living leaf. In neither case does ordinary formaldehyde take part in the reaction. The photosynthesis *in vitro* has been achieved by the action of light on carbonic acid adsorbed on a surface, and there are strong indications that a limiting surface exists in the chloroplast and is necessary for the occurrence of the normal photosynthesis. In each case a visibly coloured surface and visible light are involved. The fatigue effect observed when the living leaf is exposed to too long and intense illumination may be compared with the fatigue effect observed in the laboratory, due to poisoning of the surface by oxygen. In both processes there is a slow recovery reaction, and it appears that in both, the rate of photosynthesis must not exceed the rate of this slow reaction. It appears that the yield of carbohydrates photosynthesised *in vitro* per hr. per cm.^{2} of surface is not greatly at variance with that observed in nature. It is suggested that the constant ratio of chlorophyll-*A* to chlorophyll-*B*, observed by Willstatter and Stoll in the living leaf, is maintained by the carotin, which becomes oxidised to xanthophyll, and that, since the xanthophyll : carotin ratio tends to increase during photosynthesis, the slow recovery process present in the leaf is that in which the xanthophyll is reduced again to carotin.

L. L. Bircumshaw.

Photochemical rearrangement of acetylchloroaminobenzene. C. W. Porter and P. Wilbur (J. Amer. Chem. Soc., 1927, 49, 2145—2149).—The ultra-violet absorption spectra of acetylchloroaminobenzene and its isomeride, *p*-chloroacetanilide, are recorded. Conversion into the isomeride occurs in the solid state in the radiation of a mercury vapour lamp, and also at 100°. The change is rapid above the m. p. Mechanisms involving intermediate products cannot apply to the reaction in the solid phase.

S. K. Tweedy.

Optical sensitisation with dyes. K. Burgherr (Z. wiss. Phot., 1927, 24, 393—408).—When a molecule of sensitiser absorbs a quantum of light and enters the phototropic state, it acquires an electrical polarisation designated E{± and the positive and negative poles in the molecule act as cathode and anode in a kind of molecular electrolysis. The idea is illustrated in the photolysis of a solution of ammonium oxalate and mercuric chloride in the presence of eosin,

$$E\{^{+}_{-} + HgCl_2 \longrightarrow^{\longrightarrow CO_2} HgCl + Cl'.$$

Using silver nitrate and sucrose, glycine, or glycerol as cathodic and anodic depolarisers, respectively, the sensitising action of the following dyes has been studied: rhodamine-*B*, eosin, safranine-*G*, phenosafranine, fluorescein, methyl-violet, chromotrope-2*R*. The photolysis results in the separation of silver (which can be determined by means of ammonium thiocyanate) and the concomitant formation of oxidation products. Some silver was liberated in the binary systems silver nitrate–dye, silver nitrate–sucrose, but a larger amount was set free in the ternary systems composed of dye and depolarisers.

The sensitised photolysis very soon reaches a stationary state, apparently owing to the formation of a new anodic depolariser which begins to compete with the existing depolariser. Experiments carried out with air-containing and air-free solutions show that the most likely agent for this effect is the finely-divided silver, *i.e.*, $E\{^{+}_{-} + Ag^{\cdot} \longrightarrow^{\longrightarrow Ag^{\cdot}} Ag$

The experiments with glycine and glycerol show that these substances can be further oxidised, so that it is not possible to ascribe the stationary state to their appearance as the first decomposition products of sucrose. The investigation lends support to the inner polarisation mechanism for sensitisation.

R. A. Morton.

Light sensitivity of guaiacum resin and its possible application in photography. C.

SCHWECKENDIEK (Diss., Giessen, 1927).—Guaiaconic acid, like guaiaretic acid, is sensitive to light, the sensitivity being increased by the addition of collodion, Zapon lacquer, or a solution of sulphur in carbon disulphide. The green image is fixed with a mixture of ammonium acetate and benzene. The insolubilising action of light on guaiaretic acid is an oxidation process. CHEMICAL ABSTRACTS.

Mechanism of formation of the latent photographic image. F. C. TOY (Nature, 1927, **120**, 441).—Although the formation of the latent photographic image does not appear to be due to a complete liberation of electrons from silver bromide crystals, it appears to be closely connected with the photo-conductivity effect. Experimental evidence is adduced in support of the view that the formation of the latent image involves the transfer of valency electrons from bromide ions to silver ions, resulting in the production of metallic silver and free bromine. The observed decrease in photo-conductivity in the violet and its absence in the ultra-violet portion of the spectrum are due to the thickness of the film employed. A. A. ELDRIDGE.

Chemical reactions in the gaseous phase in electromagnetic fields of high frequency. R. MOENS and A. JULIARD (Bull. Acad. roy. Belg., 1927, [v], **13**, 201—205; cf. *ibid.*, 72).—In an attempt to investigate the chemical behaviour of gases in electromagnetic fields of high frequency, the changes produced in certain gases and gaseous mixtures by the passage of an electrodeless discharge were followed manometrically. The discharge usually appears at pressures of the order of 1 cm. and in the case of simple gases, *e.g.*, hydrogen, oxygen, nitrogen, is accompanied by an increase of pressure. On interruption of the discharge the pressure falls instantly to a value indicative of a contraction or an expansion depending on the nature of the gas and the duration and intensity of the discharge. A mixture of 2 vols. of hydrogen and 1 vol. of oxygen shows a contraction corresponding with complete conversion into water vapour. Although a mixture of 3 vols. of hydrogen and 1 vol. of nitrogen shows a slight expansion, in presence of sulphuric acid the pressure falls almost to zero. A mixture of hydrogen and carbon di(?)oxide shows a slight expansion, but returns to the initial pressure after the passage of the discharge even in presence of concentrated sulphuric acid. Mixtures of nitrogen and oxygen undergo an appreciable expansion, the pressure, however, returning to its original value on interruption of the discharge. Acetylene and benzene yield solid deposits, the pressure falling to almost zero. Ethyl ether and ethyl and amyl alcohols are decomposed and the volume is increased almost threefold. With carbon disulphide and carbon tetrachloride the discharge appears only at pressures of the order of 1 mm. J. S. CARTER.

Hydrates of lithium chlorate. L. BERG (Z. anorg. Chem., 1927, **166**, 231—236).—A *monohydrate* of lithium chlorate, $LiClO_3,H_2O$, may be prepared by cooling a solution of composition corresponding with the formula to below −25° and adding a few crystals of the hydrate $3LiClO_3,H_2O$ (A., 1926, 1014). A *trihydrate*, $LiClO_3,3H_2O$, separates from the corresponding solution at −20°. R. CUTHILL.

Phosphates. V. Hydration of sodium monometaphosphate in alkaline solution at 75°. S. J. KIEHL and H. P. COATS (J. Amer. Chem. Soc., 1927, **49**, 2180—2193; cf. this vol., 312).—The hydration of sodium monometaphosphate (for which crystallographic data are recorded) in sodium hydroxide solution was investigated at 75° in silver vessels. Both pyro- and ortho-phosphate in equimolecular quantities are end-products of the hydration: $3NaPO_3+2H_2O=Na_2H_2P_2O_7+NaH_2PO_4$. The rate of hydration increases with increase in the sodium hydroxide concentration. Pyrophosphate is precipitated in presence of orthophosphate by adjusting the hydrogen-ion concentration of the solution to 5×10^{-4} mol./litre (by addition of acetic acid) and adding zinc acetate solution of the same hydrogen-ion concentration. Orthophosphate may be determined in the filtrate. S. K. TWEEDY.

Influence of the concentration of hydrogen ions on the displacement of copper from its solutions at high pressures and temperatures. V. IPATIEV and V. IPATIEV, jun. (Ber., 1927, **60**, [*B*], 1982—1986).—The action of hydrogen on solutions of copper formate and acetate between 90° and 180° at pressures between 0 and 150 atm. and at acidities between 0 and 12·0*N* has been investigated. In neutral solution at 100° hydrolysis occurs with consequent separation of copper oxide, which is only with difficulty reduced by hydrogen. In the presence of acid, this hydrolysis is repressed and the dissolved cupric salt is reduced to the corresponding cuprous salt. If the hydrogen-ion concentration is insufficient, the cuprous salt is hydrolysed and crystalline cuprous oxide separates from the solution. If, however, the hydrogen-ion concentration is sufficient to inhibit hydrolysis, an actual displacement of copper from the cuprous salt occurs. At a sufficiently high temperature (130—180°), the anions of formic and acetic acids become decomposed with production of hydrogen, which, according to the degree of acidity of the solution, causes separation of cuprous oxide or metallic copper. H. WREN.

Reduction of copper sulphate by sodium hypophosphite. S. RAMACHANDRAN (Chem. News, 1927, **135**, 214—216).—Copper sulphate is reduced by sodium hypophosphite in aqueous solution only when acidified to a definite extent. The temperature required is the higher the greater is the proportion of hypophosphite present. C. W. GIBBY.

Composition and behaviour of precipitated copper and iron sulphides. F. FEIGL [with E. BACKER and L. ROSENBERG] (Z. anal. Chem., 1927, **72**, 32—43).—Copper sulphide, freshly precipitated by hydrogen sulphide, consists chiefly of cupric sulphide with small quantities of cuprous sulphide and sulphur, but on keeping, the cupric sulphide continues to decompose into cuprous sulphide and sulphur. The extent of the decomposition was determined by replacing the copper by mercury, boiling with sodium sulphite solution, and determining with iodine the thiosulphate formed. The pre-

cipitate obtained in an alkaline solution is a mixture of the two sulphides, but, as before, the composition of the fresh precipitate is dependent on the conditions of precipitation. The precipitate obtained by mixing a ferric salt and ammonium sulphide, of empirical formula Fe_2S_3, was treated with mercuric chloride solution. Ferrous chloride was formed and free sulphur was found in the precipitate. This indicates that the compound has the formula FeS,FeS_2, as the possible reactions with mercuric chloride are $Fe_2S_3+3HgCl_2=3HgS+2FeCl_3$, and $FeS,FeS_2+2HgCl_2=2HgS+S+2FeCl_2$. F. S. HAWKINS.

Crystallisation of some hydroxides. R. FRICKE [with C. GOTTFRIED, W. SKALIKS, A. MUNCHMEYER, and F. ENGELHARDT] (Z. anorg. Chem., 1927, **166**, 244—256).—The conditions for the production of various hydroxides in the crystalline state have been investigated. Varieties of beryllium hydroxide which give the same *X*-ray diagram but differ in crystalline form may be obtained by slow hydrolysis of sodium beryllate in aqueous solution, and by allowing a 40% solution of sodium hydroxide saturated with amorphous beryllium hydroxide at the b. p. to cool slowly. Beryllium hydroxide aged with ammonia (Haber and van Oordt, A., 1904, ii, 257) has a quite different crystal structure. The solubility in sodium hydroxide solutions at 30° of the form obtained by hydrolysis of sodium beryllate in the cold is maximal for solutions containing about 33% of sodium hydroxide; for lower concentrations the solid phase is beryllium hydroxide, whereas for higher concentrations it is sodium beryllate. One form of crystalline zinc hydroxide may be obtained by slow hydrolysis of alkali zincate solutions at the ordinary temperature, or by ageing the amorphous hydroxide under weak acids such as phenol. A metastable variety differing both in crystalline form and structure is produced by diluting zincate solutions very considerably. Zinc hydroxide precipitated with a slight excess of sodium hydroxide from a solution of a zinc salt represents a third modification. Slow hydrolysis of alkali aluminate solutions gives a form of aluminium hydroxide which at first has the crystalline structure of hydrargillite, but after keeping for some years gives an *X*-ray diagram which belongs neither to hydrargillite nor to bauxite. Specimens of magnesium hydroxide obtained by precipitating magnesium sulphate with sodium hydroxide in the cold, or by precipitating the chloride with ammonia in the cold, or by precipitating a mixed solution of magnesium and ammonium chlorides with ammonia at 60° and ageing the precipitate in contact with the supernatant liquor at 30° all have the same crystalline structure, and there seems to be no evidence for the existence of two allotropic forms as suggested by Gjaldback (A., 1925, ii, 652). R. CUTHILL.

Boric acids and alkali borates. III. Solid alkali mono- and poly-borates. H. MENZEL [with J. MECKWITZ] (Z. anorg. Chem., 1927, **166**, 63—98; cf. this vol., 937).—The literature relating to those borates of the alkali metals which can be crystallised from aqueous solution is critically reviewed, and supplemented in some cases with solubility determinations at 18° and 25° and with isothermal dehydration experiments with the hydrates. *X*-Ray diagrams and dehydration experiments show that the removal of the last molecule of water from the hydrates of sodium monoborate is accompanied by a change in the structure of the crystal. With the diborate it is apparently the last three water molecules which are of structural importance, but the pentahydrate stable above 60° appears to occupy an exceptional position. The pentahydrate of potassium pentaborate reported by Hermans (A., 1925, i, 500) seems to have been the tetrahydrate. Attempts to prepare an ammonium monoborate by treating the tetrahydrate of the diborate with ammonia have been fruitless, although it is apparently possible in this way to replace 1 mol. of the water of crystallisation with an ammonia molecule. The structure of the polyborates has been worked out with the aid of Hermans' theory of the constitution of boric acid (A., 1925, ii, 697). R. CUTHILL.

Reduction of refractory oxides by tungsten at high temperatures. H. VON WARTENBERG and H. MOEHL (Z. physikal. Chem., 1927, **128**, 439—444).—Oxides such as those of aluminium, zirconium, and thorium are reduced by metallic tungsten at 2000° in an atmosphere of nitrogen, volatile tungsten dioxide being produced. H. F. GILLBE.

Aluminium sulphate and its hydrates. Double sulphates and their components. II. F. KRAUSS and A. FRICKE (Z. anorg. Chem., 1927, **166**, 170—176).—Dehydration of the hydrate $Al_2(SO_4)_3,27H_2O$ in the tensi-eudiometer points to the existence of hydrates with 27, 18, 16, 10, and 6 mols. of water. The anhydrous salt commences to lose sulphur trioxide at 605°. R. CUTHILL.

Displacement of metals or their oxides from solutions by hydrogen under pressure. Separation of crystalline hydroxides of aluminium and chromium from solutions of their salts at high temperatures and under high pressures. V. IPATIEV and B. MOUROMTSEV (Ber., 1927, **60**, [*B*], 1980—1982).—For the separation of crystalline hydroxides of aluminium and chromium the acidity of the solution is of primary importance. A solution of the requisite nitrate, acidified with nitric acid, is placed in a golden tube (or silica tube if the temperature does not exceed 330°) and brought under pressure of hydrogen or air in the high-pressure apparatus. The temperature is varied between 320° and 360°, pressure between 200 and 370 atm., and duration between 12 and 24 hrs., although the change is complete in 12 hrs. At lower pressures amorphous products separate. Aluminium nitrate or acetate in the presence of nitric or acetic acid and hydrogen or air gives the monohydrated oxide with all the properties of the mineral diaspore. Neutral aluminium nitrate in presence of air gives a scarcely crystalline precipitate. Chromium nitrate in nitric acid solution under the influence of hydrogen gives monohydrated chromium oxide closely resembling chrome ochre. If air is used in place of hydrogen, smaller crystals are obtained and the separation is not quantitative, a portion of the oxide being converted into chromic acid. Small amounts of dark red crystals are also occasionally obtained. H. WREN.

Azidodithiocarbonic acid. IV. Ammonium and tetramethylammonium azidodithiocarbonates; tetramethylammonium thiocyanate. L. F. Audrieth, G. B. L. Smith, and A. W. Browne [with C. W. Mason] (J. Amer. Chem. Soc., 1927, **49**, 2129—2133).—*Ammonium azidodithiocarbonate*, NH_4SCSN_3, is obtained by neutralising azidodithiocarbonic acid with aqueous ammonia or, preferably, in ethereal solution, with gaseous ammonia. It is also formed by the prolonged action of carbon disulphide on aqueous ammonium azide solution (cf. Browne and Hoel, A., 1922, ii, 848). It forms white, non-deliquescent, orthorhombic plates, soluble in water, alcohol, and acetone, but insoluble in benzene; m. p. 120° (decomp.): $NH_4SCSN_3=NH_4SCN+S+N_2$. The salt becomes orange when heated at 90° or on illumination, the change in the latter case being partly reversible. *Tetramethylammonium azidodithiocarbonate* is best prepared by digesting an aqueous solution of tetramethylammonium azide with a slight excess of carbon disulphide ($NMe_4N_3+CS_2=NMe_4SCSN_3$). Its properties are similar to those of the ammonium compound; m. p. 95—98° (decomp.). Tetramethylammonium thiocyanate is conveniently prepared by boiling under reflux an alcoholic solution of tetramethylammonium azide with carbon disulphide. It does not undergo molecular rearrangement into tetramethylthiocarbamide. Crystallographic data are recorded for each of the above compounds.

S. K. Tweedy.

Formation of crystalline silicates in an aqueous medium under pressures and at high temperatures. V. Ipatiev and B. Mouromtsev (Compt. rend., 1927, **185**, 647—649; cf. A., 1926, 1219).—Silicic acid or silicate gels obtained by a double decomposition reaction may be converted into crystalline forms by heating at a constant temperature for 2—3 days in a silver tube containing hydrogen or carbon dioxide under pressure. Any oxides formed are removed by means of hydrochloric acid. The product obtained depends on the conditions, and on the presence or absence of small amounts of impurities. Thus, crystalline SiO_2 and $5SiO_2,2H_2O$ are produced using hydrogen and carbon dioxide, respectively, and silicates of magnesium, calcium, manganese, aluminium, zinc, and iron of varying compositions have also been obtained. The crystalline compound $5SiO_2,3H_2O$ was obtained from a manganese silicate gel free from any soluble manganese salt.

J. Grant.

Action of stannous chloride on silver mirror formation. O. Macchia (Chem. News, 1927, **135**, 197—200).—The formation of a silver mirror and its adherence to a glass plate are greatly facilitated by previous immersion (10 sec.) of the plate in a dilute solution (preferably 1 in 2000) of stannous chloride. The effect is attributed to the deposition of a very adherent film of gelatinous stannous hydroxide, formed by the hydrolysis of the stannous chloride, and was observed for plates of glass, cellulose, wood, and galatite.

G. A. Elliott.

Chromium carbonyl. A. Job and A. Cassal (Bull. Soc. chim., 1927, [iv], **41**, 1041—1046).—The solution obtained by the action of carbon monoxide on magnesium ethyl or phenyl bromide (this vol., 865) is hydrolysed with sulphuric acid at 0°, and the ethereal layer is separated, neutralised, and dried, after which the ether is evaporated. When magnesium ethyl bromide is used, crystals of *chromium carbonyl*, $Cr(CO)_6$, separate during the evaporation; otherwise, the residue has to be sublimed under reduced pressure. By grinding the product under benzene and resubliming at 160°, the pure carbonyl is obtained as colourless, orthorhombic crystals, d^{18} 1·77, slightly soluble in benzene and ether, but more soluble (2%) in chloroform and carbon tetrachloride, the solutions being stable only in the dark. The crystals decompose rapidly at 210° into chromic oxide; in a sealed tube they melt at 149—150° and irreversibly deposit a chromium mirror at 230°. The carbonyl is unattacked by dilute acids, bromine, and iodine; fuming nitric acid converts it into chromic nitrate and free carbon.

S. K. Tweedy.

Co-ordination compounds of quinquevalent molybdenum. R. G. James and W. Wardlaw (J.C.S., 1927, 2145—2156).—Physical and chemical properties of salts of the type $R_2[MoOCl_5]$ have been investigated, and a scheme of their hydrolysis and ionisation is outlined. The preparation of *diquinolinium molybdenyl pentachloride*, $(C_9H_8N)_2MoOCl_5,H_2O$, *monotrimethylammonium molybdenyl tetrachloride*, $NHMe_3MoOCl_4,H_2O$, and *dimolybdenum tetraoxyhydroxychloride*, $Mo_2O_4(OH)Cl,3\frac{1}{2}H_2O$ is described.

C. W. Gibby.

Oxygen compound of fluorine. P. Lebeau and A. Damiens (Compt. rend., 1927, **185**, 652—654).—In the presence of water the method for the preparation of fluorine by electrolysis of molten acid potassium fluorides below 100° results also in the production of a gaseous oxygen compound of fluorine. The compound is less active chemically than fluorine, and studies of its mixtures with oxygen point to the formula F_2O. Such mixtures have the odour of fluorine, but are stable in the presence of water and of glass even at high temperatures. The gas, which was not isolated in the pure state, liberates iodine from potassium iodide, is soluble in alkali, but only sparingly soluble in water.

J. Grant.

Chloro-acids. R. Schwarz and G. Meyer (Z. anorg. Chem., 1927, **166**, 190—212).—Attempts have been made to detect the combination of hydrogen chloride with various chlorides by determining pressure isotherms with the aid of the tensi-eudiometer. In no instance does any combination occur in absence of water, and in the case of the tetrachlorides of silicon and titanium no chloro-acid is formed owing to hydrolysis. With ferric chloride, it is probable that the compounds $Fe_2Cl_6,3HCl,9H_2O$, $Fe_2Cl_6,4HCl,11H_2O$, $Fe_2Cl_6,5HCl,12H_2O$ and $FeCl_3,3HCl,7H_2O$ are capable of existence. Hexa-aquochromic chloride forms no compounds, but dichlorotetra-aquochromic chloride dihydrate apparently gives rise to the compounds $CrCl_3,HCl,6{\cdot}5H_2O$, $CrCl_3,2HCl,8{\cdot}5H_2O$, and $CrCl_3,3HCl,10{\cdot}5H_2O$. Aluminium chloride forms no compounds.

R. Cuthill.

Manganese molybdates. F. Zambonini and V. Caglioti (Rend. Accad. Sci. fis. mat. Napoli, 1927,

[iii], **33**, 181—203).—Irrespective of variations in the method of preparation, a single compound having the formula $4(NH_4)_2O,Mn_2O_3,13MoO_3,9H_2O$, is obtained. This is identical with that described by Struve (J. pr. Chem., 1854, **61**, 449), Friedheim and Samelson (A., 1900, ii, 547), and Friedheim and Alleman (Mitt. naturf. Ges. Bern, 1904, 23). As appears from the ratio $Mn_2O_3 : MoO_3$ the manganese is to be considered present in the bi- and quadri-valent states, the formula being $[Mn^{\cdots\cdot}(Mo_2O_7)_6](NH_4)_8,Mn^{\cdot\cdot}MoO_4,9H_2O$. This confirms Struve's result that manganese in the form of Mn_2O_3 may be considered to be MnO and MnO_2, and also Péchard's suggestion that the ratio $MnO_2 : MoO_3$ is 1 : 12 in analogy to the silicomolybdates. M. Carlton.

Sublimation of iron in a vacuum. E. Botolfsen (Compt. rend., 1927, **185**, 649—650).—Iron may be sublimed in a high vacuum at temperatures below its m. p. The effect is independent of the origin of the iron and of the presence of certain substances likely to act as catalysts, and at 1300° its rate is of the order of 0·07% per hr. The sublimate takes the form of a thick deposit of metallic crystals, and is almost pure. J. Grant.

Ferric thiocyanate. K. C. Bailey (J.C.S., 1927, 2065—2069).—The red compound produced by dissolving ferric hydroxide in thiocyanic acid is found, by a repetition of the work of Tarugi (A., 1905, i, 176; 1926, 259), to be ferric thiocyanate. No evidence is obtained in favour of his formula $FeHC_3N_3S_3O_3$. C. W. Gibby.

Preparation of low-conductivity water. G. D. Bengough, J. M. Stuart, and A. R. Lee (J.C.S., 1927, 2156—2161).—Improvements in Bourdillon's still (J.C.S., 1913, **103**, 791) are described. About 4 litres of water per day can be produced, with a conductivity of 0·065 gemmho. C. W. Gibby.

Germanium. XX. Preparation of fused germanium directly from germanium dioxide. (Miss) K. M. Tressler and L. M. Dennis (J. Physical Chem., 1927, **31**, 1429—1432).—Fused, metallic germanium has been prepared by reduction of the dioxide with carbon under a flux of sodium chloride in a graphite crucible heated in an induction furnace. A 90% yield of the metal, containing approximately 1% of dioxide and other impurities in amount not greater than 0·01%, was obtained. Of the germanium lost, 70% can be recovered. Slight modifications in the method should make this loss negligible. Preparation of germanium by electrolysis of the dioxide dissolved in molten cryolite, or molten potassium fluogermanate, and by reduction of the dioxide with aluminium resulted in heavy losses of germanium as germanous oxide. L. S. Theobald.

Precautions [against explosion] in preparing lead bromate. Victor (Z. angew. Chem., 1927, 40, 841).—Fatal explosions have occurred when lead bromate, prepared by interaction of lead acetate and potassium bromate (cf. Gmelin-Kraut's "Handbuch," IV, 376) has been pulverised. The sensitivity to shock is due to the presence of diacetodiplumbous bromate (Günzel and Marcus, A., 1925, ii, 1086). W. A. Silvester.

Elementary method of qualitative analysis without the use of hydrogen sulphide, thioacetic acid, or sulphides. O. Macchia (Notiz. chim.-ind., 1927, 2, 191—196).—A detailed scheme is presented. Chemical Abstracts.

Continuous electro-conductivity titration. E. Butterworth (Mem. Manchester Phil. Soc., 1926—1927, 71, 53—62).—A new continuous-reading method of electro-conductivity titration is described, giving an accuracy of 0·2—0·3%. The sensitivity is easily controlled within wide limits. C. W. Gibby.

[Absolute] potentiometric titration. B. Cavanagh (J.C.S., 1927, 2207—2216).—A new absolute method of potentiometric titration is described for strong acids and halides, in which no potentiometer, standard cell, or normal electrode is required. It can be used for very dilute solutions and with very small quantities of liquids, and a high degree of accuracy is obtained. C. W. Gibby.

Effect of sodium hydrogen carbonate on the titration of iodine with thiosulphate. O. E. Schupp, jun. (Science, 1927, **65**, 284).—Low values, due to the formation of hypoiodite and iodide, and oxidation of the thiosulphate to sulphate, are obtained if the iodine solution is initially neutral and sodium hydrogen carbonate is added. The results for an initially acid solution containing less than *N*-sodium hydrogen carbonate are as accurate as those for a neutral solution of iodine. A. A. Eldridge.

Determination of sulphuric acid in water analysis by means of benzidine. L. W. Haase. —See B., 1927, 798.

Analysis of polythionate solutions. A. Kurtenacker and E. Goldbach (Z. anorg. Chem., 1927, **166**, 177—189).—Billeter and Wavre's sulphide method of determining trithionate (A., 1918, ii, 330), depending on the reaction $S_3O_6'' + S'' = 2S_2O_3''$, has been extended to tetra- and penta-thionates, both together and separately, and to mixtures of these with trithionate, the reactions being $S_4O_6'' + S'' = 2S_2O_3'' + S$, and $S_5O_6'' + S'' = 2S_2O_3'' + 2S$. Sulphite present along with trithionate only does not interfere with the determination if it is first caused to combine with formaldehyde, but if tetra- or penta-thionate is also present the sulphite combines with the sulphur produced in the above reactions to form thiosulphate. This difficulty may be overcome by first titrating the sulphite with iodine, or as follows. The solution for analysis is heated for 10 min. at a temperature near the b. p. with 20 c.c. of 0·4*N*-sodium sulphide and 20 c.c. of 0·4*N*-sodium sulphite, and the excess of sulphide then precipitated with zinc acetate or carbonate. An aliquot portion of the filtrate is mixed with 5 c.c. of 40% formaldehyde, acidified with 10 c.c. of 20% acetic acid, and titrated with iodine. In this case, the tetra- and penta-thionate radicals react according to the equations $S_4O_6'' + S'' + SO_3'' = 3S_2O_3''$ and $S_5O_6'' + S'' + 2SO_3'' = 4S_2O_3''$. By means of this method and those previously published (A., 1924, ii, 497, 564; 1925, ii, 239, 434, 1189; this vol., 534, 638) a mixture of tri-, tetra-, and penta-thionates, thiosulphate, hydrogen sulphite, and hydrogen sulphide can be analysed. R. Cuthill.

Volumetric determination of azoimide by oxidation with ceric sulphate in acid solution. J. MARTIN (J. Amer. Chem. Soc., 1927, **49**, 2133—2136).—The nitrometer method of determining azoimide (Sommer and Pincas, A., 1916, ii, 97) : $2Ce^{\cdots\cdot}+2HN_3=3N_2+2H^{\cdot}+2Ce^{\cdots}$, may be applied iodometrically; the reaction is carried out with the exclusion of air in a closed vessel, excess of potassium iodide is added, and the liberated iodine titrated with standard thiosulphate. Hydrazine must be absent (azoimide may be separated from it by distillation), but the ammonium ion may be present. The acid concentration must be kept low. S. K. TWEEDY.

Colorimetric determination of carbon monoxide with ammoniacal silver solution. H. KAST and A. SCHMIDT.—See B., 1927, 748.

Conversion of alkali chlorides into carbonates by means of oxalic acid. L. N. MURAVLEV (Z. anal. Chem., 1927, 72, 15—19).—The reactions involved are not quantitative. The conversion of chloride into oxalate is not complete, and the formation of carbonate from oxalate is finished only at temperatures high enough to cause loss by volatilisation. The smallest error was 0·48%. F. S. HAWKINS.

Volumetric determination of potassium. G. JANDER and O. PFUNDT (Z. anal. Chem., 1927, **71**, 417—434).—Potassium may be determined by conductometric titration with sodium perchlorate if the solution used is at least 0·3*N* with respect to potassium and the perchlorate solution is 5—6*N*. To reduce the solubility of the precipitated potassium perchlorate to a minimum the titration is carried out in a vessel cooled with ice; under these conditions the supernatant liquid above the precipitate at the end of the titration is 0·01*N* with respect to potassium. The presence of magnesium sulphate, sodium chloride, and calcium chloride is without effect on the results, so that the process is applicable to the control of liquors obtained in the potash industry. The end-point is sharp and the results are good when the solution is standardised against a potassium solution containing the same quantity of the metal as the trial. A. R. POWELL.

Determination of potassium and sodium in the presence of each other. A. MEYER (Chem.-Ztg., 1927, **51**, 778).—The metals are first weighed as chloride (or sulphate), the mixed salts dissolved, and either the chlorine is determined titrimetrically, or the sulphuric acid gravimetrically. In the latter case, to prevent the presence of traces of hydrogen sulphate, the salts should first be evaporated with ammonium carbonate. The proportions determined algebraically in the usual way are subject to a smaller error than those obtained by weighing the chlorides and sulphates. B. P. RIDGE.

Determination of sodium. D. I. PERIETEANU (Bul. Soc. chim. Romania, 1927, 9, 17—18).—Sodium is determined as the salt $3UO(C_2H_3O_2)_2,Mg(C_2H_3O_2)_2,Na(C_2H_3O_2)$ by precipitation with an acetic acid solution of magnesium and uranium acetates. After ¼ hr., the precipitate is collected in a Gooch crucible, washed three times with the reacting liquid, three times with 95% alcohol, and dried for 30 min. at 105°. Only phosphates interfere with the reaction, and small quantities of sodium can be determined. F. S. HAWKINS.

Microchemical reactions of beryllium. V. CAGLIOTI (Rend. Accad. Sci. fis. mat. Napoli, 1927, [iii], **33**, 177—180).—The usual microchemical methods of determining beryllium by means of the double oxalate of potassium and beryllium and of the chloroplatinate and sulphate are not entirely satisfactory. The most satisfactory results are obtained by Streng's reaction involving the formation of uranyl sodium beryllium acetate, $(UO_2)_3BeNa(OAc)_9.9H_2O$, as pale yellow, rhombohedral crystals. The presence of aluminium does not affect the reaction, but iron must be carefully removed.

For microchemical research the most satisfactory method of determining beryllium is by formation of beryllium acetylacetonate (cf. Jaeger, A., 1914, i, 797) as clear, colourless, monoclinic prisms which on examination under the microscope show very characteristic interference figures. M. CARLTON.

Application of Kolthoff's reaction for magnesium in plant microchemistry. H. EILERS (Chem. Weekblad, 1927, **24**, 448—450; cf. Kolthoff, this vol., 639).—The reaction with titan-yellow is not specific for magnesium in plant tissue, but may be employed if the test is carried out after removal of oils, fats, and resins on tissue before and after treatment with dilute acid, and the colorations obtained in the two cases are compared. S. I. LEVY.

Diphenylamine [acetate] as a qualitative reagent for zinc. W. H. CONE and L. C. CADY (J. Amer. Chem. Soc., 1927, **49**, 2214—2215).—The group filtrate containing chromium and zinc is acidified with acetic acid and chromium is tested for on one portion. To the remainder 5 drops of a solution of 1 g. of diphenylamine (or diphenylbenzidine) in 100 c.c. of glacial acetic acid and 5 c.c. of 0·5% aqueous potassium ferricyanide solution are added. The presence of zinc is indicated by a turbidity, the darkness of which increases with the amount of zinc present. Unless its concentration exceeds 10 mg./c.c., potassium dichromate does not influence the test. Contrary to the statement of Knop (A., 1924, ii, 351), diphenylamine sulphate immediately produces a blue coloration with potassium dichromate at concentrations greater than 0·05 mg./c.c. S. K. TWEEDY.

Rapid separation of lead and silver by a potentiometric method. E. MULLER and H. HENTSCHEL (Z. anal. Chem., 1927, 72, 1—5).—The metals are determined by titrating the solution first with sodium chloride, and observing the potentials with a silver electrode, and then with potassium ferrocyanide, using a platinum electrode. The potentials measured against a normal calomel electrode at which the titrations are finished are 0·23 volt and 0·36 volt, respectively; and the titration is carried out by applying these voltages to the cell, and titrating until no current flows. Accurate titration of the silver with potassium iodide is prevented by adsorption phenomena and the separation of lead iodide. F. S. HAWKINS.

Determination of lead in bismuth by spectrum analysis. III. E. SCHWEITZER (Z. anorg. Chem.,

1927, **165**, 364—370).—The spectrum of bismuth containing lead is coupled with that of tin containing lead by making the times of exposure of the photographic plate such that a selected line in the bismuth spectrum appears of the same intensity as a selected line in the tin spectrum. This pair of lines is chosen by photographing the spectra of tin and bismuth each containing the same relative number of atoms of lead under such conditions that the lead lines in one spectrum have the same intensity as those in the other spectrum. If the two spectra are related in this way, corresponding lead lines are always equally intense whenever the lead concentrations in the main metal are the same. The lead in a sample of bismuth may therefore be determined by coupling its spectrum with that of pure tin, and searching for a lead line and a tin line of equal intensity, as previously described (this vol., 845). R. CUTHILL.

Use of titanous chloride in the volumetric determination of copper and iron. W. G. EMMETT (J.C.S., 1927, 2059—2062).—In determining cupric or ferric salts by titration with titanous chloride in presence of potassium thiocyanate as an indicator, error may be introduced by the decomposition of ferric and cupric thiocyanates. By carrying out the titration in cold acid solution immediately after adding the thiocyanate the error may be reduced below 0·2%. The preparation of a standard copper solution by dissolving electrolytic copper in a solution of sodium peroxide in hydrochloric acid is recommended.

C. W. GIBBY.

Sensitive reaction for aluminium and colorimetric determination of this element. I. M. KOLTHOFF (Chem. Weekblad, 1927, **24**, 447—448).—1 : 2 : 5 : 8-Tetrahydroxyanthraquinone gives an intense violet coloration with aluminium compounds in faintly acid solution. The reagent is very suitable for the determination of small quantities of aluminium, especially within the limits 0·02—0·5 mg. per litre. Of the metals which interfere, copper is removed by thiosulphate, and tin, antimony, and bismuth are rendered inactive by addition of sodium tartrate; iron must be precipitated (cf. A., 1924, ii, 785).

S. I. LEVY.

Determination of manganese and magnesium in aluminium alloys. F. MUGRAUER.—See B., 1927, 783.

Potentiometric titration of iron and aluminium with bases. P. DROSSBACH (Z. anorg. Chem., 1927, **166**, 225—230).—If pure solutions of ferric or aluminium chloride lying within a certain concentration range are titrated with sodium hydroxide, the potential of a hydrogen electrode dipping into the solution changes suddenly at the equivalence point. The p_H at this point is 6·8—7·0, and the titration of ferric chloride may actually be effected with bromothymol-blue as indicator. If the chloride solutions contain free acid, the second sudden change in potential corresponds with the complete reaction of the hydroxide with both chloride and free acid. The amount of free acid in aluminium chloride solutions may be determined by direct titration, using bromothymol-blue as indicator, if the aluminium is first converted into the cryolite complex by addition of potassium fluoride, excess being avoided, and if no considerable amounts of alkali chlorides are present.

R. CUTHILL.

Analysis of iron and steel. Determination of silicon, phosphorus, sulphur, and manganese. M. MARQUEYROL and L. TOQUET.—See B., 1927, 751.

Rapid determination of nickel. G. SPACU and J. DICK (Z. anal. Chem., 1927, **71**, 442—446).—The nickel solution is diluted to 100 c.c., treated with 0·5 g. of ammonium thiocyanate for every 0·1 g. of nickel present, heated to boiling, and treated drop by drop with 1—2 c.c. of pyridine. After cooling completely, the precipitate of glistening, sky-blue prisms is collected on a filtering crucible and washed successively with water containing 4 g. of ammonium thiocyanate and 6 c.c. of pyridine per litre, 35% alcohol containing 15 c.c. of pyridine and 1 g. of ammonium thiocyanate per litre, absolute alcohol containing 5 c.c. of pyridine per 100 c.c., and ether, to 20 c.c. of which are added 2 drops of pyridine. The crucible and contents are dried in a vacuum desiccator for 10 min. and weighed. The compound, $Ni(SCN)_2,4C_5H_5N$, contains 11·95% Ni.

A. R. POWELL.

Analytical chemistry of tantalum, niobium, and their mineral associates. VII. Precipitation of tungstic acid by tannin. VIII. Separation of tungsten from tantalum and niobium. W. R. SCHOELLER and C. JAHN (Analyst, 1927, **52**, 504—514).—VII. To obtain total precipitation of tungstic acid in one operation 100—150 c.c. of the alkaline tungstate solution containing alkali chloride are neutralised with dilute hydrochloric acid to the hydrogen carbonate stage, treated with a freshly-made solution of 0·5 g. of tannin, part of which flocculates as a white precipitate if the chloride-ion concentration is high, and dilute acid is added until the solution is acid to litmus, when the brown turbidity due to the tungsten complex appears. On boiling, the precipitate becomes dark brown and flocculent, and a 5% solution of cinchonine hydrochloride (5 c.c. diluted with water) is added, boiling continued for 5 min., and after keeping in the cold for 6 hrs. the clear liquid is decanted, the precipitate mixed with pulped filter fibre, washed on the filter with 5% ammonium chloride solution containing a little tannin, dried, ignited, and weighed as WO_3.

VIII. Tungsten may be separated from tantalum and niobium, since sodium tungstate is freely soluble, whilst the tantalate and niobate are nearly insoluble in solutions of high sodium-ion concentration. Small quantities of tungsten may be separated from large quantities of earth acids by the method previously described (this vol., 32). To separate small quantities of earth acids from large quantities of tungstic acid the solution should be free from potassium ions; fusion is effected with sodium hydroxide in a nickel crucible, and the fused mass extracted with half-saturated sodium chloride solution. Sodium tantalate and niobate remain undissolved and tungstic oxide is determined by difference. Satisfactory results were obtained by both methods. D. G. HEWER.

Potentiometric method for separation of tin and antimony. H. BRINTZINGER and F. RODIS

(Z. anorg. Chem., 1927, 166, 53—59).—If a mixed solution of stannic and antimonic chlorides containing in 100 c.c. 30 g. of crystallised calcium chloride and 20 c.c. of concentrated hydrochloric acid and free from dissolved oxygen is titrated at 90—100° with chromous chloride solution, the first sudden change in the potential of a platinum electrode immersed in the solution indicates the complete reduction of the antimony salt to the tervalent state, and the second, which is relatively small, that of the tin salt to the stannous state. The addition of chromous chloride should be spread over 30—40 min., and, especially near the end-points, sufficient time should be allowed for the potential to become steady before a reading is made. R. CUTHILL.

Separation of vanadium from tungsten. S. G. CLARKE.—See B., 1927, 752.

Separation of vanadium from tungsten. S. G. CLARKE (Analyst, 1927, 52, 527).—Small amounts of vanadium may be separated from an impure tungstic oxide in steel analysis in the same way as larger amounts (B., 1927, 752), except that 50 g. of ammonium chloride should be dissolved in the solution before adding the cupferron to assist separation of the precipitate, which is collected, washed, ignited, and the residue fused with fusion mixture. The vanadium is then determined colorimetrically in the aqueous extract by the hydrogen peroxide method of Meyer and Pawletta (A., 1926, 1020). H. G. HEWER.

Sensitive test for bismuth. H. KUBINA and J. PLICHTA (Z. anal. Chem., 1927, 72, 11—14).—If dimethylglyoxime and sufficient ammonia are added to a hot very dilute bismuth nitrate or chloride solution, an intense yellow colour is developed, and in more concentrated solutions a precipitate is formed. The colour is developed with a bismuth concentration of 1 in 7×10^4. No colour is obtained with bismuth sulphate solution until a chloride is added, and arsenic, antimony, zinc, cobalt, manganese, and ferric salts interfere with the reaction. Bismuth cannot be determined by this method owing to the occlusion of salts. F. S. HAWKINS.

Volumetric determination of bismuth. W. STRECKER and A. HERRMANN (Z. anal. Chem., 1927, 72, 5—11).—The bismuth solution is added drop by drop, when boiling, to a standard solution of disodium hydrogen phosphate; the liquid is filtered when cold, neutralised with sodium hydroxide, and mixed with an excess of sodium acetate and standard silver nitrate solution. After dilution the excess of silver in an aliquot portion is titrated with ammonium thiocyanate. In a second method of determination, the bismuth solution is neutralised with ammonia until a slight turbidity appears, dilute hydrochloric acid is added, the boiling solution cleared with hydrochloric acid or ammonium chloride, and the oxychloride is precipitated with hot water. The oxychloride is dissolved in nitric acid, and the chloride determined by Volhard's method. A third method of determination consists in reducing the hot bismuth solution with magnesium, adding ammonium sulphate solution, and heating until the ammonia is removed. The reduced bismuth is then dissolved in ferric chloride solution in an atmosphere of carbon dioxide, and titrated with permanganate. Bismuth can also be determined by reducing with alkaline formaldehyde solution and titrating the excess with iodine. F. S. HAWKINS.

Thermostat heater. I. A. COWPERTHWAITE (J. Amer. Chem. Soc., 1927, 49, 2255).—The usual lamp is replaced by a resistance of graphite flakes packed in a U-tube of pyrex glass. S. K. TWEEDY.

Micropyrometer. H. VON WARTENBERG and H. MOEHL (Z. physikal. Chem., 1927, 128, 445—448).—A micropyrometer is described which may be employed at any distance above 8 cm. from the heated body and gives a sufficiently large image of such an object as the filament of an electric lamp. Its applications to the measurement of high m. p. and to the determination of the relationship between the current through an electric lamp filament and the temperature are described. H. F. GILLBE.

Apparatus for the determination of melting temperature. G. LYNN (J. Physical Chem., 1927, 31, 1381—1382).—The apparatus described by Washburn (A., 1924, ii, 344) has been modified by the addition of an electric heating coil and of removable sampling tubes. The present form may be used from temperatures below 0° to 400°; 1 c.c. of recoverable material is required, and the heating and cooling curves obtained give for the m. p. a value which is more trustworthy than that obtained by the capillary tube method, which may be up to 3° too high (Andrews, Lynn, and Johnston, A., 1926, 668). L. S. THEOBALD.

Simple automatic pipette. F. FRIEDRICHS (Chem.-Ztg., 1927, 51, 688).—A rubber bulb supplies the suction and an overflow regulates the quantity as in other automatic pipettes, but the expansion of the bulb is regulated by a rod and pressure disc, permitting accurate regulation. A side tube is provided for the eventual removal of the overflowed liquid. C. IRWIN.

Laboratory hydrogen and oxygen generator. C. G. FINK and C. L. MANTELL (Amer. Electrochem. Soc., Sept., 1927, advance copy, 5 pp.).—An apparatus is described for furnishing a continuous supply of hydrogen at constant pressure for long periods, the hydrogen being generated by electrolysis of 30% sodium hydroxide solution using nickel electrodes. H. J. T. ELLINGHAM.

Rubber stopcock lubricants for high-vacuum and other uses. M. SHEPHERD and P. G. LEDIG (Ind. Eng. Chem., 1927, 19, 1059—1061).—Lubricants compounded of rubber, "vaseline," and paraffin wax were studied. Pale crepe and smoked sheet rubber gave the best results. Good results were obtained with paraffin wax of m. p. 30—40°. For high-vacuum work a mixture of pale crepe rubber (31 parts), white "vaseline" (24 parts), and paraffin wax (5 parts) is recommended. It should be stirred for 190 hrs. at 155°, and then quickly cooled. For lighter lubricants the proportion of rubber should be less. There is evidence of chemical reaction and the time and temperature conditions stated should be precisely

followed. The lubricant retains a satisfactory consistency for 12—24 months. C. IRWIN.

Equations for design of fractionating columns. L. H. SHIRK and R. E. MONTONNA.—See B., 1927, 735.

Rapid [method of] extraction. A. G. KUHLMANN (Z. anal. Chem., 1927, **72**, 20—27).—The substance to be extracted is contained in a glass weighing bottle with a perforated bottom, which can be covered by a glass cap. The bottle rests in a constriction in the neck of a flask, which is fitted with a condenser, and contains the extracting liquid. On boiling, the vapour rises through and around the sides of the bottle, and the condensed liquid drops back into it. The extraction is rapid and quantitative, and the all-glass construction allows of the use of strong acids as extracting liquids. For a series of extractions at the temperature of the condensed liquid, a large Soxhlet apparatus can be used to hold a number of the glass bottles. Determinations of the soluble matter in linseed-oil cake and wheat flour showed good agreement with the usual Soxhlet method. F. S. HAWKINS.

One-way safety valves for vacuum pumps and gas generating apparatus. F. HEIN (Z. angew. Chem., 1927, **40**, 864—865).—The valve, of which various applications are described and figured, consists of a pipette-like vessel containing a diaphragm of sintered glass (a Jena glass filter-plate). The pores in the diaphragm are small enough to retain mercury under the pressure likely to prevail in the apparatus. The diaphragm is covered by a layer of mercury 3—4 mm. deep. W. A. SILVESTER.

Direct-reading hydrogen-ion meter. C. G. POPE and F. W. GOWLETT (J. Sci. Instr., 1927, **4**, 380—387).—An apparatus is described for obtaining direct readings of p_H values. A four-electrode valve and a potentiometer circuit are used. With a hydrogen electrode the maximum error in p_H is 0·09 and with a quinhydrone electrode 0·10. C. W. GIBBY.

Sodium voltameter. R. C. BURT (Physical Rev., 1926, [ii], **27**, 813).—The sodium voltameter, in which sodium passes through glass by electrolysis, yields results correct to 1 in 2×10^3, and probably correct to 1 in 6×10^3. A. A. ELDRIDGE.

Measurements with an absorptiometer of objective type. W. TSCHUDI (Helv. Chim. Acta, 1927, **10**, 614—619).—The absorptive powers of liquids are measured by comparing the effects recorded by a thermopile when cells containing the liquids under examination are placed between the thermopile and a constant light source. The intensity of the light transmitted by an aqueous solution of a coloured substance does not decrease with increasing concentration according to the requirements of a formula of an exponential type. Examination of the variation of the absorptive power of dilute "solutions" of silver chloride with time shows that as aggregation of the particles proceeds the absorptive power of the "solution" increases. J. S. CARTER.

Polishing and etching lead, tin, and some of their alloys for microscopical examination. J. R. VILELLA and D. BEREGEKOFF (Ind. Eng. Chem., 1927, **19**, 1049—1052).—The sample is cut with a sharp, oiled hacksaw and then ground with a series of emery papers of increasing fineness smeared with a concentrated solution of paraffin wax in kerosene. Wet polishing is carried out on soaped broadcloth with the finest levigated alumina. For etching lead and lead–antimony alloys a mixture of concentrated nitric acid (1 vol.), glacial acetic acid (1 vol.), and glycerol (4 vols.) is suitable. For lead–tin alloys twice as much glycerol is necessary. The structure is best developed by alternate polishing and etching, the etching being conducted for only a few seconds at a time. C. IRWIN.

[Diagrammatic] representation of the elements for instruction. A. PIUTTI (Rend. Accad. Sci. fis. mat. Napoli, 1925, [iii], **31**, 142—143).—A new spiral chart of the elements (cf. Oddo, A., 1925, ii, 623) is reproduced and described. E. W. WIGNALL.

Mosandrum. R. C. WELLS (J. Washington Acad. Sci., 1927, **17**, 385—388).—Mosandrum, claimed by Smith (Compt. rend., 1878, **87**, 146) as a new element, was a mixture of at least two elements—samarium and gadolinium. The history of the subject is sketched. C. W. GIBBY.

Early experiments on ultra-filtration. E. HATSCHEK (Nature, 1927, **120**, 515).—Schmidt's observation (Ann. Phys. Chem., 1856, **99**, 337) that an animal membrane is less permeable to colloids than to sugar or salts antedates Graham's papers on dialysis. A. A. ELDRIDGE.

Mineralogical Chemistry.

Distribution and transportation of chlorides in the atmosphere. F. BORDAS and A. DESFEMMES (Compt. rend., 1927, **185**, 603—605).—The chlorine contents of samples of rain-water may be considered to be an indication of the salt content of air in the neighbourhood of the sea. At Cette (Midi) the highest normal value recorded (for the dust) was 3·4% of sodium chloride, and at 35 km. from the sea 0·00267 g. per litre of water. The results depend largely on the atmospheric conditions; thus, after a dust-storm 8·41 g. per m.^{2} of sodium chloride were registered, and after a fall of snow 0·0346 g. per litre. There is no exact relationship between the number of solid particles in the air and its salt content. J. GRANT.

Chemical analysis of mud collected on the upper terrace of the Musée Océanographique at Monaco, after the storm on October 31, 1926. H. MARCELET (Compt. rend., 1927, **185**, 662—663).—The dried mud was chestnut-brown in colour, and 97·3% passed a sieve having 4900 meshes/cm.^{2}, and the remainder a sieve of 2700 meshes. It contained :

SiO_2 46·56, Al_2O_3 10·69, Fe_2O_3 6·01, CaO 18·09, MgO 2·09 SO_3 0·47, CO_2 (by difference) 16·09%. Assuming the existence of free silica, alumina, and ferric oxide, the remaining elements may be grouped as $CaCO_3$ 31·67, $CaSO_4$ 0·71, and $MgCO_3$ 4·36%.

J. GRANT.

Temperature and salinity observations in the Gulf of Aden. D. J. MATTHEWS (Nature, 1927, 120, 512).—The phosphorus content of the water in and off the Gulf of Aden is 0·03 mg. P_2O_5 per litre in the upper 50 m., increasing from 200 m. downwards to 0·143 mg. at 1750 m. The arsenic content is 0·005 mg. As_2O_3 per litre at 500—1750 m., but less than 0·001 mg. in the upper 50 m. It is probable that arsenic is removed by plankton organisms much as phosphorus is.

A. A. ELDRIDGE.

Chemical composition of the earth, of meteorites, and of the atmosphere of the sun. H. S. WASHINGTON (Bull. Nat. Res. Council, 1926, 2, II, 30—32).—The earth is considered to possess a central core of iron or iron and nickel, surrounded by a "lithosporic" shell, in which silicates are included sporadically in the metal, then by a "ferrosporic" shell in which iron occurs sporadically in silicate rock, next by a shell of peridotite, and then by the crust. The composition of the earth is given as: Fe (metal) 31·82, Ni (metal) 3·16, Co (metal) 0·23, O 27·71, Si 14·53, Mg, 8·69, Fe (silicate) 7·94, Ca 2·52, Al 1·79, S 0·64, Na 0·39, Cr 0·20, K 0·14, P 0·11, Mn 0·07, C 0·04, Ti 0·02%. Of the 11 most abundant elements in the earth, 9 are among the 11 most abundant elements in the atmosphere of the sun.

CHEMICAL ABSTRACTS.

Crystalline nature of the chief constituent of ordinary coal. C. S. FOX (Nature, 1927, 120, 547).—When thin sections of coal are examined in ordinary transmitted light, practically all of the bright coal and much of the dull coal layers appear to consist of a madder-red, somewhat granular, translucent substance ("coal substance"); in very thin sections or with strong sunlight it is golden-yellow. Pleochroism is absent, but the substance is isotropic. Sections cut perpendicularly to the planes of lamination show that the substance has the crystalline character of a uniaxial crystal. The presence of three types of minor constituents of coal: resinous substances, amorphous "mineral charcoal," and inorganic matter, is revealed. The nomenclature of the constituents of coal is discussed.

A. A. ELDRIDGE.

Zeolites from the leucites near Rome. Gismondite from Capo di Bove and pseudophillipsite from Acquacetosa. V. CAGLIOTI (Rend. Accad. Sci. fis. mat. Napoli, 1927, [iii], 33, 163—177).—A carefully selected sample of pure gismondite, d^{18} 2·277—2·279, contained SiO_2 33·89, Al_2O_3 28·14, Fe_2O_3 0·0044, CaO 13·96, BaO 0·27, SrO 0·025, K_2O 2·86, H_2O 20·76, total 99·91%, corresponding with the formula $(Ca,Ba,Sr,K_2)Al_2Si_2O_8,4H_2O$ in agreement with Zambonini and others. It is also in accord with Clark's view that gismondite is similar to hydrated anorthite.

Pseudophillipsite, d^{18} 2·257—2·259, contained SiO_2 37·35, Al_2O_3 26·27, Fe_2O_3 0·0037, CaO 12·65, BaO 0·21, SrO 0·019, K_2O 3·00, H_2O 20·32, total 100·022%, corresponding with the formula $R_2Al_4Si_5O_{18},9H_2O$. Dehydration was effected over sulphuric acid and then by heating in a current of air. On dehydration over sulphuric acid, gismondite attained equilibrium after 900 hrs. and pseudophillipsite after 450 hrs. Dehydration proceeds rapidly in the first few hours, then continues very slowly; there is no sudden break in the curve, indicating the absence of a definite hydrate. On exposure to moist air at 18·3° the lost water was reabsorbed much more rapidly than it was emitted.

On heating the minerals in dry air up to 700° the curves obtained for both minerals are continuous, showing that the water is dissolved or absorbed. After exposure to moist air for 19 hrs. at different temperatures, the amount of water reabsorbed is not in complete agreement with that evolved. Moreover there is a notable variation in the rate of absorption between 270° and 310°. Samples which have been completely dehydrated do not reabsorb water.

M. CARLTON.

Chemical composition of herschellite from Acicastello. V. CAGLIOTI (Rend. Accad. Sci. fis. mat. Napoli, 1927, [iii], 33, 156—163).—The results of previous analyses of the mineral herschellite are not concordant and it is doubtful whether the samples analysed were pure. The greatest discrepancies arise in the values obtained for calcium and sodium and potassium; these, however, may be due to the fact that the herschellite obtained from Acicastello is accompanied by phillipsite and analcime and the separation of these latter from herschellite is difficult. The mineral contains: SiO_2 44·73, Al_2O_3 21·18, Fe_2O_3 0·00126, CaO 1·65, K_2O 4·53, Na_2O 8·04, H_2O 20·11, total 100·24%. Neither barium nor strontium could be detected spectroscopically. The formula deduced from these results is $R_2Al_4Si_7O_{18},11H_2O$.

Loss of water from the mineral over sulphuric acid was 6·27%, equilibrium being attained after about 358 hrs.; the curve obtained is smooth as with other zeolites. Reabsorption of the lost water was complete after 6 hrs.' exposure to air saturated with water vapour, *i.e.*, in about 1/60 of the time required for its emission.

A sample of the mineral heated at 182° lost 11·20% of water and reabsorbed it again from a moist atmosphere in about 20 hrs. at 22°, the amount reabsorbed exceeding that emitted by 0·062%. Again the curve is characteristic of other zeolites.

M. CARLTON.

Sericite-lazulite pseudomorphs after orthoclase from Bolivia. E. V. SHANNON (J. Washington Acad. Sci., 1927, 17, 388—390).—A description of certain specimens in the U.S. National Museum.

C. W. GIBBY.

Ferrimolybdite from Bivongi (Calabria). G. CAROBBI (Rend. Accad. Sci. fis. mat. Napoli, 1927, [iii], 33, 53—57).—The yellow mineral accompanying Bivongi molybdite is ferrimolybdite (cf. Pilipenko, Festsch. Vernadsky, Moscow; Neues Jahrb. Min. Ref., 1915, 191), for which the formula $4Fe_2O_3,13MoO_3,44H_2O$ is found.

E. W. WIGNALL.

Organic Chemistry.

Mechanism of molecular rearrangements. (Mme.) Ramart-Lucas (Compt. rend., 1927, **185**, 561—563).—A theoretical explanation of common examples of molecular rearrangements involving the movement of single electron linkings. H. Burton.

Carbon monoxide and bivalent carbon. H. Scheibler (Z. angew. Chem., 1927, **40**, 1072—1081).—A review of recent work.

Synthesis of hydrocarbons of the allene series. M. Bouis (Bull. Soc. chim., 1927, [iv], **41**, 1160—1165).—Alkyl derivatives of allyl alcohol of the type $OH\cdot CHR\cdot CH{:}CH_2$ when treated with phosphorus tribromide (in presence of pyridine to prevent addition of hydrogen bromide to the double linking) yield α- and not γ-brominated derivatives, $CHR{:}CH\cdot CH_2Br$, in excellent yield. These substances are readily converted by bromine into alkylated glycerol tribromohydrins, which with solid potassium hydroxide yield epidibromohydrins, $CHRBr\cdot CBr{:}CH_2$, and from these, on treatment with zinc powder in presence of alcohol, allene derivatives may be prepared in 70—75% yield. The following substances were prepared: *α-bromo-Δ$^\beta$-pentene*, b. p. 123—124°/760 mm., d^{20} 1·2545, n_D^{20} 1·4731; *α-bromo-Δ$^\beta$-hexene*, b. p. 42—44°/10 mm., d^{16} 1·2119, n_D^{19} 1·4778; *α-bromo-Δ$^\beta$-heptene*, b. p. 62—64°/10 mm., d^{17} 1·1682, n_D^{17} 1·4760. The foregoing substances were characterised by conversion into the corresponding acetates and alcohols, viz., *Δ$^\beta$-pentenyl acetate*, b. p. 149—151°, d^{22} 0·9019, n_D^{22} 1·4219; *Δ$^\beta$-hexenyl acetate*, b. p. 171—173°, d^{18} 0·8976, n_D^{18} 1·4282; *Δ$^\beta$-heptenyl acetate*, b. p. 192—194° (corr.), d^{18} 0·8915, n_D^{18} 1·4314; *Δ$^\beta$-penten-α-ol*, b. p. 138—139°, d^{23} 0·8444, n_D^{23} 1·4359; *Δ$^\beta$-hexen-α-ol*, b. p. 158—160°, d^{16} 0·8490, n_D^{16} 1·4403; *Δ$^\beta$-hepten-α-ol*, b. p. 177—179° (corr.), d^{20} 0·8421, n_D^{20} 1·4410: the tribromohydrins prepared were *αβγ-tribromopentane*, b. p. 122—124°/18 mm., d^{19} 2·0714, n_D^{19} 1·5580; *αβγ-tribromohexane*, b. p. 127—129°/11 mm., d^{16} 1·9429, n_D^{16} 1·5506; *αβγ-tribromoheptane*, b. p. 142—143°/12 mm., d^{17} 1·8112, n_D^{17} 1·5393: epitribromohydrins, *βγ-dibromo-Δ$^\alpha$-pentene*, b. p. 173°/760 mm., d^{19} 1·7442, n_D^{19} 1·5316; *βγ-dibromo-Δ$^\alpha$-hexene*, b. p. 83—85°/9 mm., d^{14} 1·6381, n_D^{14} 1·5248; *βγ-dibromo-Δ$^\alpha$-heptene*, b. p. 108—110°/12 mm., d^{18} 1·5595, n_D^{18} 1·5200: allene derivatives, *Δ$^{\alpha\beta}$-pentadiene*, b. p. 44—45°, d^{20} 0·6890, n_D^{20} 1·4149; *Δ$^{\alpha\beta}$-hexadiene*, b. p. 78—79°, d^{17} 0·7198, n_D^{17} 1·4298; *Δ$^{\alpha\beta}$-heptadiene*, b. p. 105—106° (corr.), d^{18} 0·7410, n_D^{18} 1·4376. These allene derivatives do not precipitate ammoniacal solutions of cuprous chloride, but, like their acetylenic isomerides, they give white precipitates with mercuric chloride solutions. The action of bromine yields *αββγ-tetrabromopentane*, b. p. about 120°/3 mm., d 2·2839, n_D^{20} 1·5916, *αββγ-tetrabromohexane*, b. p. about 130°/3 mm., d^{15} 2·1873, n_D^{15} 1·5850, and *αββγ-tetrabromoheptane*, b. p. about 140°/3 mm., d^{20} 2·0675, n_D^{20} 1·5718. During attempts to prepare aryl-allene derivatives by the same synthetic method, γ-phenyl-Δ$^\alpha$-propen-γ-ol, $OH\cdot CHPh\cdot CH{:}CH_2$, yielded, with phosphorus tribromide, cinnamyl bromide, a molecular transposition again taking place, and the latter was readily converted into αβγ-tribromo-α-phenylpropane, but the treatment of this substance with solid potassium hydroxide or sodium ethoxide yielded no definite product. W. J. Powell.

Hydrogenation of squalene. M. Tsujimoto (Chem. Umschau, 1927, **34**, 256—258; cf. A., 1916, i, 786; Heilbron, Hilditch, and Kamm, this vol., 130).—Kurozame oil (from the liver of the black shark, mainly of the genus *Zameus*) on hydrogenation in the presence of a nickel catalyst yields a product, m. p. 46—47°, acid value 3·2, saponification value 82·8, iodine value 1·2, unsaponifiable matter 51·43%. The unsaponifiable portion contains dodecahydrosqualene (for which the name squalane is suggested), batyl alcohol, derived chiefly from selachyl alcohol (cf. A., 1922, i, 297), and probably hydrogenated cholesterol. Dodecahydrosqualene as isolated from the crude hydrogenated product by distillation is a colourless liquid of very low volatility, b. p. 272°/15 mm., d_4^{20} 0·8084; n_D^{20} 1·4515; flash point (Pensky–Martens apparatus) 190°. It is unchanged by treatment with sulphuric acid at 70°. W. J. Powell.

Action of cyanogen bromide on dimagnesium acetylene dibromide. A. S. Nekrassov (Ber., 1927, **60**, [*B*], 1756—1758).—Dibromoacetylidene, $CBr_2{:}C$, b. p. 76—76·5°, is prepared by the action of cyanogen bromide on dimagnesium acetylene dibromide (cf. Lawrie, A., 1907, i, 3). H. Wren.

Action of trichloroethylene, ααβ-trichloroethane, and αααβ-tetrachloroethane on magnesium phenyl bromide. L. Bert (Bull. Soc. chim., 1927, [iv], **41**, 1173—1174).—The chloro-derivatives mentioned undergo no reaction when 1 mol. of each is added to a solution of 1 mol. of magnesium phenyl bromide in anhydrous ether, even after prolonged boiling. If the ether is replaced by dry toluene and the mixture heated on the water-bath, neither trichloroethylene nor ααβ-trichloroethane reacts, but αααβ-tetrachloroethane yields a crystalline precipitate, which is not the expected ααα-trichloro-β-phenylethane. W. J. Powell.

Highly-polymerised compounds. IX. Polyvinyl acetate and polyvinyl alcohol. H. Staudinger, K. Frey, and W. Starck (Ber., 1927, **60**, [*B*], 1782—1792; cf. A., 1926, 719).—Polymerisation of monomeric vinyl acetate at low temperatures yields a viscous resin which gives highly viscous solutions and has a greater mean mol. wt. than the brittle resins which are prepared at higher temperature and give less viscous solutions. The material is thus analogous with styrene (cf. Brunner and Wehrli, Diss., Zurich, 1926). The polyvinyl acetate can be separated into fractions of greater and less solubility by suitable treatment with solvents. The more soluble portions have lower mean mol. wt. and yield less viscous solutions than the less soluble fractions. A material of mean mol. wt. 5500 has been separated into fractions of mean mol. wt. 3000, 4500, and 9000. Hydrolysis of polyvinyl acetate affords polyvinyl alcohol which resembles starch in its insolubility in organic media and (colloidal) solubility in water or formamide. Polyvinyl acetates which give highly

viscous solutions yield polyvinyl alcohols with similar properties, whereas alcohols giving less viscous solutions are derived from acetates of lower mean mol. wt. It appears, therefore, that the mean mol. wt. does not undergo change during the hydrolysis. In the polyvinyl alcohols there must therefore be present mixtures of substances in which 40—100 monomerides are united to highly-polymerised molecules. Isolation of individuals is regarded as impossible, since the physical properties of the polymerides do not differ appreciably from one another. The occurrence of materials with differing degrees of polymerisation and variation in properties which are transmitted to their derivatives contradicts the frequent assumption that association products of relatively simple compounds are present in such highly complex compounds. Polymerisation is regarded as consisting in the chemical union of the single unit molecules; thus polyvinyl alcohol is represented as $OH\cdot CH\cdot CH_2\cdot[CH(OH)\cdot CH_2]_x\cdot CH(OH)\cdot CH_2$ ($x = 40$—100). It remains uncertain in what manner the terminal valencies are satisfied, but the presence of many-membered rings is probable.

Oxidation of polyvinyl alcohol or acetate with concentrated nitric acid affords oxalic acid. The alcohol can be acetylated, but the impossibility of carrying the process to completion renders fruitless the attempt to decide whether hydrolysis of a given acetate followed by acetylation of the alcohol yields a product identical with the original material. Similar difficulties are experienced in the preparation of the *benzoate*. The *nitrate* and the *methyl ether* are described; the latter resembles methylated starch in its solubility in water and alcohol. In general, a close analogy appears to exist between polyvinyl alcohol and starch, the essential difference being the greater stability of the former and its inability to give monomeric fragments by simple processes, whereas starch readily affords dextrose or its derivatives. This is attributed to the C–C union in the alcohol and the attachment of the dextrose anhydride residues in starch in some unknown manner.

Reduction of polyvinyl alcohol by hydriodic acid gives a dark, highly-polymerised hydrocarbon which certainly is not a simple paraffin; probably ring formation has occurred. Reduction of polyvinyl bromide leads to a complex paraffin.

Attempts to prepare polyvinyl alcohol directly from acetaldehyde have not been successful, but it appears to be present in small amount in aldehyde resin.

H. WREN.

***iso*Propylacetylenylcarbinol and two stereoisomeric forms of di*iso*propylbutinediol.** W. KRESTINSKI and W. MARJIN (Ber., 1927, **60**, [*B*], 1866—1869).—The action of *iso*butaldehyde on the product of the action of acetylene on magnesium ethyl bromide gives *βη-dimethyl-Δ$^{\delta}$-octinene-γζ-diol*, $CHMe_2\cdot CH(OH)\cdot C{:}C\cdot CH(OH)\cdot CHMe_2$, m. p. 107—108° (*acetate*, b. p. 257—258°; *dibromide*, m. p. 145—146°), and its stereoisomeride, m. p. 69—70° (*acetate*, b. p. 253—256°; *dibromide*, m. p. 156—157°). As by-product, *δ-methyl-Δ$^{\alpha}$-pentinen-γ-ol*, b. p. 131—132°, d_4^{20} 0·8779, n_D 1·43569 (*silver* compound), is formed. The simultaneous production of mono- and di-hydroxy-compounds is attributed to the equilibrium $MgBr\cdot C{:}C\cdot MgBr + C_2H_2 \rightleftharpoons 2CH{:}C\cdot MgBr$ in the Grignard solution, the formation of the monohydric alcohol being therefore favoured by the presence of an excess of acetylene.

H. WREN.

Attempted application of Merling's reaction to aldehydes. Synthesis of *iso*propylacetylenylcarbinol. W. KRESTINSKI and F. SOLODKI (Ber., 1927, **60**, [*B*], 1869—1873).—δ-Methyl-Δ$^{\alpha}$-pentinen-γ-ol, b. p. 131—131·5°, d_4^{20} 0·8778, n_D^{20} 1·43539 (cf. preceding abstract), is obtained in modest yield by the action of sodamide and acetylene on *iso*butaldehyde in ether, thus establishing the enolisation of the aldehyde, $CHMe_2\cdot CHO \rightarrow CMe_2{:}CH\cdot OH$. The main products of the change are ββδ-trimethylpentane-αγ-diol, m. p. 51—52°, and γ-hydroxy-ββδ-trimethylhexaldehyde, b. p. 118—120°/16 mm., which are commonly derived from *iso*butaldehyde under the influence of alkali.

H. WREN.

Condensation of ethylene oxides with alcohols in presence of sulphuric acid as catalyst. II. E. FOURNEAU and I. RIBAS (Bull. Soc. chim., 1927, [iv], **41**, 1046—1056; cf. this vol., 131).—Ethylene oxide (1 mol.) condenses with ethylene chlorohydrin (2·5 mols.) in presence of a small amount of sulphuric acid, yielding diethylene dioxide (dioxan), β-chloroethyl β-hydroxyethyl ether, and ββ′-chloroethoxyethyl β-hydroxyethyl ether. *β-Dimethylaminoethyl β-hydroxyethyl ether*, b. p. 95°/15 mm. (*picrate*; *picrolonate*, m. p. 110°; *benzoate hydrochloride*; m-*nitrobenzoate hydrochloride*; *cinnamate hydrochloride*), is prepared from the corresponding chloro-compound and dimethylamine at 120°. *ββ′-Dimethylaminoethoxyethyl β-hydroxyethyl ether*, b. p. 135°/15 mm. (*picrate*, m. p. 45°; *picrolonate*, m. p. 74—75°; *benzoate hydrochloride*; m-*nitrobenzoate hydrochloride*, m. p. 83—84°), is obtained similarly. From epichlorohydrin and ethylene chlorohydrin there is obtained *β-chloroethyl γ-chloro-β-hydroxypropyl ether*, b. p. 123—125°/18 mm. (yield, 70%), which with dimethylamine furnishes *β-dimethylaminoethyl γ-dimethylamino-β-hydroxypropyl ether*, b. p. 120°/18 mm. (*dihydrochloride*, m. p. 210°). Ethylene chlorohydrin and *as*-methylethylethylene oxide in presence of sulphuric acid give only methylethylacetaldehyde(?), and a substance, b. p. 75°/18 mm., probably a substituted dioxan. In the absence of acid, at 100° for 4—8 days, there is produced a condensation product which on treatment with dimethylamine furnishes *β-dimethylaminoethyl β-hydroxy-β-methyl-n-butyl ether*, b. p. 115°/20 mm. (*picrate*, m. p. 75°; *benzoate hydrochloride*; m-*nitrobenzoate hydrochloride*, m. p. 96°; *cinnamate hydrochloride*). Several of the above hydrochlorides are local anæsthetics.

H. BURTON.

Infra-red absorption spectra of organic compounds of sulphur. I. Aliphatic mercaptans and sulphides. F. K. BELL (Ber., 1927, **60**, [*B*], 1749—1756).—Measurements are recorded of the infra-red absorption spectra between 1·0 and 12·0 μ of *n*-propyl, *n*-butyl, and *iso*amyl mercaptan and the corresponding sulphides. Four sharply-defined absorption bands which are present in the spectra of all these mercaptans suffer uniform displacement towards the region of greater wave-length by passage

from the mercaptan to the corresponding sulphide. The occurrence of a sharp band at 3·8 in the absorption spectra of the mercaptans which is not present in those of the sulphides affords a qualitative method for the discrimination between aliphatic mercaptans and sulphides; the origin of the band cannot be satisfactorily explained. H. WREN.

Preparation and hydrolysis of esters by the distillation method. II. Preparation of *iso*amyl acetate. L. GAY, P. MION, and M. AUMERAS (Bull. Soc. chim., 1927, [iv], **41**, 1027—1040).—Mixtures of acetic acid (0·48 mol.) and *iso*amyl alcohol (0·52 mol.) with a small amount of sulphuric acid on distillation with a Vigreux column give (*a*) a binary mixture of water (0·788) and *iso*amyl acetate (0·212 g.-mol.), practically free from acetic acid and the alcohol, (*b*) a small intermediate fraction which is mainly water, and (*c*) pure *iso*amyl acetate. The binary mixture also passes over first if the acid or alcohol is in excess, but the difficulty of separation of the acetate is increased. The results agree with the theory previously enunciated (this vol., 14). H. BURTON.

Hydrogenation of oleic acid with active hydrogen. H. I. WATERMAN and S. H. BERTRAM (Chem. Umschau, 1927, **34**, 255—256).—The main reaction between electrically activated hydrogen and oleic acid leads to the formation of polymerised products. The work has been repeated using larger quantities of a sample of oleic acid containing only 0·3—0·5% of saturated fatty acids as an impurity. The amount of stearic acid obtained after treatment with activated hydrogen is considerably greater than that present in the original oleic acid, indicating that hydrogenation also takes place to some extent. W. J. POWELL.

Formation of lactic acid from sugar by the action of alkalis. [Determination of lactic acid in aqueous solutions.] W. WINDISCH, P. KOLBACH, and H. RUCKDESCHEL (Woch. Brau., 1927, **44**, 405—410, 417—422, 429—434, 441—446; cf. Kiliani, A., 1882, 715, 827; Meisenheimer, A., 1908, i, 319).—A detailed account of the production of lactic acid from invert-sugar, dextrose, and lævulose by the action of various alkalis. The effects of change of temperature, times of heating, alkali and sugar concentrations have been studied. The best yields recorded are of the order of 50—60%, agreeing with the value quoted by Meisenheimer (*loc. cit.*). For the determination of lactic acid in aqueous solution, the acid is first extracted by ether in a Partheil–Rose apparatus, full details of which are given, and then oxidised to acetaldehyde by standard potassium permanganate solution. The method is accurate ±1% for quantities of 0·04—0·5 g., but is less accurate for smaller amounts. H. BURTON.

Configurational relationships of α-hydroxybutyric and lactic acids. P. A. LEVENE and H. L. HALLER (J. Biol. Chem., 1927, **74**, 343—350).—*d*-α-Hydroxybutyric acid, $[\alpha]^{22}$ +2·3° (*barium* salt, $[\alpha]_D$ −5·6°), was converted into the *ethyl* ester, $[\alpha]^{22}_D$ −3·8°, which, on reduction, gave l-*butane*-αβ-*diol*, b. p. 94—96°/12 mm., $[\alpha]_D$ −7·4° in alcohol (*diphenylcarbamate*, m. p. 121—123°, $[\alpha]^{22}_D$ −19·8° in alcohol). d-*Butane*-αβ-*diol*, b. p. 91—91·5°/13 mm., $[\alpha]^{22}$ +12·4° in alcohol, prepared by reduction of hydroxymethyl ethyl ketone with fermenting yeast (*diphenylcarbamate*, m. p. 125—127°, $[\alpha]^{20}_D$ +23·7° in alcohol), gave l-α-*bromo*-β-*hydroxybutane*, b. p. 61—63°/12 mm., $[\alpha]^{22}_D$ −11·8°, which, on reduction, yielded d-*methylethylcarbinol*, $[\alpha]^{22}$ +13·0° (*phenylcarbamate*, m. p. 61—63°, $[\alpha]_D$ +26·5° in alcohol). *d*-α-Hydroxybutyric acid is therefore configurationally related to *d*-lactic and *d*-β-hydroxybutyric acids. C. R. HARINGTON.

Condensation of α-hydroxy- and keto-acids under the influence of the combined action of catalysts. V. IPATIEV and G. RAZUBAIEV (Ber., 1927, **60**, [*B*], 1971—1973; cf. A., 1926, 1124).—Sodium glycollate when heated under pressure in aqueous solution with hydrogen in the presence of an aluminium oxide–nickel oxide catalyst yields succinic acid by condensation and acetic acid by hydroxyl reduction. The main reaction consists in decomposition of the molecule into carbonate, methane, carbon dioxide, water, succinic and formic acids; this decomposition increases markedly with increasing temperature. An oil with an intense odour and a small quantity of acids of high b. p. are also produced. Pyruvic acid undergoes condensation more readily, but the temperature should not exceed 230°, above which the yield of the main condensation product (methylsuccinic acid) sinks rapidly and products are formed which resinify rapidly when exposed to air. Lactic acid is regarded as primary product of the change (cf. *loc. cit.*). H. WREN.

Unsaturation phenomena of acetylenic acids and esters. I. Constitution of ι-ketoundecoic acid. W. W. MYDDLETON and A. W. BARRETT (J. Amer. Chem. Soc., 1927, **49**, 2258—2264; cf. Chuit and others, this vol., 40).—Treatment of dehydroundecenoic acid (cf. Krafft, A., 1896, i, 665) with mercuric acetate in glacial acetic acid affords *mercuric* κκκ-*triacetoxymercuri*-ι-*ketoundecoate* (I). Ethyl dehydroundecenoate yields similarly *ethyl* κκκ-*triacetoxymercuri*-ι-*ketoundecoate*. Treatment of (I) with concentrated hydrochloric acid affords ι-ketoundecoic acid, m. p. 59·5° (*ethyl* ester, b. p. 169—170°/12 mm.; *semicarbazone*, m. p. 136·5°) (cf. Welander, A., 1895, i, 447). The *oxime* of the acid, m. p. 68—69°, is converted by concentrated sulphuric acid into a mixture, m. p. 65—72°, of the isomerides $NHMe{\cdot}CO{\cdot}[CH_2]_8{\cdot}CO_2H$ and $NHAc{\cdot}[CH_2]_8{\cdot}CO_2H$. Treatment of Δ^9-undecinoic acid with mercuric acetate yields a mixture of *mercuric diacetoxymercuriketoundecoates*, which, on hydrolysis with hydrochloric acid, affords the above ι-ketoundecoic acid, together with an isomeride, presumably *θ-ketoundecoic acid*, m. p. 43·5°. Mercuration of the ethyl esters of the above acids proceeds analogously. F. G. WILLSON.

Unsaturation phenomena of acetylenic acids and esters. II. Reaction between mercuric acetate and some acetylenic acids and esters. W. W. MYDDLETON, R. G. BERCHEM, and A. W. BARRETT (J. Amer. Chem. Soc., 1927, **49**, 2264—2269; cf. preceding abstract).—Treatment of stearolic, ricinoleic, and behenolic acids with mercuric acetate in glacial acetic acid yields, respectively, *mercuric diacetoxymercuriketostearate*, *diacetoxymercurihydroxyketostearate*, and *diacetoxymercuriketobehenate*, which,

on treatment with hydrochloric acid, yield θ-ketostearic, ζ-hydroxy-θ-ketostearic, and θ-ketobehenic acids (cf. Baruch, A., 1894, i, 170, 171; Goldsobel, A., 1895, i, 81; Holt, A., 1892, 812). Mercuration of methyl behenolate proceeds analogously, but definite compounds could not be obtained similarly from γ-butinene-αα-dicarboxylic acid and γ-butinene-α-carboxylic acid. F. G. Willson.

Existence and preparation of methyl orthocarbonate. H. von Hartel (Ber., 1927, **60**, [*B*], 1841).—*Methyl orthocarbonate*, m. p. −5·5°, b. p. 114°, $d_{13\cdot5}^{18\cdot5}$ 1·0232, n_{D}^{16} 1·3864, is readily obtained by the action of trichloronitromethane on sodium methoxide in pure methyl alcohol. It volatilises to a marked extent with methyl alcohol or ether. H. Wren.

Preparation of ethoxalyl chloride. L. Bert (Bull. Soc. chim., 1927, [iv], **41**, 1165—1166; cf. A., 1926, 56; Barré, this vol., 228).—In the preparation of ethoxalyl chloride by the action of phosphorus pentachloride on ethyl oxalate, yields of 80% may be obtained provided that the starting materials are of a high degree of purity. The phosphorus pentachloride is best prepared beforehand from phosphorus trichloride and chlorine in the flask used for the reaction with ethyl oxalate. W. J. Powell.

Lanthanum, cerous, praseodymium, neodymium, and samarium maleates. L. Coniglio (Rend. Accad. Sci. fis. mat. Napoli, 1927, [iii], **33**, 80—82).—*Salts* of the general formula $[(CH\cdot CO_2\cdot)_2]_3R_2,10H_2O$, where R is $Ce^{\cdots}$, Pr, Nd, La, or Sm, are prepared, of which the respective solubilities of the anhydrous salts in water at 25° are 8·05, 6·05, 5·64, 4·19, and 1·45 g. per 100 g. of solution. E. W. Wignall.

C_4-Saccharinic acids. IV. Preparation of the two *dl*-αβ-dihydroxybutyric acids. J. W. E. Glattfeld and S. Woodruff (J. Amer. Chem. Soc., 1927, **49**, 2309—2315; cf. A., 1925, i, 881).—The α-chloro-β-hydroxybutyric acid obtained from crotonic acid by a modification of the method of Melikoff and Zelinsky (A., 1888, 1056) yields, when treated as the barium salt in aqueous solution with silver oxide, an αβ-dihydroxybutyric acid, (I), m. p. 81·5°. Oxidation of crotonic acid with permanganate yields an αβ-dihydroxybutyric acid, $(+1H_2O)$ (II), m. p. 73·5—74·5° (cf. Fittig and Kochs, A., 1892, 956), also obtained by the oxidation of crotonic acid with chlorate in presence of osmium tetroxide (cf. Milas and Terry, A., 1925, i, 780). The following derivatives of (I) and (II) respectively were prepared: *phenylhydrazides*, m. p. 103° and 129·5°; *o-tolylhydrazides*, m. p. 103° and 111·5°; and *barium* and *silver* salts. F. G. Willson.

Combined action of catalysts (nickel oxide and aluminium oxide) on solutions of substituted hydroxysuccinic acids under high pressure of hydrogen and at high temperatures. G. Razubaiev (Ber., 1927, **60**, [*B*], 1976—1980).—The behaviour of sodium lactate under the conditions expressed in the title (cf. A., 1926, 1124) has been explained by the scheme: $2OH\cdot CHMe\cdot CO_2H \longrightarrow CO_2Na\cdot CMe(OH)\cdot CHMe\cdot CO_2Na \longrightarrow CO_2Na\cdot CMe{:}CH\cdot CO_2Na \longrightarrow CO_2Na\cdot CHMe\cdot CH_2\cdot CO_2Na$, but α-hydroxy-αβ-dimethylsuccinic acid could not be detected among the products. The sodium salts of α-hydroxy-αβ-dimethylsuccinic, α-hydroxy-α-methylsuccinic, and α-hydroxy-α-methyl-β-ethylsuccinic acids have been subjected to the same treatment. In each case methylsuccinic acid is produced in 25—30% yield. In addition, fission of the molecule occurs with production of methane, carbonate, and a series of monobasic acids. Formic and acetic acids are invariably produced, the yield being highest (45%) with α-hydroxy-α-methylsuccinic acid and lowest (16%) with α-hydroxy-α-methyl-β-ethylsuccinic acid. The yield of higher monobasic acid increases in the inverse order; with α-hydroxy-α-methyl-β-ethylsuccinic acid butyric acid is obtained in 30% yield, due to fission between the α- and β-carbon atoms. In all cases an intensely odorous oil, similar to that derived from sodium lactate (*loc. cit.*), is produced in quantity too small for extended examination. H. Wren.

Reduction of polybasic α-hydroxy-acids under the influence of the combined action of catalysts. V. Ipatiev and G. Razubaiev (Ber., 1927, **60**, [*B*], 1973—1976; cf. A., 1926, 1124, and preceding abstract).—The action of hydrogen under pressure on heated solutions of sodium malate, tartrate, and citrate in the presence of aluminium oxide and nickel oxide is characterised by reduction of the hydroxyl group by hydrogen with production of the corresponding saturated polybasic acid and decomposition of the molecule into monobasic acids. The first change is observed only with malic and tartaric acids, which give succinic acid in 50% yield and very small amount respectively. Decomposition of the acids affords formic and acetic acids, carbon dioxide, and methane. Methylsuccinic acid is obtained from citric acid in rather more than 30% yield. H. Wren.

Catalytic reduction of *d*-gluconic acid to *d*-glucose. J. W. E. Glattfeld and E. H. Shaver (J. Amer. Chem. Soc., 1927, **49**, 2305—2308).—*d*-Gluconic acid was treated in faintly acid aqueous solution at the ordinary temperature with hydrogen under a pressure of 17 lb./sq. in., in presence of platinum oxide. Glucosazone was isolated from the reaction mixtures in amounts corresponding with 14—28% yields of dextrose, the latter also being obtainable in crystalline condition. F. G. Willson.

Behaviour of aldehydeacetals on hydrogenation. Formation of ethers from acetals. F. Sigmund and G. Marchart (Monatsh., 1927, **48**, 267—288).—Hydrogenation of benzaldehydediethylacetal at 180° by the Sabatier and Senderens process yields benzyl ethyl ether (45%), b. p. 185—187°. From phenylacetaldehydedimethylacetal there is produced methyl β-phenylethyl ether (50%), b. p. 189—190°. Similarly, heptaldehydediethylacetal yields ethyl heptyl ether (61%), b. p. 165—167°; *heptaldehydedi-n-propylacetal*, b. p. 112·5°/9 mm., affords *n*-propyl heptyl ether (64%), b. p. 182·5—183°; *heptaldehydedi*isobutylacetal, b. p. 126·6° (corr.)/10 mm., gives isobutyl *heptyl ether* (64%), b. p. 194—196°; *phenylacetaldehydedi-n-propylacetal*, b. p. 136·6° (corr.)/12 mm., furnishes β-*phenylethyl* n-*propyl ether* (80%),

b. p. 225—227° (corr.); and cinnamaldehydediethylacetal yields ethyl γ-phenylpropyl ether, b. p. 220—222°. H. BURTON.

α-Bromo- and α-hydroxy-aldehydes. R. DWORZAK and P. PEIFFERLING (Monatsh., 1927, 48, 251—266).—Bromination of parapropaldehyde with 2 atoms of bromine at −10 to −5°, followed by treatment with alcohol, yields the acetal of α-bromopropaldehyde. With 4 atoms of bromine there are produced *αα-dibromopropaldehydeacetal*, b. p. 91°/9 mm., together with a substance, b. p. 130°/2—3 mm., probably *αβγ-tribromo-α-methylvaleraldehyde alcoholate*. Bromination of paraheptaldehyde with 1 mol. of bromine at −6°, with subsequent treatment by alcohol, furnishes *α-bromoheptaldehyde*, b. p. 62°/2 mm., and its *acetal*, b. p. 92°/1 mm.

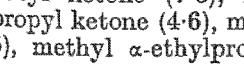
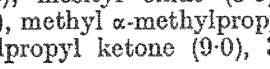
Hydrolysis of the bromoacetals with water yields the corresponding hydroxyaldehyde. Thus from the acetals of α-bromopropaldehyde, αα-dibromopropaldehyde, and α-bromoheptaldehyde there were obtained α-hydroxypropaldehyde, pyruvaldehyde, and a dimeric form of *α-hydroxyheptaldehyde*. H. BURTON.

Solvatochromism of the ketones. J. S. P. BLUMBERGER (Chem. Weekblad, 1927, 24, 454—462).—It is proposed to employ the term "solvatochromism" to cover all the phenomena of molecular addition between organic compounds and organic and inorganic compounds, since the term "halochromism," which should be restricted to cases of addition analogous to salt formation, has been hitherto employed very loosely. The theories put forward to account for the various cases of addition are considered and criticised. S. I. LEVY.

Stability of acetone to light. K. WIESLER (Z. angew. Chem., 1927, 40, 1023—1024).—One drop of 0·1% potassium permanganate solution per 10 c.c. of acetone was used to test for the presence of oxidisable impurities. Pure acetone, which remained stable to this permanganate for 5 hrs., decolorised it in 6—7 min. after 4 hrs.' exposure to a mercury vapour lamp; on distilling, pure acetone stable to potassium permanganate was obtained as the main distillate, but the last runnings contained a quantity of a viscous substance too small to identify. Exactly similar effects were obtained by repeating the whole experiment with this main distillate, indicating that the sensitivity of acetone to light is due to its actual decomposition, and not to some impurity previously present. S. J. GREGG.

Composition of acetone oil. H. SUIDA and H. POLL (Monatsh., 1927, 48, 167—192; cf. Wolfes, A., 1891, 819; Pringsheim and Bondi, A., 1925, i, 1072).—Examination of 18 fractions obtained from acetone oil, having b. p. 55—60°/760 mm. to 48—51°/15 mm., shows the following constituents to be present (figures indicate percentage of substance in ketone oil boiling within these temperatures: acetone (2·3), methyl ethyl ketone (5·8), methyl *iso*propyl ketone (2·1), methyl propyl ketone (32·6), methyl butyl ketone (14·5), ethyl propyl ketone (0·6), methyl *iso*butyl ketone (7·6), mesityl oxide (3·8), propyl *iso*propyl ketone (4·6), methyl α-methylpropyl ketone (7·6), methyl α-ethylpropyl ketone (9·0), 3-methyl-Δ^3-hexen-5-one (12·5), and methyl *n*-amyl ketone (4·6). An equimolecular mixture of calcium acetate and calcium butyrate yields on distillation acetone, mesityl oxide, methyl ethyl, methyl propyl, ethyl propyl, and dipropyl ketones. If 4·5 mols. of calcium acetate are used to 1 mol. of calcium butyrate the products are acetone, methyl ethyl and methyl propyl ketones. H. BURTON.

Trifluoroacetone. F. SWARTS (Bull. Acad. roy. Belg., 1927, [v], 13, 175—180).—Trifluoroacetone, b. p. 21·9°, d^0 1·282 (*hydrogen sulphite*; *monohydrate*, m. p. 51°; *semicarbazone*, m. p. 127°; *oxime*, m. p. −1·5°, b. p. 102·5—103°, $d^{10\cdot5}$ 1·3042, $n_\alpha^{10\cdot5}$ 1·34636, $n_\beta^{1\cdot5}$ 1·3528), may be prepared by boiling ethyl trifluoroacetoacetate (this vol., 646) with 10% sulphuric acid, or more conveniently by decomposing the crude sodium salt of the ester with excess of dilute sulphuric acid. Catalytic reduction with hydrogen yields *trifluoroisopropyl alcohol*. The depression of the b. p. consequent on the substitution of three fluorine atoms in a methyl group adjacent to a carbonyl group is always of the order of several degrees, but varies considerably with the nature of the compound considered. J. S. CARTER.

Action of amines and ammonia on acetylenic γ-diketones. G. DUPONT (Bull. Soc. chim., 1927, [iv], 41, 1167—1169; cf. A., 1914, i, 701; Ruhemann and Cunnington, J.C.S., 1899, 75, 954).—Acetylenic γ-diketones, *e.g.*, dibenzoylacetylene, react readily, not only with secondary amines, but also with the majority of primary amines and even with ammonia to give compounds the analyses of which indicate that addition of 1 mol. of ammonia or amine to the triple linking takes place. The following were prepared: *α-amino-αβ-dibenzoylethylene*, m. p. 142°; *α-amino-αβ-ditoluoylethylene* (?), m. p. 138° (not analysed); *α-amino-αβ-dianisoylethylene*, m. p. 107°: from aniline, *α-anilino-αβ-dibenzoylethylene*, m. p. 131° (+0·5C_6H_6, m. p. 121°); *α-anilino-αβ-dianisoylethylene*, m. p. 138°: from *o*-toluidine, *α-o-toluidino-αβ-dibenzoylethylene*, a yellow, crystalline precipitate (m. p. omitted); from piperidine, *α-piperidino-αβ-dibenzoylethylene*, m. p. 181°, *α-piperidino-αβ-dianisoylethylene* (?), m. p. 164—165°. Neither diphenylamine nor hydrazine gave a crystalline derivative with any of the three acetylenic diketones used. With phenylhydrazine and dibenzoylacetylene a *derivative*, m. p. 160°, NHPh·NH·CBz:CHBz or NH_2·NPh·CBz:CHBz, was obtained. This substance loses 1 mol. of water on fusion, yielding a *product*, m. p. 138°, probably  or  W. J. POWELL

[Action of amines and ammonia on acetylenic γ-diketones.] J. BALLET (Bull. Soc. chim., 1927, [iv], 41, 1170; cf. preceding abstract).—Methylamine reacts with dibenzoylacetylene in benzene solution with evolution of heat, forming *α-methylamino-αβ-dibenzoylethylene*, m. p. 121°; dimethylamine under the same conditions affords *α-dimethylamino-αβ-dibenzoylethylene*, m. p. 144°, in quantitative yield; the *β-naphthylamine* derivative has m. p. 143°. The *product* formed by the interaction of 1 mol. of benzidine with 2 mols. of diketone has m. p. 205—210° (in m. p. tube) and m. p. 169° (Maquenne block),

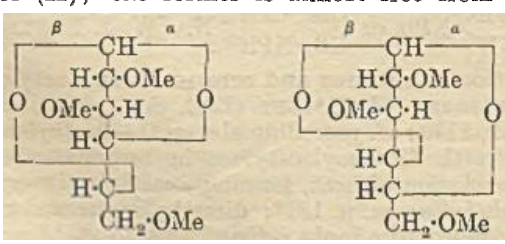
whilst the *pyrrole* derivative has m. p. 175°. *o*-Aminophenol did not appear to react. W. J. POWELL.

Spectrographic investigations on carbohydrates in the ultra-violet. L. KWIECIŃSKI and L. MARCHLEWSKI (Z. physiol. Chem., 1927, **169**, 300; cf. this vol., 291).—The conclusion of Niederhof (this vol., 396) that sugars containing an aldehyde or a ketone grouping have an absorption band at 2800 Å. is refuted. Very pure preparations of dextrose and galactose show a continuous absorption and this band is evident only with less pure preparations. The results are not quite so definite with lævulose, but the absorption band becomes much weaker as the preparation is purified. A. WORMALL.

Percentage formula of pentosans. G. SCHORSCH (Papier-Fabr., 1927, **25**, 576—577).—The formula $(C_5H_8O_4)_n$ for the pentosans, due to Tollens, cannot be regarded as definitely established. A critical examination of results given in the literature shows that elementary analysis of amorphous and ash-containing preparations is not conclusive, whilst the C-value given by Tollens and Wheeler is the arithmetic mean of the theoretical C-values of $C_5H_8O_4$ and $C_{10}H_{18}O_9$. That a hexosan formula is improbable is shown by the results of other investigators on the hydrolysis of xylan, no dextrose or other hexose having been found, hence only $C_5H_8O_4$, $C_{10}H_{18}O_9$, or similar anhydride formula need be considered. The hydrolysis of xylan to xylose does not illuminate the problem, since 100% yields of xylose are never obtained. The usual determinations of xylan by its yield of furfuraldehyde phloroglucide show that no 100% value is obtained, calculated on the dry, ash-free substance, in spite of the fact that no other sugars than pentoses can ever be found. The Tollens method for the determination of pentoses in xylose and arabinose was worked out experimentally on crystallised pure products, and the above anomalies are removed only by the use of other calculation factors. With these, together with hydrolysis formulæ, it is shown that all xylan values within the ordinary limits of experimental error give 100%, which points to $(C_{10}H_{18}O_9)_n$ as the composition of the pentosans. B. P. RIDGE.

Oxygen bridges in sugars. III. Anhydrides of βγζ-trimethylglucose. Attempted synthesis of trimethylcellulose. F. MICHEEL and K. HESS (Ber., 1927, **60**, [*B*], 1898—1906; cf. A., 1926, 1230; this vol., 43).—If trimethylcellulose is a 2 : 3 : 6-trimethylanhydroglucose it must possess the constitution (I) or (II); the former is almost free from strain,

(I.)



(II.)

whereas in the latter the strain is very great. The two anhydrides are obtained as follows. 2 : 3 : 6-Trimethylglucose is converted by acetic anhydride and sodium acetate into amylene-oxidic 1 : 4-*diacetyl*-2 : 3 : 6-*trimethyl*-β-*glucose*, m. p. 67—68°, $[\alpha]^{19}$ —8·7° in chloroform, re-converted into 2 : 3 : 6-trimethylglucose by 5% hydrochloric acid. It is converted by hydrogen chloride in the presence of acetyl chloride at —15° to —18° into amylene-oxidic 1-*chloro*-4-*acetyl*-2 : 3 : 6-*trimethyl*-α-*glucose*, b. p. 143—146°/0·04 mm., $[\alpha]^{20}$ +146·9° in chloroform, which with alcoholic trimethylamine affords amylene-oxidic 4-*acetyl*-2 : 3 : 6-*trimethylglucosidotrimethylammonium chloride*, $[\alpha]_D^{19}$ —3·7° in chloroform, to which the β-configuration is assigned. If this material is treated with warm barium hydroxide solution ring closure occurs with production of 2 : 3 : 6-trimethylglucose anhydride in 62% yield. The product is a mobile liquid, b. p. 107—108°/0·05—0·07 mm., which shows the expected mol. wt. in solution, does not reduce Fehling's solution, but reacts immediately with cold permanganate. It contains about 75% and 25%, respectively, of the trimethylanhydroglucoses (I) and (II). When treated with 1% methyl-alcoholic hydrogen chloride at the atmospheric temperature it gives 2 : 3 : 6-trimethylmethylglucoside, only one anhydride ring being opened, whilst the other is stable. Separation of the glucoside and unchanged anhydride has not been effected, but the presence of each is established by the methoxyl content of the preparation and the results of further methylation by methyl sulphate and subsequent hydrolysis of the product with 5% aqueous hydrochloric acid to amylene-oxidic 2 : 3 : 4 : 6-tetramethylglucose and amylene-oxidic 2 : 3 : 6-trimethylglucose. It appears certain that neither of the trimethylanhydroglucoses is identical with trimethylcellulose and that either the cryoscopic behaviour of the latter in glacial acetic acid solution must be ignored or that the constitution of trimethylcellulose cannot be based on the production of 2 : 3 : 6-trimethylglucose. H. WREN.

***d*-Glucose-ζ-chlorohydrin and its derivatives.** B. HELFERICH and H. BREDERECK (Ber., 1927, **60**, [*B*], 1995—2001).—The triphenylmethyl ether of acetyl-*d*-glucose or acetyl-α-methylglucoside is converted into triacetyl-α-methylglucoside-6-chlorohydrin in the manner described previously, except that the triphenylmethyl group is removed in the form of its sparingly soluble bromide and is then transformed by aqueous hydrochloric acid into d-*glucose*-ζ-*chlorohydrin*, m. p. 135—136° (corr.), $[\alpha]_D$ +78·3° to +35·0° in aqueous solution; the *osazone* is described. Similarly, β-*tetra-acetyl*-d-*glucose*-6-*chlorohydrin*, m. p. 114—115° (corr.), $[\alpha]_D^{18}$ +17·6° in chloroform, is prepared by the action of phosphorus pentachloride on β-tetra-acetyl-*d*-glucose 6-triphenylmethyl ether; the mother-liquors obtained in the preparation of the latter compound yield small quantities of a crystalline material, m. p. 120—126°, consisting mainly of the corresponding α-tetra-acetate, which may be converted into α-*tetra-acetyl*-d-*glucose*-6-*chlorohydrin*, m. p. 162—164°, $[\alpha]_D^{20}$ +111·6° in chloroform. β-Tetra-acetyl-*d*-glucose-6-chlorohydrin is transformed by phosphorus pentachloride and aluminium chloride in chloroform into 1 : 6-*dichlorotriacetyl*-d-*glucose*, m. p. 156° (corr.), $[\alpha]_D^0$ +196·8° in chloroform, and by hydrogen bromide in glacial acetic acid at 0° into 6-*chloro*-1-*bromotriacetyl*-d-*glucose*, m. p. 165—166° (corr.), $[\alpha]^{20}$ +209·0° in chloroform; *tri-*

acetyl-d-*glucose*-6-*chlorohydrin*, m. p. 125° after softening at 118°, $[\alpha]_D^{19}$ +18·1° in chloroform, and *triacetyl*-β-*methylglucoside*-6-*chlorohydrin*, m. p. 141°, are derived from the bromo-compound by treatment with silver carbonate and acetone or silver oxide and methyl alcohol, respectively. Anhydrous hydrogen fluoride converts β-tetra-acetyl-*d*-glucose-6-chlorohydrin into 1-*fluorotriacetyl*-d-*glucose*-6-*chlorohydrin*, m. p. 151—152° (corr.), $[\alpha]_D^{20}$ +106·95° in chloroform, from which 1-*fluoroglucose*-6-*chlorohydrin*, decomp. 138° according to the rate of heating, $[\alpha]_D^{20}$ +88·8° in aqueous solution, is derived. H. WREN.

Synthesis of maltose. A. PICTET and H. VOGEL (Helv. Chim. Acta, 1927, **10**, 588—593).—See this vol., 752.

Constitution of the disaccharides. XV. Sucrose. J. AVERY, W. N. HAWORTH, and E. L. HIRST (J.C.S., 1927, 2308—2318).—The adoption of the amylene-oxide formula for normal fructose is justified by the reference of crystalline derivatives of its degradative oxidation products to standard compounds of known constitution. Cautious oxidation of tetramethyl-γ-fructose with nitric acid (*d* 1·42) followed by esterification of the product yields essentially the lactol ethyl ester, $C_{11}H_{20}O_7$, $[\alpha]^{24}$ +25·8° in water, which after methylation yields the amide, $C_{10}H_{19}O_6N$, m. p. 99—100°, identical with that obtained from the corresponding methyl ester (this vol., 859). Oxidation of the lactol ethyl ester with alkaline permanganate followed by esterification of the product with methyl alcohol gives an ester, $C_7H_{14}O_5$, $[\alpha]^{20}$ +19° in water, from which hydroxydimethoxybutyramide, m. p. 104—105°, $[\alpha]_I^{19}$ +33° in water, is obtained. Application of Weerman's reaction to this amide indicates that it is not an α-hydroxy-compound (A., 1917, i, 546). Since the amide is not oxidised by nitric acid as it would be if it were a γ-hydroxy-compound, it is probably the β-hydroxy-compound. The lactol acid, prepared by hydrolysis of the lactol ethyl ester described above, is oxidised in dilute sulphuric acid solution with barium permanganate to give *d*-trimethylarabonolactone, m. p. 32—33°, $[\alpha]_D$ +44·5 to +25·5° in water in 18 days. The m. p. of this substance is identical with and the rotatory power equal and opposite to that of the *l*-isomeride already obtained (this vol., 750). Oxidation of the lactol methyl ester yields the same product. G. A. C. GOUGH.

Transformation of a β-glucoside into an α-glucoside. B. HELFERICH and A. SCHNEIDMÜLLER (Ber., 1927, **60**, [*B*], 2002—2005).—*d*-β-Methylglucoside is converted by successive treatments with triphenylmethyl chloride in pyridine and acetic anhydride into *triacetyl*-β-*methyl*-d-*glucose* 6-*triphenylmethyl ether*, m. p. 126° (corr.), $[\alpha]_D^{22}$ +32·0° in pyridine. The position of the triphenylmethyl group is established by the conversion of the compound by phosphorus pentabromide (2 mols.) into acetodibromoglucose (yield, 23%) and by phosphorus pentachloride into *triacetyl*-d-β-*methylglucoside*-6-*chlorohydrin*, m. p. 141° (corr.), $[\alpha]_D^{19}$ −9·8° in pyridine, from which d-β-*methylglucoside*-6-*chlorohydrin*, m. p. 156—157° (corr.), $[\alpha]_D^{17}$ −48·7° in water, is derived. The constitution of this substance is established by its hydrolysis to *d*-glucose-6-chlorohydrin and the anhydroglucose of Fischer and Zach. It is remarkable that *d*-β-methylglucoside-6-chlorohydrin (like the majority of *d*-β-methylglucosides containing a substituent in the 6-position) is indifferent towards emulsin. Treatment of triacetyl-β-methyl-*d*-glucose 6-triphenylmethyl ether with phosphorus pentabromide (1 mol.) leads unexpectedly to *d*-α-methylglucoside-6-bromohydrin in addition to decomposition products, the yield being 12%. Transformation does not appear to occur when tetra-acetyl-*d*-methylglucoside is melted with phosphorus pentabromide, and isomerisation therefore appears at any rate to be facilitated by simultaneous change at the 6 carbon atom. A somewhat similar instance of transformation under more drastic conditions has been recorded by Irvine (J.C.S., 1905, **87**, 901). H. WREN.

Synthetic glucosides of pyrimidine derivatives. III. A. HAHN and W. LAVES (Z. Biol., 1926, **85**, 280—288).—The *tetra-acetyl*-d-*glucoside* of 2-*methylanilino*-6-*oxypyrimidine* has been isolated as a crystalline compound, m. p. 145°, $[\alpha]^{20}$ −45·04° in toluene, by the action of the silver salt of 2-methylanilino-6-oxypyrimidine on a xylene solution of tetra-acetobromoglucose at 155°. From this substance 2-methylanilino-6-oxypyrimidine-*d*-glucoside, m. p. 116—118° (indef.), $[\alpha]_D^{18}$ −66·39° in alcohol, has been isolated after deacetylation with methyl-alcoholic ammonia.

The *tetra-acetyl*-d-*glucoside* of 2-*methylanilino*-6-*oxy*-5-*methylpyrimidine*, m. p. 143—145° (indef.), $[\alpha]_D^{20}$ −63·9 in benzene, has been isolated in an analogous manner from the silver salt of 2-methylanilino-6-oxy-5-methylpyrimidine. By deacetylation with methyl-alcoholic ammonia, 2-*methylanilino*-6-*oxy*-5-*methylpyrimidine*-d-*glucoside*, m. p. 135—136°, $[\alpha]_D^{22}$ −57·54°, is formed.

The *picrate*, m. p. 109—110°, of the *tetra-acetylglucoside* of 2-*ethylthiol*-6-*oxypyrimidine* has been prepared by the addition to a saturated aqueous solution of picric acid of a boiling alcoholic solution of the condensation product of tetra-acetobromoglucose and 2-ethylthiol-6-oxypyrimidine. The free *glucoside*, m. p. 103°, $[\alpha]_D^{22}$ −13·73°, is described. Deacetylation of this substance with methyl-alcoholic ammonia produces 2-*ethylthiol*-6-*oxypyrimidine*-d-*glucoside*, m. p. 144—145°, $[\alpha]_D$ −68·47°; its hydrolysis by emulsin proves it to be a β-glucoside. None of these synthetic glucosides reduces Fehling's solution until after fission with dilute hydrochloric acid except 2-methylanilino-6-oxypyrmidine-*d*-glucoside, which, although stable in alkaline solution, is hydrolysed into its components by keeping in neutral aqueous solution. E. A. LUNT.

Nitrogenous glucosides. K. JOSEPHSON (Ber., 1927, **60**, [*B*], 1822—1826).—Silver phthalimide is conveniently prepared by the gradual addition of alcoholic sodium hydroxide to a hot aqueous-alcoholic solution of silver nitrate and phthalimide. With acetobromoglucose in boiling xylene it yields phthalimide as sole isolable product. *Silver saccharin* and acetobromoglucose afford *tetra-acetylglucosidosaccharin*, $C_6H_4<\begin{matrix}CO\\SO_2\end{matrix}>N\cdot C_6H_7O_5Ac_4$, m. p. 154° (corr.), $[\alpha]$

—40·2° in chloroform. It is converted by barium hydroxide into *o-glucosidosulphamidobenzoic acid*, $C_6H_{11}O_5{\cdot}NH{\cdot}SO_2{\cdot}C_6H_4{\cdot}CO_2H$, [α] +2·8° in water (corresponding *sodium* salt, incipient decomp. 119°, [α] —14·9° in water), which readily reduces Fehling's solution. Hydrolysis with methyl-alcoholic ammonia appears to convert tetra-acetylglucosidosaccharin into glucosidosaccharin, which passes readily into *o*-glucosidosulphamidobenzamide. H. WREN.

Amphoteric nature of cellulose. E. OMAN (Papir-Journalen, 1927, **15**, 91—96, 107—110, 116—120).—The chemical activity of cellulose is demonstrated by its reduction, by chemical combination, of the acidity or alkalinity of dilute aqueous solutions. The extent to which hydrogen ions are taken up by the cellulose is variable, and dependent on the hydrogen-ion concentration of the water.

CHEMICAL ABSTRACTS.

Cellulose. XXX. Acetolysis of cellulose by hydrogen bromide and acetyl bromide. Degradation to a trihexosan. K. HESS and F. MICHEEL (Annalen, 1927, **456**, 69—86; cf. Hess, Weltzien, and Kunau, A., 1924, i, 146).—By the action of hydrogen bromide and acetyl bromide cellulose acetate undergoes complete fission into brominated dextrose derivatives in 15 days at 0° or in 10—12 days at 4—6°. The progress of the acetolysis is followed (i) polarimetrically, (ii) by bromine determinations, (iii) by mol. wt. determinations. The bromine content of the final product (above 24%) is greater than required for dextrose monobromide acetate (19·5% Br); more than half this bromine reacts with silver acetate and is thus attached to the C_1 atom of an aldehydic sugar. The mol. wt. of the final product, freed from cellobiose bromide acetate, is 630—380 (disaccharide 700, dextrose 410, as bromide acetate). Cellobiose bromide acetate under similar conditions is practically unattacked by 5% hydrogen bromide in acetyl bromide, but by 7·5% at 15° it is converted after treatment with silver acetate into equal amounts of dextrose penta-acetate and a dextrose bromide acetate.

The final product of complete acetolysis of cellulose acetate with 6% hydrogen bromide in acetyl bromide at 5° for 17 days, on acid hydrolysis under special conditions, yields a water-soluble *trihexosan*, $(C_6H_{10}O_5)_3,H_2O$, m. p. 184—189° (decomp.), $[\alpha]_D^{17}$ +90·5° in water, $[\alpha]_D^{19}$ +96·8° in methyl alcohol, which is without reducing action on Fehling's solution. The trihexosan forms crystalline additive products with toluene and xylene and is thus separated from the reducing sugars which accompany it. It is purified by fractional crystallisation of the *acetate*, $C_{36}H_{48}O_{24}$, m. p. 123—126°, $[\alpha]_D^{9}$ +86·6° in chloroform, which is a nona-acetate of a trisaccharide anhydride. Celloglucosan is not present in the products of acid hydrolysis. Methylation of trihexosan with methyl sulphate and alkali gives smoothly the *nonamethyltrihexosan*, m. p. 84—91°, $[\alpha]_D^{13}$ +94·8° in chloroform, which on hydrolysis yields only βγζ-trimethyldextrose. Trihexosan must thus have one of the constitutions assigned by Irvine to cellulose, from which, however, it differs completely.

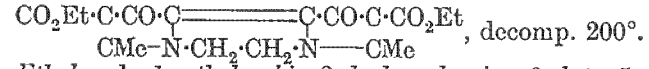
C. HOLLINS.

Aminohydroxy-compounds which show the biuret reaction. III. Separation of γ-amino-β-hydroxybutyric acid into optically active components. M. TOMITA and Y. SENDJU (Z. physiol. Chem., 1927, **169**, 263—277; cf. Tomita and Fukagawa, A., 1926, 1235).—*dl*-γ-Amino-β-hydroxybutyric acid has been resolved into the active components by means of the brucine salts of the benzoyl derivative. The amino-acid is benzoylated and an alcoholic solution of brucine is added. After some days at 0°, *brucine benzoyl*-l-γ-*amino*-β-*hydroxybutyrate*, m. p. 87°, separates as colourless plates, whilst colourless needles of the *brucine benzoyl*-d-γ-*amino*-β-*hydroxybutyrate*, m. p. 41°, are obtained from the mother-liquor. The former brucine salt yields two isomeric l-γ-*benzamido*-β-*hydroxybutyric acids*, m. p. 172°, $[\alpha]_D^{20}$ —7·59° and m. p. 114° and $[\alpha]_D^{9}$ —11·84° (+1H₂O, m. p. 80—81°); the other brucine salt gives two d-γ-*benzamido*-β-*hydroxybutyric acids*, m. p. 178°, $[\alpha]^{20}$ +4·08°, m. p. 116° and $[\alpha]^{20}$ +10·0° (+1H₂O, m. p. 78—80°). Hydrolysis of the benzoyl compounds with hydrobromic acid yields two l-γ-*amino*-β-*hydroxybutyric acids*, m. p. 213°, $[\alpha]^{20}$ —3·40° and m. p. 212°, $[\alpha]_D^{20}$ —21·06°, respectively, and two d-γ-*amino*-β-*hydroxybutyric acids*, m. p. 214°, $[\alpha]_D^{20}$ +3·21° and m. p. 214° (decomp.), $[\alpha]^{20}$ +18·30°, respectively. The d- and l-γ-*amino*-β-*hydroxybutyric acids* all give positive biuret reactions. On exhaustive methylation they yield two l-γ-*trimethyl*-β-*hydroxybutyrobetaines*, $[\alpha]_D^{20}$ —7·25° (*gold* salt, m. p. 151—152°, $[\alpha]_D^{20}$ —20·98°, *gold* salt, m. p. 155°, *platinic* salt, m. p. 220°, and *mercury* salt, m. p. 204°, respectively, the second compound being identical with carnitine, and two d-γ-*trimethyl*-β-*hydroxybutyrobetaines*, $[\alpha]^{20}$ +8·42°, *gold* salts, m. p. 150—151°, $[\alpha]_D$ +20·20°, and m. p. 155°, respectively.

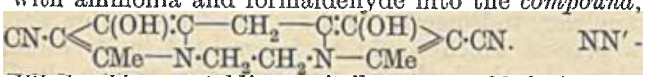
A. WORMALL.

Acylation of derivatives of *NN'*-ethylenebis-β-aminocrotonic acid and similarly constituted substances. E. BENARY (Ber., 1927, **60**, [*B*], 1826—1836; cf. A., 1923, i, 37, 201; this vol., 45).—In general, *C*-derivatives cannot be obtained from compounds of αγ-diketones with bases of the type NHR'·CR:CHX by means of acid chlorides, whereas they are prepared from substances in which X represents an ester, nitrile, or acid amide group. From the former compounds the preparation of β-hydroxypyrroles cannot therefore be effected.

Ethyl *NN'*-ethylenebis-β-aminocrotonate is converted by chloroacetyl chloride and pyridine in presence of ether into *ethyl -ethylenebis*-β-*amino*-α-*chloroacetylcrotonate*, $[{-}CH_2{\cdot}NH{\cdot}CMe{:}C(CO{\cdot}CH_2Cl){\cdot}CO_2Et]_2$, m. p. 124°, which is transformed by potassium hydrogen sulphide into ethyl 4-hydroxy-2-methylthiophen-3-carboxylate, m. p. 64·5—66° (cf. A., 1915, i, 576), and passes when heated into the *compound* $\left[\begin{matrix}O\text{—}CO\\ \diagup\quad\diagdown\\ CH_2{\cdot}CO\end{matrix}\!>\!C{:}CMe{\cdot}NH{\cdot}CH_2{-}\right|$ m. p. 290° (decomp.). It is transformed by alcoholic ammonia into *ethyl* 1 : 1'-*ethylenebis*-3-*hydroxy*-5-*methylpyrrole*-4-*carboxylate*, decomp. 180—200° after darkening at 160°. The aqueous solution of the latter ester is converted by ferric chloride into the *pyrroline* derivative,


, decomp. 200°. *Ethyl* 1 : 1 *ethylenebis-2-hydroxylamino-3-keto-5-methylpyrroline-4-carboxylate*, m. p. 168° (decomp.) after darkening at 160°, and *ethyl* 1 : 1′-*ethylenebis-2-nitrimino-3-keto-5-methylpyrroline-4-carboxylate* (anhydrous and dihydrate), decomp. about 198°, are described.

Diacetonitrile is readily transformed by ethylenediamine in acetic acid solution into NN′-*ethylenebisdiacetonitrile*, $[CN\cdot CH{:}CMe\cdot NH\cdot CH_2-]_2$, m. p. 194—195°, which, with chloroacetyl chloride and pyridine, affords NN′-*ethylenebis-2-chloroacetyldiacetonitrile*, m. p. 220°; it is transformed by successive treatment with ammonia and formaldehyde into the *compound*,



NN′-*Ethylenebis-α-acetyldiacetonitrile*, m. p. 230°, is converted by phenylhydrazine into 1-*phenyl-3* : 5-*dimethylpyrazole-4-nitrile*, m. p. 89—90°, identified by hydrolysis to 1-phenyl-3 : 5-dimethylpyrazole-4-carboxylic acid.

Acetylacetone–ethylenediamine, chloroacetyl chloride, and pyridine afford NN′-*ethylenebis*-N-*chloroacetyl-acetylacetonamine*, $[CHAc{:}CMe\cdot N(CO\cdot CH_2Cl)\cdot CH_2-]_2$, m. p. 108°, which is converted by alcoholic alkali hydroxide into NN′-*ethylenebis*-N-*hydroxyacetylacetylacetonamine*, m. p. 275° (decomp.) after darkening at 260°. -*Ethylenebis*-N-*benzoylacetylacetonamine*, m. p. 192°, N-*benzoylbenzoylacetonamine*, m. p. 114°, N-*acetylbenzoylacetonamine*, m. p. 101°, and NN′-*ethylenebisbenzoylacetonamine*, m. p. 183°, are described. Chloroacetylacetylacetonamine is converted by potassium hydrogen sulphide into *thiobis*-N-*acetylacetylacetonamine*, $S[CH_2\cdot CO\cdot NH\cdot CMe{:}CHAc]_2$, m. p. 123°; it does not appear to give a pyrrole derivative with alcoholic ammonia.

Formylacetonanil and formylacetophenonanil give O-*chloroacetyl* derivatives, m. p. 137·5° and 144°, respectively. *Formylacetophenonanilphenylhydrazone*, m. p. 225—226°, is described. H. Wren.

So-called "diethyl dicyanoglutaconate" and some derivatives. Y. Urushibara (Bull. Chem. Soc. Japan, 1927, **2**, 236—241; cf. this vol., 345).—In the condensation of ethyl cyanoacetate with chloroform and sodium ethoxide, excess of the latter two compounds gives an improved yield of ethyl sodio-αγ-dicyanoglutaconate. From the silver derivative of this compound an *ammonium* derivative, $C_{11}H_{12}O_4N_2,NH_3,2H_2O$, losing 1 mol. of water at 130°, was obtained (cf. Ruhemann and Browning, J.C.S., 1898, **73**, 283). An attempt to synthesise the true ethyl dicyanoglutaconate by heating together ethyl cyanoacetate, ethyl orthoformate, and acetic anhydride yielded ethyl sodiodicyanoglutaconate, the desired product possibly having been formed initially. Methyl cyanoacetate and chloroform condensed with sodium methoxide in methyl alcohol, giving *methyl sodio-αγ-dicyanoglutaconate*, $C_9H_7O_4N_2Na,H_2O$, from an acidified solution of which *methyl αγ-dicyanoglutaconate semihydrate*, $(+0{\cdot}5H_2O)$, m. p. 225°, was precipitated. This compound yielded an indefinite bromine derivative from which *αγ-dicarbomethoxyglutaconamide picrate*, $C_9H_{12}O_6N_2,C_6H_2(NO_2)_3\cdot OH$, was obtained. B. W. Anderson.

New reference compounds in the sugar group. Methylamides of *d*-, *l*-, and *i*-dimethoxysuccinic acids and of *l*-arabo- and *i*-xylo-trimethoxyglutaric acids. W. N. Haworth and D. I. Jones (J.C.S., 1927, 2349—2353).—d-*Dimethoxysuccinomethylamide* has m. p. 205°, $[\alpha]_D^{15}$ +132·6° in water. *Methyl* l-*dimethoxysuccinate*, b. p. 83°/0·07 mm., n_D^{18} 1·4345, $[\alpha]_D$ −78·8° in methyl alcohol, gives l-*dimethoxysuccinamide*, m. p. 278° (decomp. 294°), and l-*dimethoxysuccinomethylamide*, m. p. 205°, $[\alpha]_D^{15}$ −131·8° in water. i-*Dimethoxysuccinomethylamide* has m. p. 210°. Methyl i-trimethoxyglutarate, b. p. 102—104°/0·09 mm., n_D 1·4402, obtained by the cautious oxidation of trimethyl δ-xylonolactone with nitric acid (*d* 1·42) followed by esterification with methyl-alcoholic hydrogen chloride, gives i-*xylo-trimethylglutaramide*, m. p. 195—198° after darkening at 195°, and i-*xylo-trimethoxyglutaromethylamide*, m. p. 167—168°. Trimethyl δ-arabonolactone, m. p. 45°, $[\alpha]_D^{15}$ +179° in water, prepared from trimethyl-β-methylarabinoside, is similarly oxidised to give finally *methyl* l-*arabono-trimethoxyglutarate*, b. p. 105°/0·14 mm., $[\alpha]^{20}$ +37·6° in water, +41·2 in methyl alcohol; l-*arabono-trimethoxyglutaramide*, m. p. 230° (decomp.), and l-*arabono-trimethoxyglutaromethylamide*, m. p. 172°, $[\alpha]_D^{18}$ +59·9° in water, are described. G. A. C. Gough.

Nitroalkylguanidines. T. L. Davis and S. B. Luce (J. Amer. Chem. Soc., 1927, **49**, 2303—2305; cf. this vol., 863).—The following nitroalkylguanidines, obtained from nitroguanidine and the corresponding amines in aqueous solution, are described: *nitromethyl-*, m. p. 160·5—161·0°; *-dimethyl-*, m. p. 193·6—194·5°; -n-*propyl-*, m. p. 98·0—98·5°; -iso*propyl-*, m. p. 154·8—155·6°; -iso*butyl-*, m. p. 121·0—121·5°; -n-*amyl-*, m. p. 98·8—99·3°; -iso*amyl-*, m. p. 145·5 146·2°, and -tert.-*amyl-guanidine*, m. p. 154·8—155·6°. F. G. Willson.

Methylation with diazomethane. M. Nierenstein (Ber., 1927, **60**, [*B*], 1820—1821).—Ethylene glycol does not react with diazomethane. Its monoacetate is readily converted by the reagent into β-methoxyethyl acetate, b. p. 143—144°. The latter substance is hydrolysed by alcoholic ammonia to β-methoxyethyl alcohol, which cannot be methylated by diazomethane. Triphenylmethyl chloride, β-methoxyethyl alcohol, and pyridine afford *triphenylmethyl β-methoxyethyl ether*, m. p. 104°. H. Wren.

Reaction between lithium *n*-butyl and organic halogen compounds. C. S. Marvel, F. D. Hager, and D. D. Coffman (J. Amer. Chem. Soc., 1927, **49**, 2323—2328; cf. A., 1926, 1232).—Treatment of lithium *n*-butyl with *n*-heptyl bromide in light petroleum affords *n*-undecane. Methylene iodide yields similarly *n*-nonane, whilst β-bromostyrene affords *α-phenyl-*Δ^{α}-n-*hexene*, b. p. 97—100°/8 mm., d_0^{25} 0·9455, n_D^{25} 1·5377, together with *trans-trans-*αδ-diphenyl-$\Delta^{\alpha\gamma}$-butadiene (cf. Rebuffat, A., 1891, 76). The initial deep coloration of the reaction mixture supports the view that the products of the last reaction are derived from intermediately formed free radicals. Lithium *n*-butyl and triphenylmethyl

chloride yield mainly *ααα-triphenyl-n-pentane*, m. p. 153—154°, b. p. 170—180°/0·01 mm. *o*- and *m*-Bromotoluenes yield similarly toluene, but *p*-bromotoluene affords *p*-butyltoluene in 75% yield. Definite products could not be obtained from lithium *n*-butyl and α-chloropyridine, trimethylene bromide, carbon tetrachloride, *o*-dichlorobenzene, hexabromobenzene, and tetrachloroethylene. F. G. WILLSON.

Magnesium diethyl and its reaction with acetyl chloride. H. GILMAN and F. SCHULZE (J. Amer. Chem. Soc., 1927, 49, 2328—2330).—The production of magnesium diethyl from magnesium powder and mercury diethyl at 130° is greatly facilitated by the presence of a small proportion of mercuric chloride (cf. Lohr, A., 1891, 682; Fleck, A., 1893, i, 622). Magnesium diethyl reacts with ethereal acetyl chloride with production of methyldiethylcarbinol (cf. Fleck, *loc. cit.*). F. G. WILLSON.

Pyrogenic dissociation of certain aromatic compounds under pressure of hydrogen and by the combined action of catalysts. V. IPATIEV and N. ORLOV (Ber., 1927, 60, [*B*], 1963—1971).—The dissociation of a series of substances has been investigated in the presence of a catalyst (aluminium oxide, alone or with addition of oxide of copper or iron) to depress the temperature of dissociation and in an atmosphere of hydrogen to combine with the dissociated fragments. The initial pressure of the hydrogen is about 70 atm. and a minimum temperature of 400° is necessary to ensure a reasonably rapid action. Under these conditions, diphenyl ether is partly decomposed into phenol, traces of benzene, and a non-volatile resin. Phenol affords benzene in 20% yield. *o*-Cresol gives very little resin and about 30% of a mixture of benzene and toluene. Pyrocatechol yields benzene, much phenol, and a brittle resin. Aniline decomposes into benzene, ammonia, and a little diphenylamine; the change appears reversible, since aniline is produced in small amount from benzene and aqueous ammonia. Triphenylmethane gives benzene and a little diphenylmethane; the latter substance is more stable, giving only a small proportion of benzene. Naphthalene and a mixture of hydrocarbons are derived from tetrahydronaphthalene; diphenyl readily yields benzene. Acenaphthene affords naphthalene and liquid hydrocarbons, together with saturated gaseous hydrocarbons. Anthracene is converted almost completely into coke. Mesitylene appears to suffer loss of methyl groups to some extent. The uniform production of substances with simply constructed molecules is noteworthy. Solvent naphtha is converted into benzene, toluene (accompanied by xylenes or ethylbenzene), naphthalene, and small amounts of resin; phenols appear to be formed in very small quantity. Coal-tar heavy oil affords "light petroleum," benzene, toluene, xylene, naphthalene, and, probably, polymerised products. H. WREN.

Pyrogenic dissociation of phenanthrene in the presence of hydrogen under pressure. N. A. ORLOV (Ber., 1927, 60, [*B*], 1950—1956).—Phenanthrene is decomposed when heated at about 500° in the presence of hydrogen under initial pressure of about 75 atm. and aluminium oxide mixed with copper, nickel, or iron oxide yielding disubstituted benzenes containing very little benzene, naphthalene, methylnaphthalene, 2-ethylnaphthalene, dihydrophenanthrene, and unchanged phenanthrene. Dissociation occurs therefore with intermediate production of dihydrophenanthrene and fission of one ring with the formation of naphthalene and alkylnaphthalenes, the process representing the converse of the synthesis of phenanthrene from naphthalene and ethylene. The second possible mode of dissociation, into diphenyl and ethylene, does not appear to be realised in these experiments, as indicated by the almost complete absence of benzene and toluene from the products. Probably the dissociation of phenanthrene into naphthalene is caused by its tendency to isomerise to the symmetrical anthracene, a process which would be interrupted in its initial stages by the hydrogen and thus give rise to alkylnaphthalenes. It is probable that a dynamic isomerism exists between 9 : 10-dihydrophenanthrene and the dihydro-product formed by addition of hydrogen to the neighbouring ring. H. WREN.

Nitration of xylene with dilute nitric acid in presence of mercury. E. I. ORLOV (Ukraine Chem. J., 1926, 2, 370—375).—See A., 1926, 1130.

Nitration of cumene. L. BERT and P. C. DORIER (Bull. Soc. chim., 1927, [iv], 41, 1170—1171; cf. A., 1926, 56, 285).—The observation of Vavon and Callier (this vol., 455) that nitration of cumene by the Pictet method yields almost exclusively the *p*-nitro-derivative is confirmed. W. J. POWELL.

Arylsulphur chlorides and arylsulphuranilides. E. GEBAUER-FULNEGG (J. Amer. Chem. Soc., 1927, 49, 2270—2275).—Treatment of 2 : 5-dichlorothiophenol with chlorine in cold carbon tetrachloride affords 2 : 5-*dichlorochlorothiolbenzene*, b. p. 92°/3 mm., which, on treatment with aniline in chloroform or carbon tetrachloride, yields 2 : 5-*dichlorobenzenesulphenanilide*, m. p. 85°. p-*Chlorochlorothiolbenzene*, b. p. 94°/6 mm., was prepared analogously, and converted by treatment with aminoazobenzene into the corresponding substituted p-*chlorobenzenesulphenamide*, red, m. p. 188°. Treatment of 4-chloro-2-nitrochlorothiolbenzene with methylaniline in absolute ether affords 4-*chloro-2-nitrobenzenesulphenmethylanilide*, non-crystalline, red, and an analogous substituted 4-*chloro-2-nitrobenzenesulphenamide*, brownish-red, was also obtained from 2 : 4-diaminoazobenzene. A study of absorption spectra indicates that 4-chloro-2-nitrochlorothiolbenzene, its anilide, and 4-chloro- and 2 : 5-dichloro-chlorothiolbenzenes have similar structures, whilst 2 : 5-dichlorobenzenesulphenanilide has a structure differing from these. Variations in colour amongst these derivatives are ascribed to "approached quinonoid structures" of the molecules concerned (cf. Lecher and Holschneider, A., 1924, i, 728). F. G. WILLSON.

Oxidising action of "chloramine-*T*" [sodium *p*-toluenesulphonchloroamide]. G. SCHIEMANN and P. NOVAK (Z. angew. Chem., 1927, 40, 1032—1033).—Contrary to Engelfeldt's statement (A., 1923, i, 454), "chloramine-*T*" is stable on boiling a 10% aqueous solution for 3 hrs., and elimination of sodium hypo-

chlorite does not occur. Oxidation by "chloramine-*T*" in acid solution is represented by the equations $2C_6H_4Me\cdot SO_2NaNCl+2H^{\cdot}=C_6H_4Me\cdot SO_2\cdot NH_2+C_6H_4Me\cdot SO_2\cdot NCl_2+2Na^{\cdot}$; $C_6H_4Me\cdot SO_2\cdot NCl_2+2H_2O=C_6H_4Me\cdot SO_2\cdot NH_2+HOCl$, whilst in neutral solution it follows the equation, $C_6H_4Me\cdot SO_2NaNCl+H_2O=C_6H_4Me\cdot SO_2\cdot NH_2+NaCl+O$. In alkaline solution only does elimination of sodium hypochlorite occur. In agreement with Chattaway (J.C.S., 1905, **87**, 145) and Engelfeldt (*loc. cit.*) the constitution of "chloramine-*T*" is given as $C_6H_4Me\cdot SO(:NCl)\cdot ONa,3H_2O$.

S. J. Gregg.

Bivalency of carbon. I. Displacement of chlorine from diphenylchloromethane. *s*-Tetraphenyldimethyl ether. A. M. Ward (J.C.S., 1927, 2285—2295).—The chlorine group in diphenylchloromethane is displaced by ethyl alcohol or aqueous ethyl alcohol, both alone and in the presence of sodium hydroxide, to give mainly benzhydryl ethyl ether together with benzhydrol. The velocity coefficients of the reactions at 25° and at 35° under each of the above conditions and also in an experiment where alcoholic sodium ethoxide was used are those of a unimolecular reaction. Thus the sodium compounds, which merely accelerate the reaction, play no direct part in the displacement. It is suggested that the slowest reaction is the ionisation of the diphenylchloromethane, which is followed by the rapid reactions of the diphenylmethyl ion with hydroxyl and ethoxyl ions to give benzhydrol and benzhydryl ethyl ether (cf. Nef, A., 1898, i, 102). Benzhydrol gives *s*-tetraphenyldimethyl ether on boiling with dilute hydrochloric acid; on raising the concentration of the acid the yield of this product falls and diphenylchloromethane finally becomes the principal product. Boiling 2*N*-hydrochloric acid is without action on *s*-tetraphenyldimethyl ether, but the concentrated acid, or better ethereal hydrogen chloride, converts it into diphenylchloromethane.

G. A. C. Gough.

Reduction of 2-nitrofluorene. F. E. Cislak, I. M. Eastman, and J. K. Senior (J. Amer. Chem. Soc., 1927, **49**, 2318—2322).—Reduction of 2-nitrofluorene with zinc dust and calcium chloride in boiling aqueous alcohol affords 2 : 2′-azoxyfluorene, orange-yellow, m. p. 279° (decomp.). Owing to its insolubility, the latter can be reduced to 2-aminofluorene only by zinc dust and hydrochloric acid in phenol solution. If this reduction is carried out with glacial acetic acid instead of hydrochloric acid, at below 40°, the product appears to be the result of an *o*-semidine rearrangement of the corresponding hydrazo-derivative. It is colourless, has m. p. 257—258° (decomp.) after becoming red at 240—245°, and is considered to be either 2′-*amino*-2 : 3′-*difluorenylamine* or 2-*amino*-1 : 2′-*difluorenylamine*. When boiled with acetic anhydride, it yields an oxygen-free compound, m. p. 179°, to which the corresponding alternative constitutions, 3-(2-*fluorenyl*)-2-*methyl*-2 : 3-*fluoreniminazole* and 1-(2-*fluorenyl*)-2-*methyl*-1 : 2-*fluoreniminazole*, are ascribed. F. G. Willson.

Preparation and constants of phenylpropinene and certain of its homologues. L. Bert and P. C. Dorier (Bull. Soc. chim., 1927, [iv], **41**, 1171—1173).—A reply to Bourguel's criticisms (this vol., 337) of the authors' work on this subject (A., 1925, i, 803, 1373; 1926, 391). W. J. Powell.

System acetanilide–propionanilide. E. C. Gilbert and L. Clarke (J. Amer. Chem. Soc., 1927, **49**, 2296—2299).—The f.-p. curve of mixtures of acetanilide and propionanilide shows that a compound, m. p. 79·2—79·4°, almost completely dissociated in the liquid state, is formed between the two substances, but the shape of the curve does not permit the composition of this compound to be determined (cf. Hurd, A., 1924, i, 140). F. G. Willson.

Tautomerism of the amidines. VII. Methylation of benzenyl-*p*-nitrodiphenylamidine [*N*-phenyl-*N*′-*p*-nitrophenylbenzamidine]. C. Chew and F. L. Pyman (J.C.S., 1927, 2318—2323).—N-*Phenyl*-N′-p-*nitrophenylbenzamidine*, m. p. 184° (corr.; *hydrochloride*, m. p. 261°), prepared by an application of the method of Hill and Cox (this vol., 144), and methyl iodide give a 28·8% yield of *N*-phenyl-*N*′-*p*-nitrophenyl-*N*-methylbenzamidine, and 24·9% of the *N*′-methyl isomeride. These results confirm the suggestion (Pyman, J.C.S., 1923, **123**, 3359; A., 1926, 1156) that the preferential alkylation of the nitrogen atom attached to an aryl group of *N*-aryl-*N*′-alkylbenzamidines is due to the tendency of the aryl group to attract the double linking into the αβ-position. If the difference in basicity of the two nitrogen atoms (which must be considerable in the present case) determined the proportion of the isomerides in the methylation product, a large preponderance of one isomeride would be expected. N-*Phenyl*-N′-p-*nitrophenyl*-N-*methylbenzamidine*, m. p. 138° [corr.; *picrate*, m. p. 206° (corr.)], prepared by the interaction of *p*-nitrobenzanilide-iminochloride (free from traces of hydrogen chloride) and methylaniline in dry ethereal solution, could not be prepared by the method of Hill and Cox. N-*Phenyl*-N′-p-*nitrophenyl*-N′-*methylbenzamidine* [oil; *hydrochloride* +EtOH, m. p. 226° (corr.; with effervescence); *hydriodide*, m. p. 225° (corr.); *picrate*, m. p. 194° (corr.)], was obtained by the method of Hill and Cox, but could not be isolated from the products of the interaction of benzanilide-iminochloride and *p*-nitromethylaniline.

G. A. C. Gough.

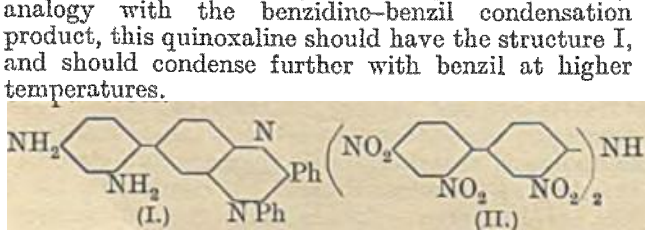
Crystalline products formed by the action of aromatic amines on thiosemicarbazide and its derivatives. H. Macurevitsch (Bull. Soc. chim., 1927, [iv], **41**, 1065—1074).—The mol. wt. of the crystalline substances of high m. p. obtained by the action of aniline, *o*-, *m*-, and *p*-toluidines on hydrazodithiodicarbonamide, and of *o*-toluidine on phenylhydrazodithiodicarboxylamide (this vol., 777), have been determined in various solvents, and the values obtained show that the formulæ previously assigned to them should be halved. On heating with benzophenone chloride these compounds do not give blue colorations (see Tschugaev, A., 1902, i, 630), and it is concluded that the groupings $\cdot CS\cdot NH_2$ and $\cdot CS\cdot NH\cdot$ are not present in their molecules. The suggestion that these compounds are substituted tetrazines is abandoned, and they are formulated as thio-1 : 2 : 4-triazoles, formed by elimination of 1 mol. of hydrogen sulphide from the intermediate

substance NH_2·CS·NH·NH·CS·NHR, which is obtained from 1 mol. of the amine and 1 mol. of hydrazodithiodicarboxylamide, by elimination of ammonia. H. BURTON.

Determination of the amino-group in nitroarylamines. I. Determination of nitroaniline and nitroacetanilide. N. SEMIGANOVSKY (Z. anal. Chem., 1927, **72**, 27—30).—The amine is refluxed with sodium hydroxide solution, which, throughout the analysis, is never more concentrated than 25%, and the ammonia evolved is collected and titrated with standard acid. When the amine is completely decomposed, the water-jacket of the reflux condenser is disconnected, the ammonia being distilled over through a second condenser. The results obtained agree within 0·2%. F. S. HAWKINS.

Determination of secondary nitrosoamine groups. K. LEHMSTEDT (Ber., 1927, **60**, [*B*], 1910—1912).—Reduction of nitrosoamines by mercury and concentrated sulphuric acid does not generally proceed quantitatively, since the acid frequently causes partial conversion into the *C*-nitroso-compound. Reduction may, however, be effected with ferrous chloride and hydrochloric acid in boiling solution: $NR'R''·NO+HCl+FeCl_2=NHR'R''+FeCl_3+NO$. The liberated nitric oxide is measured. The results are generally somewhat low, since reduction to ammonia occurs to some extent and a little nitric oxide usually remains in the evolution flask. *C*-Nitroso- and *C*-nitro-groups do not cause complication. Analyses of di*iso*butyl-, phenylmethyl-, diphenyl-, piperidyl-, and acetylphenylnitrosoamines are recorded. H. WREN.

Orientation effects in the diphenyl series. IV. Reduction of Bandrowski's and of Strakosch's dinitrobenzidines, and condensation of the products with benzil. Nitration of 2-nitrodiacetylbenzidine and of 4 : 4′-dibromodiphenyl. R. J. W. LE FÈVRE, D. D. MOIR, and E. E. TURNER (J.C.S., 1927, 2330—2339).—The observation of Brady and McHugh (*ibid.*, 1923, **123**, 2047) that Bandrowski's dinitrobenzidine, m. p. 233° (originally supposed to be 3 : 3′-dinitrobenzidine, but recently shown to be the 2 : 3′-derivative, m. p. 236—237°; Le Fèvre and Turner, A., 1926, 946), yields the same quinoxaline, m. p. 313° (corr.), as 3 : 3′-dinitrobenzidine (Strakosch's dinitrobenzidine) when reduced and subsequently treated with benzil has been verified, but the yield from Bandrowski's dinitrobenzidine is small. The latter is very difficult to purify, and it is shown by examining artificial mixtures that any sample of m. p. 233° or lower contains 2% or more of Strakosch's dinitrobenzidine, which is sufficient to account for the quinoxaline formed. Samples of Bandrowski's dinitrobenzidine, m. p. 237° (uncorr.), yield no quinoxaline. By analogy with the benzidine–benzil condensation product, this quinoxaline should have the structure I, and should condense further with benzil at higher temperatures.



Actually, when heated in the solution in which it is formed, it undergoes further condensation with production of what is evidently a mixture (m. p. range about 30°).

4-Bromo-4′-nitrodiphenyl was nitrated to give 4-*bromo*-3 : 4′-*dinitrodiphenyl*, m. p. 135°, which on further nitration yielded 4-bromo-2′ : 3 : 4′-trinitrodiphenyl (Le Fèvre and Turner, A., 1926, 1029). Small quantities of the latter compound were readily converted into 2′ : 3 : 4′-*trinitro*-4-*aminodiphenyl* (m. p. 192—193°) on heating in a sealed tube with alcoholic ammonia, but the large-scale conversion proved unsatisfactory. On dissolving 4-bromo-2′ : 3 : 4′-trinitrodiphenyl in boiling nitrobenzene and passing in dry ammonia, 4 : 4′-*bis*-o*p*-*dinitrophenyl*-2 : 2′-*dinitrodiphenylamine* (II), m. p. 256—257°, was obtained. Under the same conditions, picryl chloride yielded trinitroaniline, 1-chloro-2 : 4-dinitrobenzene gave 2 : 4-dinitroaniline, 2 : 5-dichloronitrobenzene was unaffected, and 4 : 4′-dibromo-2 : 3′-dinitrodiphenyl was partly converted into the corresponding bromo-amino-compound.

From the nitration product of 2-nitrodiacetylbenzidine, which is mainly 2 : 3′-dinitrodiacetylbenzidine (Le Fèvre and Turner, *loc. cit.*), 2 : 5 : 3′-*trinitrobenzidine*, dark red, m. p. 276° (*diacetyl* derivative, m. p. above 300°), was obtained in the form of the sparingly soluble *sulphate*. The constitution of this base was proved by its conversion by the perbromide method into 4 : 4′-*dibromo*-2 : 5 : 3′-*trinitrodiphenyl*, m. p. 251—252°, which reacted readily with piperidine to give 2 : 5 : 3′-*trinitro*-4 : 4′-*dipiperidinodiphenyl*, m. p. 160°. The occurrence of this trinitrobenzidine shows that some 2 : 5-dinitrodiacetylbenzidine must be formed in the nitration of 2-nitrodiacetylbenzidine, since the 2 : 3′-compound is unaffected by even more drastic nitrating conditions than those used. Nitration of 4 : 4′-dibromo-2 : 3′-dinitrodiphenyl yielded 4 : 4′-*dibromo*-2 : 3′ : 5′-*trinitrodiphenyl*, m. p. 176—177°, which with piperidine afforded 4-*bromo*-2 : 3′ : 5′-*trinitro*-4′-*piperidinodiphenyl*, m. p. 194° (cf. Lellmann, A., 1883, 343). 3 : 4′-*Dinitro*-4-*anilinodiphenyl* has m. p. 155—156°, 3 : 2′ : 4′-*trinitro*-4-*anilinodiphenyl*, m. p. 190—191°, and 3 : 2′ : 4′-*trinitro*-4-*methylanilinodiphenyl*, m. p. 212°. W. J. POWELL.

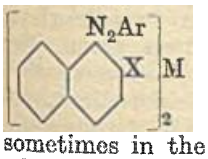
Compounds of aromatic *p*-diamines with sulphur dioxide. I. G. FARBENIND. A.-G.—See B., 1927, 742.

The two *p*-nitroazoxybenzenes. A. ANGELI and D. BIGIAVI (Atti R. Accad. Lincei, 1927, [vi], **5**, 819—823).—When treated with excess of bromine in presence of a very small quantity of iron filings, *p*-nitroazoxybenzene (*a*), m. p. 148° (cf. Angeli and Alessandri, A., 1911, i, 1045), yields (1) the *tribromo*-derivative, $C_6H_2Br_3·N:NO·C_6H_4·NO_2$, m. p. 206—208°, which is obtained also on brominating monobromonitroazoxybenzene, m. p. 203°, in the cold, and (2) the isomeric *p*-nitroazoxybenzene (*b*). Under similar treatment, the latter yields a monobromo-compound, $C_{12}H_8O_3N_3Br$, m. p. 135—137°, which may be identical with the compound, m. p. 127°, described by Valori (Atti R. Accad. Lincei, 1912, [v], **21**, i, 794). T. H. POPE.

Reduction of nitro-compounds by aromatic ketols. I. Some *p*-azoxy-compounds. H. B. NISBET (J.C.S., 1927, 2081—2086).—Hot alcoholic solutions of benzoin, anisoin, or furoin reduce aromatic nitro-compounds to the corresponding azoxy-compounds in the presence of a trace of sodium methoxide or ethoxide. The ketols are oxidised to the 1 : 2-diketones. In this way the following azoxy-compounds are prepared: p-*azoxybenzylidene-aniline*, decomp. 226° (sintering at 185°); p-*azoxy-benzylidene*-p-*toluidine*, m. p. 217° (decomp.; sintering at 189—190°); p-*azoxybenzylidene*-p-*aminoaceto-phenone*, m. p. 217° (decomp.; sintering at 187°); p-*azoxybenzonitrile*, m. p. 221°; p-*azoxystilbene*, m. p. 271—272° (decomp.; sintering at 259°); p-*azoxy*-2-*nitrostilbene*, m. p. 208—210°; p-*azoxy*-2 : 3′-*dinitro-stilbene*, m. p. 212°; p-*azoxy*-2 : 6-*dinitrostilbene*, m. p. 270°; p-*azoxy*-2-*nitro*-4′-*methoxystilbene*, m. p. 208°; p-*azoxy*-2-*nitro*-3′ : 4′-*methylenedioxystilbene*, m. p. 230°; p-*azoxy*-2 : 6-*dinitro*-4′-*methoxystilbene*, m. p. 297° (decomp.); p-*azoxy*-2-*nitro*-4′-*dimethylamino-stilbene*, unmelted at 305°. Methyl and ethyl *p*-azoxy-cinnamates may conveniently be prepared by this method. The nitrostilbenes were prepared by a modification of Bishop and Brady's method (J.C.S., 1922, 121, 2367; cf. A., 1916, i, 24) and of them the following are new: 2 : 4 : 4′-*trinitrostilbene*, m. p. 234—235°; 2 : 4-*dinitro*-3′ : 4′-*methylenedioxystilbene*, m. p. 178—180°; 2 : 4 : 6-*trinitro*-4′-*methoxystilbene*, m. p. 167—168°; 2 : 4-*dinitro*-4′-*dimethylamino-stilbene*, m. p. 181° (*chloroplatinate*, m. p. 211°).

G. A. C. GOUGH.

Metallic derivatives of azo-compounds. G. B. CRIPPA (Gazzetta, 1927, 57, 497—504).—The metallic complexes formed by the union of an atom of copper, nickel, or cobalt with 2 mols. of arylazo-β-naphthylamine or arylazo-β-naphthol and obtained either by the action of the metal ammonium sulphate on the amino- or hydroxy-azo-derivatives in alcoholic suspension or by boiling solutions of the aminoazo-derivatives in aniline or nitrobenzene with powdered nickel or cobalt exhibit properties which suggest for these complexes formulæ of the type annexed, where X=NH_2 or OH. These complexes yield the azo-derivative when treated with dilute mineral acid or acetic acid, sometimes in the cold; but they remain unchanged when boiled in a strongly alkaline medium. Neither the complexes derived from the benzeneazonaphthols nor the aminocupric complexes are obtainable by the latter of the two methods mentioned, but are readily formed by the former method.



[With U. MARTEGANI.]—*Cupridi*-p-*anisylazo*-β-*naphthol*, $C_{34}H_{28}O_4N_4Cu$, forms burnt-sepia needles, m. p. 271°; the corresponding *nickel* and *cobalt* complexes have m. p. 279° and 265°, respectively. *Cupri*-, *nickelo*-, and *cobalto-di*-o-*anisoleazo*-β-*naphthols* have m. p. 225°, 300° (decomp.), and 254° (decomp.), respectively. *Cupri*-, *nickelo*-, and *cobalto-di*-p-*phenetoleazo*-β-*naphthols* have m. p. 267°, 265°, and 224°, respectively. The corresponding *complexes* from o-*phenetoleazo*-β-*naphthol* have m. p. 219°, 295°, and ; from *p*-anisoleazo-β-naphthylamine, 157°, 257°, and 236°; from *o*-anisoleazo-β-naphthylamine, 170°, 226—228°, and 167°, and from *p*-phenetoleazo-β-naphthylamine, 186°, 267°, and 212°. T. H. POPE.

Action of hydrazines on semicarbazones. III. W. BAIRD and F. J. WILSON (J.C.S., 1927, 2114—2117; cf. A., 1926, 1141).—That the thermal decomposition of acetone-δ-anilinosemicarbazone to give acetone-phenylhydrazone and 4-aminourazole, $\begin{matrix}CO\cdot NH\cdot NH\\ |\\ N(NH_2)\cdot CO\end{matrix}$ (previously described in error as 1-aminourazole), proceeds through the intermediate formation of acetonecarbohydrazone and diphenylcarbohydrazide, is confirmed by the formation of the same final products by the interaction of the hypothetical intermediates. Some dimethylketazine is formed in both reactions probably by the decomposition of the carbohydrazone. In a similar way pinacolin-δ-anilinosemicarbazone affords pinacolinphenylhydrazone, pinacolinazine, and 4-aminourazole; benzylidene-δ-anilinosemicarbazone affords benzaldehydephenylhydrazone and 4-aminourazole; acetone-δ-diphenylaminosemicarbazone affords acetonediphenylhydrazone, dimethylketazine, and 4-aminourazole. In the last decomposition some of the intermediate compound, tetraphenylcarbohydrazide (Acree, A., 1903, i, 861), was actually isolated. *Pinacolinazine*, b. p. 213—216°/17 mm., was identified by comparison with the synthetic product obtained by the interaction of alcoholic solutions of hydrazine hydrate and pinacolin. Attempts to prepare δ-anilinothiosemicarbazones by the interaction of the thiosemicarbazones of acetone, acetophenone, and dibenzyl ketone with phenylhydrazine resulted in the formation of thiosemicarbazide and the ketonephenylhydrazones. *Dibenzyl ketone thiosemicarbazide*, m. p. 165—166°, and *methyl ethyl ketone* δ-*anilinosemicarbazide*, m. p. 137°, are also described. G. A. C. GOUGH.

Azides. A. ANGELI (Atti R. Accad. Lincei, 1927, [vi], 5, 732—736).—The molecular structure of the azides is discussed. The fact that the presence of a small proportion of acid effects the isomerisation of the nitroso-derivative obtained from benzylmethylhydrazine, $CH_2Ph\cdot N(NO)\cdot NHMe \longrightarrow CH_2Ph\cdot NH\cdot NMe\cdot NO$, renders it possible that the formation of phenyl azide by the action of an acid on nitrosophenylhydrazine is accompanied by a similar change: $NO\cdot NPh\cdot NH_2 \longrightarrow NHPh\cdot NH\cdot NO \longrightarrow NPh{:}N{:}N$. An analogous transformation is possible in the conversion of the sodium derivative of nitrosophenylhydrazine into *iso*diazo-oxides and nitrous oxide by the action of alcoholic nitrite solution: $NH{:}NPh{:}N\cdot OH \longrightarrow NO\cdot N{:}NPh{:}N\cdot OH \longrightarrow NPh{:}N\cdot OH + N_2O$. It appears likely that the tautomeric form of nitrosophenylhydrazine belongs to a group of compounds which contain a quinquevalent nitrogen atom united to the aromatic nucleus, such as $O{:}NPh{:}O$, $O{:}NH_2Ph$, $O{:}NPh{:}NH$, $O{:}NPh{:}N\cdot OH$.

T. H. POPE.

Diazo hydroxides. L. CAMBI (Atti R. Accad. Lincei, 1927, [vi], 5, 837—840).—Our knowledge of the structure of the alkali salts of the normal diazohydroxides is in agreement with the structural formula ascribed by Angeli to these hydroxides themselves (A., 1926, 947). Hantzsch's views on this question are refuted. T. H. POPE.

Organic compounds of quinquevalent bismuth. G. CHARRIER (Atti R. Accad. Lincei, 1927, [vi], 5, 889—892).—In hydrochloric acid solution, bismuth trichloride reacts with aryldiazonium chlorides giving stable crystalline compounds containing quinquevalent bismuth: $BiCl_3+ArN_2Cl\longrightarrow ArN_2BiCl_4$. The chlorine atoms in these chlorobismuthates are readily replaceable by sulphuric or nitric residues. *Benzenediazonium chlorobismuthate*, $N_2Ph\cdot BiCl_4$, has m. p. 85—87° (decomp.); the *toluene-o-diazonium* compound, m. p. 115—120° (decomp.); *toluene-m-diazonium*, m. p. 120° (decomp.); *toluene-p-diazonium*, m. p. 120° (decomp.); *p-methoxybenzenediazonium*, m. p. 145—147° (decomp.); *p-chlorobenzenediazonium*, m. p. 105—107° (decomp.); *p-bromobenzenediazonium*, m. p. 135—140° (decomp.). T. H. POPE.

Halogenated tertiary amines. C. S. MARVEL, W. H. ZARTMAN, and O. D. BLUTHARDT (J. Amer. Chem. Soc., 1927, 49, 2299—2303).—Treatment of boiling diethylamine with γ-phenoxypropyl bromide affords *diethyl-γ-phenoxypropylamine*, (I), b. p. 147—150°/20 mm., d_4^{20} 0·9425, n_D^{20} 1·4987 [*hydrochloride*, m. p. 98—102° (decomp.)], together with *diethyldi-γ-phenoxypropylammonium bromide*, m. p. 77·5—79°. When boiled with hydrobromic acid under such conditions that water and phenol are continuously boiled off, (I) yields *diethyl-γ-bromopropylamine hydrobromide*, hygroscopic, m. p. 91—94°. Treatment of the latter in ethereal solution with concentrated aqueous sodium hydroxide affords the corresponding *base*, (II), b. p. 60—64°/7mm., d_4^{25} 1·1524, n_D^{25} 1·4580, which isomerises rapidly when kept into a *quaternary ammonium bromide*, m. p. 180—185°, presumably an 8-membered ring compound (cf. Knorr and Roth, A., 1906, i, 457). Condensation of (II) with ethyl sodiomalonate in absolute alcohol affords *ethyl γ-diethylaminopropylmalonate*, b. p. 163—170°/23 mm., d_4^{25} 0·9686, n_D^{25} 1·4380. Treatment of δ-phenoxy-*n*-butylamine with ethyl bromide and aqueous sodium hydroxide yields *diethyl-δ-phenoxybutylamine*, b. p. 152—158°/21 mm., d_4^{25} 0·9424, n^{25} 1·4975, from which *diethyl-δ-bromobutylamine*, b. p. 68—70°/6 mm., d_4^{25} 1·0187, n_D^{25} 1·4415 (*hydrobromide*, hygroscopic, m. p. 62—68°), was obtained as above. When kept, the latter isomerises, presumably into *diethylpyrrolidinium bromide*, m. p. 170—175°. *Ethyl δ-diethylaminobutylmalonate* has b. p. 170—175°/24 mm., d_4^{25} 0·9621, n_D^{25} 1·4468. F. G. WILLSON.

Nuclear carboxylation of aromatic amines. A. P. TERENTIEV and A. M. RUBINSTEIN (Ber., 1927, 60, [*B*], 1879—1882).—Magnesium powder, activated by iodine, reacts readily with *o*-anisidine in the absence of air, giving the compound $(OMe\cdot C_6H_4\cdot NH)_2Mg$, which is transformed by carbon dioxide at 150° into *magnesium* N-*o-anisylcarbamate*. If the latter compound is heated with an excess of *o*-anisidine at 250—270° it is converted into 3-*amino*-2-*methoxybenz-o-anisidide*, m. p. 178° (NN′-*di-o-anisylcarbamide* has m. p. 182°); the *formyl* derivative, m. p. 133°, is more stable than the anisidide itself. Hydrolysis of the anisidide gives *o*-anisidine and 3-*amino*-2-*methoxybenzoic acid*, m. p. 153°, identified by de-amination and subsequent oxidation to phthalic acid. H. WREN.

Nitrosation of phenols. IV. 3 : 5-Dichlorophenol. H. H. HODGSON and J. S. WIGNALL (J.C.S., 1927, 2216—2221; cf. Hodgson and Moore, *ibid.*, 1923, **123**, 2499).—During numerous unsuccessful attempts, both direct and indirect, to nitrosate 3 : 5-dichlorophenol, it was found that the supposed 3 : 5-dichloro-4-nitrosophenol obtained by Blanksma (Rec. trav. chim., 1908, 27, 25) as a by-product in the conversion of 3 : 5-dichloroaniline into the phenol, and by Willstatter and Schudel (A., 1918, i, 399) by the action of nitrous acid on sodium 3 : 5-dichlorophenoxide, is identical with 3 : 5-*dichloro*-4-*nitrophenol*, m. p. 150° (*acetate*, m. p. 99°), obtained together with 3 : 5-*dichloro*-2-*nitrophenol*, m. p. 51°, by direct nitration of 3 : 5-dichlorophenol. 3 : 5-Dichloro-2-nitrophenol does not form a hydrate (cf. 3-chloro-2-nitrophenol, Hodgson and Moore, A., 1926, 281). 3 : 5-*Dichloro*-2-*aminophenol*, m. p. 132°, and 3 : 5-*dichloro*-4-*aminophenol*, m. p. 154°, are prepared by reduction of the nitrophenols with sodium hyposulphite. 3 : 5-*Dichloro*-2-*nitroanisole*, m. p. 75°, and 3 : 5-*dichloro*-4-*nitroanisole*, m. p. 70°, were prepared by methylation of the appropriate nitrophenol. The latter by reduction with tin and hydrochloric acid gives 3 : 5-*dichloro*-p-*anisidine*, m. p. 71°, from which 3 : 5-*dichloro*-4-*nitrosoanisole*, m. p. 125°, was obtained by oxidation with Caro's acid. On hydrolysis with concentrated sulphuric acid, it gives colourless 3 : 5-*dichloro*-4-*nitrosophenol*, m. p. 165°, dissolving in alkali with a green colour. It resembles the nearly colourless 3-chlorobenzoquinone-4-oxime (Hodgson and Moore, *loc. cit.*) and is possibly better formulated as 3 : 5-dichlorobenzoquinone-4-oxime. No evidence of conversion or of geometrical isomerism was obtained.

3 : 5-Dichloro-*p*-anisidine may be prepared from 3-chloro-4-nitroanisole by simultaneous reduction and chlorination with tin and concentrated hydrochloric acid, whilst iron and acetic acid effect normal reduction to 3-chloro-*p*-anisidine (cf. Hodgson and Handley, A., 1926, 515). The latter on oxidation yields 3-*chloro*-4-*nitrosoanisole*, deep green, m. p. 59°. Since 3 : 5-dichloro-4-nitrosoanisole is colourless, whilst 3-chloro-4-nitrosoanisole is deep green, the suppression of colour may be ascribed to the chlorine atom in the 5-position. 3 : 5-Dichlorodimethylaniline is nitrated by nitrous acid in formic acid solution, yielding 3 : 5-*dichloro*-4-*nitrodimethylaniline*, m. p. 142°. The direct nitrosation of 3-chloro-5-iodophenol was attempted without success. W. J. POWELL.

Complex metallic ammines. IX. Introduction of nitrophenol radicals into cobaltammine complexes. Distinctive behaviour of mononitrophenoxides. J. C. DUFF and E. J. BILLS (J.C.S., 1927, 2365—2375).—Unlike *o*- and *m*-nitrophenoxides, sodium *p*-nitrophenoxide reacts with aquopentamminocobaltic nitrate to give p-*nitrophenoxopentamminocobaltic* p-*nitrophenoxide* [I; X=*p*-$C_6H_4(NO_2)\cdot O$·]. This compound is hydrolysed in

(I.) $[Co(NH_3)_5X]X_2$ $[Co(NH_3)_5,H_2O]X_3$ (II.)

(III.) $[Co(NH_3)_5X](OH)X$

presence of platinised electrodes to $[H_2O\cdot Co(NH_3)_5]X_3$. Sodium 2 : 4- and 2 : 6-dinitrophenoxides give simple

aquopentammino-salts, *aquopentamminocobaltic* 2 : 4-*dinitrophenoxide* ($+3H_2O$), and *aquopentamminocobaltic* 2 : 6-*dinitrophenoxide* [II; $X=C_6H_3(NO_2)_2\cdot O\cdot$]. Sodium picrate gives *picratopentamminocobaltic picrate* ($+3H_2O$) [I; (cf. Morgan and King, J.C.S., 1922, **121**, 1723). This compound is alternatively prepared by reaction of picric acid with carbonatopentamminocobaltic nitrate. If the latter be present in excess, however, a basic salt, *picratopentamminocobaltic hydroxypicrate* [III; $X=C_6H_3(NO_2)_3\cdot O\cdot]+2H_2O$, is produced.

Sodium *m*-nitrophenoxide reacts with bisaquobisethylenediamminocobaltic bromide, giving *bis*-m-*nitrophenoxobisethylenediamminocobaltic* m-*nitrophenoxide* +m-*nitrophenol* [IV; $X=m\text{-}C_6H_4(NO_2)\cdot O\cdot]+H_2O$.

(IV.) $[X_2\cdot Co\ en_2]X,HX$ $\left|\begin{matrix}X\\HX\end{matrix}Co\ en_2\right]X_2$ (V.)

The *o*-isomeride gives o-*nitrophenol*-o-*nitrophenoxobisethylenediamminocobaltic* o-*nitrophenoxide* [V; $X=o\text{-}C_6H_4(NO_2)\cdot O\cdot](+H_2O)$. Sodium *p*-nitrophenoxide yields, under varying conditions, four compounds: (A) p-*nitrophenol*-p-*nitrophenoxobisethylenediamminocobaltic* p-*nitrophenoxide* (V) ($+3H_2O$); (B) *aquo*-p-*nitrophenoxobisethylenediamminocobaltic* p-*nitrophenoxide* (VI) ($+2H_2O$); (C) *aquo*-p-*nitrophenoxobisethylenediamminocobaltic* p-*nitrophenoxide*+p-*nitrophenol* (VII) ($+H_2O$); and (D) *bis*-p-*nitrophenoxobisethylenediamminocobaltic* p-*nitrophenoxide* + p-*nitrophenol* (IV) ($+2H_2O$). The compounds (B) and (C) are changed in dilute solution in presence of platinised electrodes into (D).

(VI.) $\left[\begin{matrix}H_2O\\X\end{matrix}Co\ en_2\right]X_2$ $\left[\begin{matrix}X\\H_2O\end{matrix}Co\ en_2\right]X_2,HX$ (VII.)

(VIII.) $\left[\begin{matrix}H_2O\\X\end{matrix}Co\ en_2\right]OH$

The colour reactions of the compound (A) and of the corresponding *o*-nitrophenol derivative are regarded as indicating a quinonoid structure for the nitrophenol molecule which is linked up with the cobalt in the complex through residual valency. Sodium *m*-nitrophenoxide, on the other hand, is not quinonoid in structure. Sodium 2 : 4- and 2 : 6-dinitrophenoxides react with bisaquobisethylenediamminocobaltic bromide to give *aquo*-2 : 4-*dinitrophenoxobisethylenediamminocobaltic* 2 : 4-*dinitrophenoxide* (VI) ($+1H_2O$) and *aquo*-2 : 6-*dinitrophenoxobisethylenediamminocobaltic hydroxy*-2 : 6 *dinitrophenoxide* (VIII). Sodium picrate gives *aquopicratobisethylenediamminocobaltic picrate* (VI) ($+4H_2O$). M. Clark.

Detection and determination of thymol. F. W. Klingstedt and E. Sundstrom (J. pr. Chem., 1927, [ii], **116**, 307—313).—Whilst thymol ethyl and methyl ethers are unaffected either by alcoholic hydrogen chloride or by dilute aqueous alcoholic sodium nitrite, the two reagents together yield nitrosothymol. This has m. p. 169—170° (higher than that usually given), but is reduced to aminothymol of the accepted m. p. The best yields (93 and 90%, respectively) of the nitroso-compounds are obtained by the action of aqueous sodium nitrite on a solution of thymol or its methyl ether in alcohol–water–acetic acid. The ethers of carvacrol and *o*-cresol, and anisole yield no nitroso-derivatives and the reaction thus forms the basis for the approximate determination of thymol in carvacrol; it is shown that carvacrol obtained from sodium cymenesulphonate contains no thymol, the sulphonic acid group entering exclusively the position *ortho* to the methyl group. J. W. Baker.

Direct introduction of substituents in aromatic mercaptans. T. van Hove (Bull. Acad. roy. Belg., 1927, [v], **13**, 206—224; cf. this vol., 555).—Attempts to brominate *p*-thiocresol in carbon tetrachloride solution were unsuccessful, the resulting product being di-*p*-tolyl disulphide, m. p. 45·2°, converted into *p*-nitrobenzoic acid by dilute nitric acid. Under similar conditions *p*-methylthioltoluene yields 3-*bromo*-4-*methylthioltoluene*, m. p. —16°, b. p. 275—275·5°, d_4^{15} 1·4696. Proof of the constitution of this compound is afforded by the preparation of the same substance from the corresponding mercaptan obtained from 3-bromo-*p*-toluidine by Leuckart's method (A., 1890, 603). Oxidation with acid permanganate gives 3-*bromo*-4-*methylsulphonyltoluene*, m. p. 99—100°, and 3-*bromo*-4-*methylsulphonylbenzoic acid*, m. p. 202—203°. Bromination of thioanisole in carbon disulphide solution results in the formation of the additive *compound*, $C_6H_4Br\cdot SMeBr_2$, m. p. 90—91°, which is readily hydrolysed to form *p*-bromophenylmethylsulphoxide, m. p. 83°, previously described (*loc. cit.*). Bromination of *p*-bromothioanisole in carbon tetrachloride solution at the b. p. gives a *dibromo*-derivative, m. p. 48°, oxidised by acid potassium permanganate to the corresponding *sulphone*, $C_6H_3Br_2\cdot SO_2Me$, m. p. 121—122°. 4-*Methylthiolphenetole*, m. p. 21·5°, b. p. 250—251°, is prepared by treating the corresponding mercaptan, obtained from *p*-phenetidine by Leuckart's process, with methyl sulphate. Bromination in carbon tetrachloride solution yields, among other products as yet unidentified, 2-*bromo*-4-*methylthiolphenetole*, m. p. 17·4°, b. p. 301—302°, d_4^{17} 1·4454. The constitution of this compound is established by its preparation from the corresponding mercaptan obtained from 2-bromo-*p*-phenetidine. J. S. Carter.

Relative directive powers of groups of the forms RO and RR′N in aromatic substitution. VI. Nitration of *m*- and *p*-chlorobenzyl ethers of guaiacol. A. E. Oxford and R. Robinson (J.C.S., 1927, 2239—2244).—The directive powers of substituted benzyloxy-groups are studied by putting them separately in competition with methoxyl, and it has been shown that the directive powers of the *m*- and *p*-nitrobenzyloxy-groups are approximately equal (67; MeO=100; A., 1926, 397). By the nitration of *m*- and *p*-chlorobenzyl ethers of guaiacol, and analysis of the products, which behave thermally as binary mixtures, it is now found that the *m*-chlorobenzyloxy-group has the directive power 69, and *p*-chlorobenzyloxy- 82. The close approach of the directive power of *m*-chlorobenzyloxy- to that of *m*-nitrobenzyloxy- shows that the electron affinity of chlorine is almost as strong as that of the nitro-group, whilst the higher value for *p*-chlorobenzyloxy- is interpreted as being due to conjugation. The

following were prepared: 2-m-*chlorobenzyloxyanisole*, m. p. 46—47°, b. p. 207—208°/15 mm.; 4-*nitro*-2-m-*chlorobenzyloxyanisole*, m. p. 129—130·5°; 5-*nitro*-2-m-*chlorobenzyloxyanisole*, m. p. 121°; 2-p-*chlorobenzyloxyanisole*, m. p. 70° (a crystallographic description is given); 4-*nitro*-2-p-*chlorobenzyloxyanisole*, m. p. 115—117°; 5-*nitro*-2-p-*chlorobenzyloxyanisole*, m. p. 120—120·5° (crystals described). The nitration product of 2-*m*-chlorobenzyloxyanisole contains 41% and that of 2-*p*-chlorobenzyloxyanisole 45% of the 5-nitro-isomeride. The m. p. of mixtures of the 4- and 5-nitro-isomerides in each case are given. W. J. POWELL.

Chlorination of creosol. W. QVIST [with G. WUK] (Ber., 1927, 60, [*B*], 1847—1850).—Creosol, dissolved in glacial acetic acid, is converted by chlorine in the dark or in diffused daylight at 20—25° into 2 : 5 : 6-*trichlorocreosol*, m. p. 130—131°, which, in alcoholic solution, can readily be titrated with alkali hydroxide in the presence of phenolphthalein. Further chlorination at 100° affords *pentachloro*-3 : 4-*diketotetrahydrotoluene* (anhydrous, monohydrate, and dihydrate, m. p. 86—88°). H. WREN.

Fission of the methylenedioxy-group. E. SPATH and H. QUIETENSKY (Ber., 1927, 60, [*B*], 1882—1890).—With the object of elucidating the most promising conditions for the removal of the methylenedioxy-group from methylene ethers with the subsequent isolation of the dihydroxybenzene thereby produced, the behaviour of piperonylic acid, pyrocatechol methylene ether, and dihydrosafrole has been investigated. The action of concentrated acids on these compounds gives complex condensation products of the liberated formaldehyde and phenolic substance. It is therefore necessary to conduct operations in the presence of a compound which reacts more readily than the liberated *o*-dihydroxybenzene with formaldehyde. For this purpose phloroglucinol may be replaced by the cheaper resorcinol or phenol. Methylene ethers of phenolic bases may be hydrolysed by treatment with sulphuric acid (*d* 1·39) at 100° in the presence of phloroglucinol or resorcinol. If the methylene ether and the fundamental phenol are only slowly sulphonated at the ordinary temperature, the change can frequently be effected by concentrated sulphuric acid with addition of phloroglucinol, resorcinol, or phenol. If these methods give poor yields it is advisable to try the effect of fuming hydrochloric acid at 100—130° in a sealed tube in the presence of phenols which combine with formaldehyde. In the absence of other groups capable of reacting with magnesium methyl iodide, the methylenedioxy-compound may be transformed by the Grignard reagent into the monoethyl ether, which is subsequently hydrolysed by hydriodic acid. H. WREN.

Photoactivity of cholesterol. J. STŘÍTESKY (Biochem. Z., 1927, 187, 388—397).—Ultra-violet rays have a much stronger effect on cholesterol than *X*-rays and the latter are a little stronger than sunlight. The photo-activity is due to the production from cholesterol in the presence of oxygen of a volatile substance and is probably dependent on the presence of the double linking, since, whereas cholesterol and its stearate and benzoate are photo-activated, cholesterol dibromide is not. The effect increases with rise in temperature, cholesterol at temperatures above its m. p. showing photo-activity without irradiation due to spontaneous oxidation. P. W. CLUTTERBUCK.

Phosphorus derivatives of sterols. H. VON EULER and A. BERNTON (Ber., 1927, 60, [*B*], 1720—1725).—Cholesterol is converted by successive treatments with phosphorus trichloride and water into cholesteryl phosphite, m. p. 158—159° (*aniline* salt, $C_{33}H_{52}NPO_3$, m. p. 170°), transformed by bromine into the *dibromo*-compound, m. p. 148°, also obtained by brominating cholesterol and treating the product with phosphorus trichloride. Acetic anhydride converts the ester into cholesteryl acetate, m. p. 114°. Cholesterol and phosphoryl chloride in benzene afford dicholesteryl phosphate, m. p. 195—199°, which is also obtained when phosphoryl chloride is added to an equivalent quantity of cholesterol in pyridine. If, however, a solution of cholesterol in pyridine is slowly added to the chloride in the same solvent and the product is treated with water, *monocholesteryl phosphate*, m. p. 195—196°, is produced. The latter ester is precipitated from alcoholic solution by cadmium chloride; its *sodium* salt is described. H. WREN.

Action of phosphorus pentabromide on the isomeric β-methoxyphenylethyl alcohols. J. B. SHOESMITH and R. J. CONNOR (J.C.S., 1927, 2230—2234).—With phosphorus pentabromide in benzene solution the isomeric β-methoxyphenylethyl alcohols give nuclear-brominated derivatives of the expected β-methoxyphenylethyl bromides, the orientation of which has been proved by elimination of hydrogen bromide and subsequent oxidation to the corresponding bromomethoxybenzoic acid. β-o-*Methoxyphenylethyl alcohol*, b. p. 130—131°/11 mm., prepared from *o*-bromoanisole (Grignard, A., 1905, i, 593; Shoesmith and Connor, this vol., 962) yields β-5-*bromo*-2-*methoxyphenylethyl bromide*, m. p. 55°, b. p. 160—165°/12 mm.: β-m-*methoxyphenylethyl alcohol*, b. p. 135—137°/12 mm., affords β-6-*bromo*-3-*methoxyphenylethyl bromide*, b. p. 163—165°/13 mm.; β-*p*-methoxyphenylethyl alcohol, b. p. 138—140°/11 mm., m. p. 24°, gives β-3-*bromo*-4-*methoxyphenylethyl bromide*, b. p. 187—188°/19 mm., with excess of phosphorus pentabromide, whilst with a limited quantity, β p-*methoxyphenylethyl bromide*, b.p. 130—131°/11 mm., is obtained. All these bromides are non-pungent and non-lachrimatory. β-Phenylethylamine with nitrous acid in hydrochloric acid solution gives considerable quantities of β-phenylethyl chloride, whilst with nitrous acid in sulphuric acid solution poor yields of the alcohol are obtained. *m*-Methoxybenzaldehyde with nitromethane and alkali yields m-*methoxy*-ω-*nitrostyrene*, light yellow, m. p. 93—94°, which on treatment with zinc dust and acetic acid affords m-*methoxyphenylacetaldoxime*, m. p. 92·5—93°. Reduction of the latter by means of sodium amalgam yields a small quantity of β-*m*-methoxyphenylethylamine, but this substance is more readily prepared by the method of Haworth, Perkin, and Rankine (A., 1924, i, 1098). A trustworthy method for the preparation of *o*-methoxybenzaldehyde from salicylaldehyde is described. W. J. POWELL.

Reactions of sodium compounds of aromatic ketones. I. Synthesis of triarylcarbinols and of triarylmethane dyes. E. H. RODD and F. W. LINCH (J.C.S., 1927, 2174—2178).—*pp'*-Tetramethyldiaminobenzophenone (Michler's ketone) reacts with sodium in an inert solvent to form a *sodio*-compound, which in turn reacts with aromatic chloro-compounds, if these are concurrently added, to give the sodium salt of a triarylcarbinol. The reaction constitutes a new synthesis of triarylcarbinols and of dyes from them. Michler's ketone in this way affords the following substances: from chlorobenzene, *pp'*-tetramethyldiaminotriphenylcarbinol; from *o*-chlorotoluene, pp'-*tetramethyldiaminodiphenyl-o-tolylcarbinol*, m. p. 132·5°, and in presence of toluene, pp'-*tetramethyldiaminodiphenylbenzylcarbinol* (see following abstract), m. p. 190° [basification of the oxalate of the former substance with ammonia yields pp'-*tetramethyldiaminodiphenyl-o-tolylmethylamine*, m. p. 163°, and reduction with zinc and 2*N*-hydrochloric acid yields *pp'*-tetramethyldiaminodiphenyl-*o*-tolylmethane, m. p. 102° (cf. Noelting and Saas, A., 1913, i, 522; Noelting and Gerlinger, A., 1906, i, 607)]; from 4-chloro-*m*-xylene, pp'-*tetramethyldiaminodiphenyl-m-4-xylylcarbinol*, m. p. 145°; from *p*-chloroanisole, pp'-*tetramethyldiaminodiphenyl-p-anisylcarbinol*, m. p. 153°; from β-chloronaphthalene, pp'-*tetramethyldiaminodiphenyl-β-naphthylcarbinol*, m. p. 181°; from α-chloronaphthalene, pp'-*tetramethyldiaminodiphenyl-α-naphthylcarbinol*, m. p. 167° (basification of the oxalate with ammonia gives pp'-*tetramethyldiaminodiphenyl-α-naphthylmethylamine*, m. p. 186°). The *sodio*-compound of *pp'*-tetraethyldiaminobenzophenone reacts with β-chloronaphthalene to afford pp'-*tetraethyldiamino-β-naphthylcarbinol*, m. p. 177°. The carbinols form green salts with acids which dye tannin-mordanted cotton bright green shades.

G. A. C. GOUGH.

Reactions of sodium compounds of aromatic ketones. II. Their reaction with methyl and methylene groups and their products of decomposition. E. H. RODD and F. W. LINCH (J.C.S., 1927, 2179—2188).—A toluene solution of Michler's ketone reacts with sodium to give *pp'*-tetramethyldiaminodiphenylbenzylcarbinol (preceding abstract) and Michler's hydrol together with small amounts of *p*-dimethylaminobenzoic acid, hexamethyltriaminotriphenylcarbinol, and dimethylaniline. This new type of reaction may be expressed:

$$2(NMe_2\cdot C_6H_4)_2CO+2Na+PhMe=(NMe_2\cdot C_6H_4)_2CH\cdot ONa+(NMe_2\cdot C_6H_4)_2C(ONa)\cdot CH_2Ph.$$

Acids form blue salts with the benzylcarbinol and, on heating, convert it into ββ-pp'-*tetramethyldiaminodiphenylstyrene*, m. p. 135°. Oxidation with lead peroxide of the benzylcarbinol yields phenylacetic acid, and of the styrene, first a blue dye, then benzaldehyde. By extension of this reaction to substances containing a methylene group, the following are prepared: from *pp'*-tetramethyldiaminodiphenylmethane, *octamethyltetra-aminotetraphenylethanol*, m. p. 255°, oxidised to a violet dye by lead peroxide and converted by warm sulphuric acid into the corresponding ethylene, m. p. 314—316°; from *pp'*-tetraethyldiaminobenzophenone and *pp'*-tetramethyldiaminodiphenylmethane, αα-4 : 4'-*tetraethyldiaminodiphenyl*-ββ-4 : 4'-*tetramethyldiaminodiphenylethan-α-ol*, m. p. 228°; from *pp'*-tetramethyldiaminobenzophenone and *pp'*-tetraethyldiaminodiphenylmethane, αα-4 : 4'-*tetramethyldiaminodiphenyl*-ββ-4 : -*tetraethyldiaminodiphenylethan-α-ol*, m. p. 229—230° (corresponding *ethylene*, m. p. 212°); from acenaphthene and Michler's ketone, 4 : 4'-*tetramethyldiaminodiphenylacenaphthenylcarbinol*, m. p. 232° (dehydrated by boiling aqueous hydrochloric acid to 4 : 4'-*tetramethyldiaminodiphenylmethyleneacenaphthene*, m. p. 209°); from fluorene, 4 : 4'-*tetramethyldiaminodiphenylmethylenefluorene*, m. p. 239—240°. The last compound is formed by dehydration of the carbinol at a stage in the preparation not determined.

Toluene is unattacked when less than 1 atomic proportion of sodium is taken for the reaction with Michler's ketone in toluene solution, the principal products being Michler's hydrol, *p*-dimethylaminobenzoic acid, and crystal-violet base.

G. A. C. GOUGH.

[Tetraphenylethane dyes.] F. KEHRMANN (Ber., 1927, **60**, [*B*], 1913—1914).—The tetraphenylethane dyes described by Wizinger (this vol., 764) can readily be formulated as quinonoid di-imonium or dioxonium salts; there is no evidence in favour of the carbonium structure.

H. WREN.

Colour and chemical constitution. XXI. Methyl derivatives of the phenolphthaleins. J. MOIR (Trans. Roy. Soc. S. Africa, 1927, **14**, 233—236).—Since the complete series of bromine derivatives of phenolphthalein could not be obtained (cf. A., 1921, ii, 365), the author has prepared and examined ten of the possible methyl derivatives, and, in addition, phenoltetrahydro-α-naphtholphthalein (λ 584) phenolthymolphthalein (λ 578), phenolcarvacrolphthalein (λ 580), thymolphthalein (λ 597), carvacrolphthalein (λ 601), *pp'*-phenol-α-naphtholphthalein (λ 601), *pp'*-α-naphtholphthalein (λ 650), phenol-8-hydroxyquinolinephthalein (λ 598), and phenol-6-iodo-*o*-cresolphthalein (λ 576). All the values found for these sixteen compounds agree within experimental error with the values obtained by adding to the number 554 tho calculated additive value for each substituent (cf. A., 1921, ii, 6; 1923, ii, 108). Comparison of the value of λ calculated for 2 : 3-diethylphenolphthalein (577) with that observed for phenoltetrahydro-α-naphtholphthalein (584) indicates that the effect of ring closure of the two adjacent ethyl groups into the *cyclo*butane ring is only +7, a result in agreement with previous observations on the absorptions of dihydroxyxanthhydrol and succinylfluorescein. Phenol-*p*-cresolphthalein shows a band at λ 563, phenol-*as-m*-xylenolphthalein, 573, phenol-*as-o*-xylenolphthalein, 578, phenol-*p*-bromophenolphthalein, 559, phenolbromo-*o*-cresolphthalein, 570, phenolbromo-*p*-cresolphthalein, 569, phenol-*s*.-*m*-xylenolphthalein, 572, phenol-ψ-cumenolphthalein, 581, phenol-β-naphtholphthalein, 570, broad, phenol-2-α-naphtholphthalein, 612, whence the additive effects appear to be, 3- and 5-methyl-, 11; 3- and 5-bromo-, 7; 4-methyl, 13; 6-methyl-, 7.

R. BRIGHTMAN.

Pinabietic acid. O. ASCHAN and P. LEVY [with H. BRUNOTTE] (Ber., 1927, **60**, [*B*], 1923—1927).—Pinabietic acid yields tetrahydroxyabietic acid when

oxidised by potassium permanganate and *iso*phthalic acid when treated with warm nitric acid. The production of the tetrahydroxy-acid establishes the presence of a common component in pinabietic acid and abietic acid from American colophony, whereas the production of *iso*phthalic and *trans*-hexahydrophthalic acids from the two parent acids is evidence against the presence of one and the same compound in each. H. WREN.

Manasse's ketonic acid, $C_{10}H_{16}O_3$, from camphorquinone. M. BREDT-SAVELSBERG, K. ZAUNBRECHER, and L. KNIEKE (Ber., 1927, **60**, [*B*], 1801—1808; cf. A., 1903, i, 45).—The ketonic acid, $C_{10}H_{16}O_3$, obtained from camphorquinone by the method of Manasse and Samuel (*loc. cit.*) has m. p. 67—68° (+H_2O), b. p. 150°/3 mm. (anhydrous); the semicarbazone, decomp. 220° and methyl ester, m. p. 81—83° (cf. Gibson and Simonsen, A., 1925, i, 919), are described. The *ethyl* ester, b. p. 115—117°/3 mm., $d^{11.3}$ 1·0382, $n^{11.3}$ 1·46858, $[\alpha]_D^{18}$ +38·52°, yields two isomeric *semicarbazones*, needles and leaflets, decomp. 216·4°. The acid is proved to be 2 : 2 : 3-*trimethylcyclohexan*-4-*one*-1-*carboxylic acid* (cf. Gibson and Simonsen, *loc. cit.*) by the ability of its methyl and ethyl esters to yield *benzylidene* derivatives, b. p. 180°/1·75 mm. and 150—155°/0·3 mm., respectively, thus proving the presence of the ·CO·CH_2· group in the ring. Bromination of the anhydrous acid in chloroform solution without cooling gives the *dibromoketonic acid*, $C_{10}H_{14}O_3Br$, m. p. 158—159° (decomp.), whereas at 0° the *monobromolactone*, $C_{10}H_{13}O_3Br$, m. p. 116—117°, is obtained, converted by cold sodium carbonate solution into the *substance*, $C_{10}H_{12}O_3$, m. p. 211—212°. 2 : 2 : 3-Trimethyl*cyclo*hexan-4-ol-1-carboxylic acid, m. p. (anhydrous) 132—134°, prepared by reduction of the ketonic acid by sodium amalgam in the presence of carbon dioxide, is converted by acetic anhydride at 140—150° into a mixture of the corresponding *acetyl* derivative, $C_{12}H_{20}O_4,H_2O$, m. p. 85—87°, and the *anhydride*, $[C_9H_{16}(OAc)\cdot CO]_2O$, m. p. 115—116°. H. WREN.

Spectrophotometric comparison of natural and synthetic thyroxines. E. ABDERHALDEN and E. ROSSNER (Z. physiol. Chem., 1927, **169**, 223—225).—The absorption curves of natural thyroxine and a commercial synthetic preparation (Hoffman–La Roche) prepared by the method of Harington and Barger (this vol., 358) appear to be identical. A. WORMALL.

Suggested mechanism of the splitting of the *cyclo*propane ring by bromine. B. H. NICOLET and H. SATTLER (J. Amer. Chem. Soc., 1927, **49**, 2066—2071).—The action of bromine on ethyl *cyclo*propane-1 : 1-dicarboxylate affords *ethyl* 2-*bromo*cyclo*propane*-1 : 1-*dicarboxylate* (I), b. p. 135—140°/15 mm., and ethyl bromo-β-bromoethylmalonate (II), b. p. 146—151°/10 mm., neither of which could be obtained free from the other by repeated fractionation. The former preponderates when the reaction is carried out at a low temperature. Hydrolysis of (II) with boiling aqueous hydrobromic acid, with subsequent treatment of the product with silver oxide, affords αγ-dihydroxybutyric acid, which is also obtained in the same way from (I). It is therefore concluded that (I) is the primary product of the above bromination, (II) being subsequently produced from (I) by the action of the hydrobromic acid liberated. Bromination of *cyclo*propane-1 : 1-dicarboxylic acid in carbon tetrachloride in ultra-violet light affords bromo-β-bromoethylmalonic acid. In chloroform, the product is a viscous oil, which loses carbon dioxide on distillation, with formation of 2-*bromocyclopropane*-1-*carboxylic acid*, b. p. 140°/20 mm. Bromination of ethyl 1-cyano*cyclo*propane-1-carboxylate affords *ethyl* 2-*bromo*-1-*cyano*cyclo*propane*-1-*carboxylate*, and *ethyl* αγ-*dibromo*-α-*cyanobutyrate*, b. p. 136—140°/11 mm. Bromine is without action, in ultra-violet light, on cyano*cyclo*propane and 1-cyano*cyclo*propane-1-carboxylic acid. Hypochlorous and hypobromous acids and iodine monochloride do not react with *cyclo*propane-1 : 1-dicarboxylic acid or 1-cyano*cyclo*propane-1-carboxylic acid. F. G. WILLSON.

Catalytic reduction of certain hydrophthalic anhydrides. F. P. MAZZA [with G. DI MASE, A. CALÒ, and A. CREMONA] (Rend. Accad. Sci. fis. mat. Napoli, 1926, [iii], **32**, 137—146).—See this vol., 664, 665.

Nature of the alternating effect in carbon chains. XXI. Directive influence of the groups $-CH_2\cdot CH(CO_2Me)_2$, $-CH{:}C(CO_2Me)_2$, $-C(CO_2Me){:}CH_2$, and $-CH{:}CH\cdot CH{:}C(CO_2Me)_2$ in aromatic substitution. J. W. BAKER and A. ECCLES (J.C.S., 1927, 2125—2133).—The following nitrations were effected by addition of the ester to nitric acid (*d* 1·49; 10 times the weight of ester) at −15° and the proportion of isomerides in the product determined by oxidation to the nitrobenzoic acids (this vol., 454). Methyl benzylmalonate gave 8% of *m*- and 68% of *p*-nitro-derivative; *methyl benzylidenemalonate*, b. p. 174—177°/15 mm., m. p. 41°, prepared by the condensation of benzaldehyde and methyl malonate, gave 3% of *m*- and 67% of *p*-nitro-derivative (65% of methyl *p*-nitrobenzylidenemalonate isolated); methyl atropate gave 5% *m*- and 55% p-*nitro*-derivative (m. p. 110°); methyl cinnamylidenemalonate gave less than 1% of *m*- and 40% of *p*-nitro-derivative. Partial decomposition of the nitration product takes place in the last case unless the nitration mixture is poured into alkaline ice-water, the precipitate removed and rapidly dried in a vacuum. These results are in agreement with the previous observations (*loc. cit.*) as to the propagation of the *m*-orienting effect of the fractional dipoles of the carboxyl groups through the side-chain. The following compounds were prepared for comparative purposes: *methyl* p-*nitrobenzylidenemalonate*, m. p. 136—137°, from *p*-nitrobenzaldehyde and methyl malonate; *methyl* m-*nitrobenzylidenemalonate*, m. p. 99—100°; *methyl* o-*nitrobenzylidenemalonate*, m. p. 65—66°; *methyl* o-*nitrobenzylmalonate*; m-*nitrobenzylmalonic acid*, m. p. 164° (decomp.; *amide*, m. p. 203°; *methyl* ester, oil), prepared from *m*-nitrobenzyl chloride, methyl malonate, and sodium methoxide in methyl alcohol; *methyl di*-m-*nitrobenzylmalonate*, m. p. 162—162·5° (by-product in the previous preparation); *methyl* p-*nitrobenzylmalonate*, m. p. 82·5—83·5°; *methyl cinnamylidenemalonate*, m. p. 67°, obtained by esterification of the acid; *methyl* m-*nitro*-

cinnamylidenemalonate, m. p. 125—126°, prepared by condensation of *m*-nitrocinnamaldehyde and methyl malonate; *methyl o-nitrocinnamylidenemalonate*, m. p. 114°; *methyl p-nitrocinnamylidenemalonate*, m. p. 146—147°. G. A. C. GOUGH.

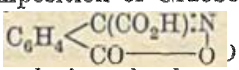
Diphenyl series. VII. Relative stability of optically active diphenic acids. F. BELL and P. H. ROBINSON (J.C.S., 1927, 2234—2239).—The "obstacle" theory advanced to account for the asymmetry of certain diphenyl derivatives (cf. this vol., 876) is supported by new experiments on optically active diphenic acids. As may be predicted, 6-nitrodiphenic acid, with only three groups in the central position, is optically less stable than 4 : 4′ : 6 : 6′-tetranitrodiphenic acid, which resists racemisation by boiling acetic anhydride to a much greater extent. *d*-6-Nitrodiphenic acid has $[\alpha]_{5461}$ +65·2° (*c*=3·01 in ethyl alcohol), $[\alpha]_{5461}$ −434° (*c*=4·73 in 0·426*N*-sodium hydroxide); *l*-6-nitrodiphenic acid has $[\alpha]_{5461}$ −66·4° (*c*=4·91 in ethyl alcohol), $[\alpha]_{5461}$ +433° (*c*=4·69 in 0·261*N*-sodium hydroxide); *l*+*dl*-tetranitrodiphenic acid, m. p. 224—226°, has $[\alpha]_{5461}$ −138·5° (*c*=1·7 in ethyl alcohol), whilst *d*-tetranitrodiphenic acid, m. p. 226—227°, has $[\alpha]_{5461}$ +142·3° (0·3696 g. in 20 c.c. of ethyl alcohol). By the action of thionyl chloride on *l*-6-nitrodiphenic acid, the *l*+*dl*-dichloride, m. p. 65—68°, $[\alpha]_{5461}$ −209·5°, is obtained. Attempts to resolve 5-nitrodiphenic acid (Schmidt and Lumpp, A., 1909, i, 34) and 2 : 2′-dinitrodiphenyl-4 : 4′-dicarboxylic acid were unsuccessful. 5-Nitrodiphenic acid readily forms an *anhydride*, m. p. 193—195°, and with sulphuric acid easily undergoes condensation forming *6(?)-nitrofluorenone-4-carboxylic acid*, m. p. 282°, whilst 4 : 4′ : 6′-trinitrodiphenic acid is unaffected by sulphuric acid at 160°. 5-Nitrofluorenone-4-carboxylic acid (Moore and Huntress, this vol., 665) cannot be resolved by crystallisation of its morphine or quinidine salts, this result being interpreted as indicating that the 4 : 5-positions of fluorene are further apart than are the 6 : 6′-positions in a diphenic acid. *2 : 5 : 7(?)-Trinitrofluorenone-4-carboxylic acid*, obtained by the action of nitric acid (*d* 1·5) at 100° on 5-nitrofluorenone-4-carboxylic acid, has m. p. 254—255°; the *quinine* salt of 4-nitrodiphenic acid has m. p. 180° (indef.), $[\alpha]_{5461}$ +106·4°, but the liberated 4-nitrodiphenic acid is inactive. W. J. POWELL.

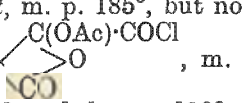
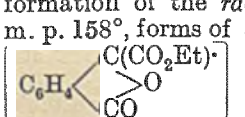
Constitution of acids formed by decomposition of cholic acid. W. BORSCHE (Z. physiol. Chem., 1927, **169**, 306—307).—A reply to the criticism by Wieland (this vol., 767) of a previous paper (Borsche and Frank, this vol., 459). A. WORMALL.

Constitution of the bile acids. XII. Cholamine, amides of cholic and deoxycholic acids. W. BORSCHE and A. SCHWARZ (Ber., 1927, 60, [*B*], 1843—1846).—Repetition of the work of Curtius (A., 1906, i, 400) and of Bondi and Müller (A., 1906, i, 633) has confirmed the transformation of ethyl cholate into cholylethylurethane, but the conversion of the latter substance into cholamine could not be effected and the identity of the latter compound appears insufficiently established. The following derivatives of cholic acid have been prepared by shaking freshly-prepared cholazide in aqueous suspension with the requisite amine; amide (+3H_2O), m. p. 136°, resolidifying at 180° and again melting at 220°; *methylamide* (+H_2O), m. p. 186°; *dimethylamide*, m. p. 179°; *ethylamide*, m. p. 159°; *propylamide*, m. p. 146°; *allylamide*, m. p. 144°; *benzylamide*, m. p. 240°; *piperidide*, m. p. 246°. *Deoxycholamide*, m. p. 186° after softening at 162°, *deoxycholmethylamide*, m. p. 168°, and *deoxycholdimethylamide*, m. p. 203°, are described. H. WREN.

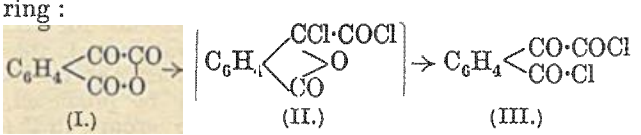
Tautomerism in the phthalonic and phthalidecarboxylic acid series. A. CORNILLOT (Ann. Chim., 1927, [x], **7**, 275—313, and **8**, 120—205; cf. this vol., 562).—The relations between phthalonic acid and its anhydride and their derivatives and compounds of the phthalidecarboxylic acid series afford little evidence of tautomerism or of the existence of desmotropic mixtures of isomerides. Throughout this series of compounds each grouping of substituents appears to involve a characteristic redistribution of the affinity capacities and in any reaction a new and independent distribution takes place. This behaviour is attributed to the unstable nature of the linkings of the carbon atom occupying the α-position with respect to the aromatic ring, this quaternary lactonic carbon being surrounded by saturated radicals, and also to the strong residual affinity of the ketonic oxygen. In consequence, compounds of this series cannot saturate their affinity capacities in either the ketonic or the lactonic structure. The complex affinities of the keto-lactonic system lead the authors to propose partial valency formulæ (cf. Skraup, A., 1919, i, 598), which are non-rigid and indicate the energy conditions of the linkings.

Oxidation of tetralin in aqueous suspension at 64—68° by addition of potassium permanganate affords only 56% (cf. von Braun and Braunsdorf, A., 1924, i, 48) of the theoretical yield of phthalonic acid, m. p. 148—149° (hydrate, +2H_2O, m. p. 37°). The acid is dibasic with thymol-blue, phenolphthalein, or litmus as indicators, but only monobasic with methyl-orange (cf. Tcherniac, A., 1898, i, 263; 1917, i, 33). Anomalies observed in the dissociation of phthalonic acid in aqueous solution are attributed to anomalies in the mobility of the ions $C_6H_4\langle^{C(OH)\cdot CO_2}_{CO}\rangle O$ and $C_6H_4\langle^{CO\cdot O}_{CO_2}\rangle C\cdot$, the structure of the monobasic ion affording an explanation of the weakness of the acid ($K=9\times10^{-5}$) as compared with benzoic acid. It is suggested that the increased conductivity observed by Boeseken (A., 1921, i, 844) on addition of boric acid is due to hydration and formation of boric acid complexes with the neutral molecule only of phthalonic acid, the proportion of neutral molecules decreasing as the dilution increases. In view of the readiness with which phthalonic acid undergoes hydration, no conclusions as to the structure of the anhydrous acid can be reached from the reactions of phthalonic acid in aqueous solution. With hydroxylamine in neutral aqueous solution phthalonic acid appears to afford first an oxime hydrate, $CO_2H\cdot C_6H_4\cdot C(OH)(NH\cdot OH)\cdot CO_2H$, which is unstable and affords phthalic acid derivatives by loss of

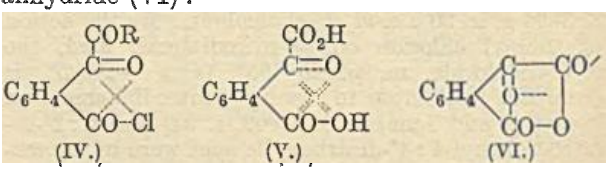
carbon dioxide. The corresponding *oxime acetate*, $CO_2H{\cdot}C_6H_4{\cdot}C(OAc)(NH{\cdot}OH){\cdot}CO_2H$, obtained in cold acetic acid, decomposes at 100° into phthalimide, water, acetic acid, and carbon dioxide, but no phthalimide was observed in the decomposition of Graebe and Trümpy's anhydro-oxime,  (A., 1898, i, 318). In alkaline solution the latter oxime afforded phthalamic acid, for which a theoretical explanation is offered. With hydroxylamine hydrochloride and sodium acetate in acetic acid at 100°, phthalonic acid affords, in addition to the anhydro-oxime, a little of a neutral substance subliming at 250°, $C_{22}H_{14}O_7N_4$ or $C_{22}H_{16}O_7N_4$. Dehydration of the oxime hydrate with cold acetic anhydride yields *o*-cyanobenzoic acid; dehydration at 20° also affords the nitrile, and it is suggested that an unstable oxime, $CO_2H{\cdot}C_6H_4{\cdot}C(N{\cdot}OH){\cdot}CO_2H$, forms an intermediate stage in all cases, the *anti*-form of which readily cyclises to the known anhydro-oxime, the *syn*-form of which affords the nitrile at 20°, or phthalamic acid at 0°. Formation of phthalamic acid from the anhydro-oxime at 100° is attributed to simple oxidation of the phthalonic acid by hydroxylamine.

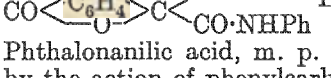
Phthalonic anhydride, m. p. 190—191° (decomp.), is best obtained by dehydration of the acid with acetyl chloride. Using acetic anhydride, the reaction product may contain, according to the duration of heating, up to 50% of *α-acetoxyphthalide-α-carboxylic acid*, decomp. 180°, also obtained by suspending phthalonic anhydride in glacial acetic acid; it is decomposed by water or alcohol into phthalonic acid and acetic acid or ethyl acetate. With aniline it forms a *salt*, m. p. 185°, but no anilide; from the *chloride*,  , m. p. 112°, the *ethyl*, m. p. 110°, and *methyl*, m. p. 112°, esters are obtained. On prolonged contact with acetic anhydride, phthalonic anhydride affords *αα-diacetoxyhomophthalic anhydride*, m. p. 240° (decomp.), a reaction which is attributed to the residual affinity of the carbonyl oxygen in presence of electronegative groups. With phosphorus pentachloride in toluene, phthalonic anhydride affords *α-chlorophthalide-α-carboxyl chloride*, m. p. 70°, hydrolysed in moist air to *α-chlorophthalide-α-carboxylic acid*, m. p. 132—133°. The *methyl* ester has m. p. 92°, the *ethyl* ester, m. p. 48°, b. p. 164°/5 mm., and the *anilide*, m. p. 137·5°. With aluminium chloride in benzene, the ethyl ester affords *ethyl α-phenylphthalide-α-carboxylate*, m. p. 70°, together with a little benzhydrol-*o*-carboxylic acid, which on hydrolysis with alcoholic potassium hydroxide yields α-phenylphthalide. The methyl ester similarly affords methyl α-phenylphthalide-α-carboxylate, an oil, b. p. 275°/9 mm. (decomp.). These reactions support the lactone structure for the acid and its derivatives. Further support for this structure is afforded by the formation of the *racemic*, m. p. 188°, and *inactive*, m. p. 158°, forms of *ethyl bis-α-phthalide-α-carboxylate*,  by the action of zinc methyl iodide on ethyl α-chlorophthalide-α-carboxylate in toluene at 30°; the inactive form is also obtained with zinc ethyl iodide. On hydrolysis with alcoholic potassium hydroxide, both isomerides afford phthalonic acid and phthalide-α-carboxylic acid.

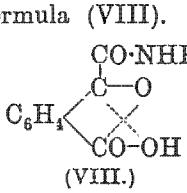
The foregoing facts indicate a lactone structure for phthalonic acid, but the formation of α-chlorophthalide-α-carboxylic acid (III) from phthalonic anhydride (I) involves the opening of the glutaric ring:

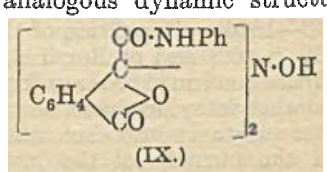

(I.) (II.) (III.)

possibly an unstable intermediate chloride (II) is first formed (cf. Haller and Guyot, A., 1900, i, 170). The formation of α-chlorophthalide-α-carboxyl chloride from phthalonic acid is, however, more easily interpreted on the basis of a ketonic structure for phthalonic acid. The authors propose the term "mesomerism" for the structural relationships of this type, and structural formulæ involving partial valencies are proposed for the chlorophthalidecarboxylic derivatives (IV), phthalonic acid (V), and phthalonic anhydride (VI):


(IV.) (V.) (VI.)

Phthalonic dianilide, m. p. 217—218°, affords with phenylcarbimide a *derivative*,  (VII), m. p. 203·5°. Phthalonanilic acid, m. p. 180°, is readily obtained by the action of phenylcarbimide on phthalonic acid in ether. With aniline in alcoholic solution it affords, in addition to the dianilide, a colloidal acidic *substance* (N, 8%), which is possibly a polymeric form of the anil of phthalonanilic acid, $[CO_2H{\cdot}C_6H_4{\cdot}C(NPh){\cdot}CO{\cdot}NHPh]_n$, a reaction which would indicate that phthalonanilic acid can react in the ketonic form, the predominating reactivity being, however, lactonic. The dianilide is also obtained when phthalonanilic acid is warmed with 60% acetic acid containing a little hydrochloric acid. On alkaline hydrolysis α-chlorophthalide-α-carbanilide readily affords phthalonanilic acid; the reverse reaction takes place with thionyl chloride in benzene, a part of the phthalonanilic acid undergoing dehydration to *N*-phenylphthalonimide, m. p. 218·5°. This result indicates that the constitution of phthalonanilic acid is intermediate between the lactonic and the ketonic structures, and supports a valency formula (VIII). The analogous dynamic structure


(VIII.)


(IX.)

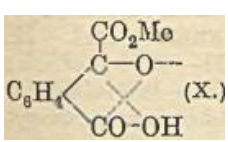
for α-chlorophthalide-α-carbanilide is further supported by the formation from this substance, under the influence of alcoholic pyridine, of *N*-phenyl-

phthalonimide. With hydroxylamine in neutral alcoholic solution phthalonic acid affords only neutral products (the normal ketoxime, $C_6H_4<^{N\ H)\cdot CO\ NHPh}_{CO_2H}$, being therefore absent), an *oxime*, m. p. 168°, which dissolves in dilute potassium hydroxide, and on hydrolysis with hydrochloric acid affords phthalic acid, aniline, and ammonia, together with a smaller amount of a *substance*, m. p. 168°, for which the structure (IX) is proposed. The oxime, m. p. 168°, is evidently α-hydroxylaminophthalide-α-carboxyanilide. Both substances are also formed from hydroxylamine and phthalonanilic acid in aqueous solution, but not in alcoholic solution or with excess of hydroxylamine. With excess of phthalonanilic acid no oxime is formed, but the substance, m. p. 168°, accompanied by a little phthalanil; the latter substance is formed in about 50% yield in 60% acetic acid. Since the reaction medium is without dehydrating properties, the appearance of phthalanil suggests that the phthalonanilic acid has reacted in its ketonic form,

$$C_6H_4\text{–}C\cdot CO\cdot NHPh$$
$$CO\cdot O\cdot N$$

With semicarbazide in aqueous or alcoholic solution phthalonanilic acid affords no definite substance; in acetic acid α-*semicarbazidophthalide-α-carbonanilide*, decomp. at 180°, and an acidic *substance*, m. p. 250° (decomp.), possibly the semicarbazone, $CO_2H\cdot C_6H_4\cdot C(CO\cdot NHPh):N\cdot NH\cdot CO\cdot NH_2$, are formed.

Methyl hydrogen phthalonate, $(C_6H_4<^{CO\cdot CO_2Me}_{CO_2H}$, m. p. 94°, in aqueous solution is a moderately strong acid ($K=1\cdot36\times10^{-4}$), probably having the structure $CO_2H\cdot C_6H_4\cdot C(OH)_2\cdot CO_2Me$, analogous to the hydrate of phthalonic acid. With semicarbazide it affords a normal *semicarbazone*, m. p. 200° (decomp.), together with traces of *methylphthalazonecarboxylate*, m. p. 207°; the latter is obtained quantitatively by the action of hydrogen chloride in methyl alcohol on the semicarbazone and its formation establishes the ketonic structure of the semicarbazone. Acetic anhydride at 100°, however, converts the ester into methyl α-acetoxyphthalide-α-carboxylate, m. p. 112°, and thionyl chloride and phosphorus pentachloride give almost quantitative yields of the corresponding α-chlorophthalidecarboxylic ester, reactions indicating a lactonic structure for the hydrogen ester. The dynamic structure (X), involving a mobile hydroxyl group, is proposed. Methyl α-methoxyphthalide-α-carboxylate, m. p. 66°, obtained by the action of methyl iodide on silver phthalonate with phosphorus pentachloride in toluene, affords methyl α-chlorophthalide-α-carboxylate and, with semicarbazide, methyl phthalazonecarboxylate. Potassium methoxide in ethereal solution converts the lactonic ester into *methyl phthalonate*, $CO_2Me\cdot C_6H_4\cdot CO\cdot CO_2Me$, which does not crystallise at −15°, affords a normal *semicarbazone*, m. p. 250° (decomp.), and with phosphorus pentachloride in toluene is converted into methyl αα-dichlorohomophthalate. Esterification of phthalonic acid in presence of hydrogen chloride at 0° affords an uncrystallisable oil, which by the action of semicarbazide is shown to be a mixture of the neutral lactonic and ketonic esters. In alcoholic solution in presence of sulphuric acid methyl α-chlorophthalide-α-carboxylate affords only the neutral lactonic ester, and there is no evidence that the lactonic and ketonic esters are to be regarded as desmotropic forms. R. BRIGHTMAN.



Action of aminoacetals on phenols. II. O. HINSBERG and R. MEYER (Ber., 1927, 60, [*B*], 1914—1916).—The product of the action of aminoacetal on gallic acid, regarded previously as *r*-β-amino-α-hydroxy-α-carboxytrihydroxyphenylethane (A., 1923, i, 556), is shown to be the *anhydride* of 2-β-*amino*-α-*hydroxyethylgallic acid*, $(OH)_3C_6H<^{CH(CH_2\ NH_2)}_{CO}>O$; the hydrochloride, m. p. 288°, and the *acetyl* derivative, $C_{17}H_{17}O_9N$, m. p. 173—174°, are described. Gallic acid and methylaminoacetal similarly afford the *anhydride* of 2-β-*methylamino*-α-*hydroxyethylgallic acid* (*hydrochloride*, m. p. 275—276°; *acetyl* derivative, $C_{18}H_{19}O_9N$, m. p. 172—173°). Pyrogallol is converted by successive treatments with concentrated sulphuric acid and aminoacetal into the *anhydride* of 3 : 4 : 5-*trihydroxy*-2-β-*amino*-α-*hydroxyethylbenzenesulphonic acid* (*hydrochloride*, $+1\cdot5H_2O$). H. WREN.

Structure of the condensation products of o-phthalaldehydic acids with phenols and phenol ethers. VIII. M. M. BRUBAKER and R. ADAMS (J. Amer. Chem. Soc., 1927, 49, 2279—2296; cf. this vol., 362).—Condensation of opianic acid with phenol in presence of 73% sulphuric acid at not above 30° affords 5 : 6-*dimethoxy*-2-*o-hydroxyphenylphthalide* (I), m. p. 177—178° (*methyl ether*, m. p. 103—104°), together with the corresponding *p*-hydroxy-derivative, m. p. 155—156° (cf. Bistrzycki, A., 1894, i, 600; 1899, i, 151). Opianic acid and anisole yield similarly 5 : 6-*dimethoxy*-2-*p-methoxyphenylphthalide*, m. p. 93—95°. Bromination of (I) in glacial acetic acid affords 5 : 6-dimethoxy-2-(5′-bromo-2′-hydroxyphenyl)phthalide (cf. Jacobson and Adams, A., 1925, i, 272). Condensation of opianic acid with *o*-bromophenol yields 5 : 6-*dimethoxy*-2-(3′-*bromo*-4′-*hydroxyphenyl*)*phthalide*, m. p. 207—208°, which is also obtained by brominating, in chloroform, the crude product from the condensation of opianic acid with phenol. Opianic acid and *o*-bromoanisole yield similarly 5 : 6-*dimethoxy*-2-(3′-*bromo*-4′-*methoxyphenyl*)-*phthalide*, m. p. 141° after softening, or melting and resolidifying, at 136·5—137°, whilst 3-bromo-*o*-cresol affords analogously 5 : 6-*dimethoxy*-2-(5′-*bromo*-4′-*hydroxy*-3′-*methylphenyl*)*phthalide*, m. p. 178—179° after melting and resolidifying at 163—164°. The latter is also obtained by brominating the condensation product from opianic acid and *o*-cresol (cf. Jacobson and Adams, A., 1925, i, 1076). Condensation of opianic acid with *m*-cresol yields (presumably) 5 : 6-*dimethoxy*-2-(4′-*hydroxy*-2′-*methylphenyl*)*phthalide*, m. p. 191·5—192·5°. Bromination of the crude product from the condensation of opianic acid with anisole, in chloroform, yields 5 : 6-*dimethoxy*-2-(5′-*bromo*-2′-*methoxyphenyl*)*phthalide*, m. p. 157—158°, which is also obtained by condensation of opianic acid with *p*-bromoanisole, or by bromination of the

above methyl ether. 2-(5′-*Bromo*-2′-*methoxyphenyl*)-*phthalide*, m. p. 137·5—138·5°, and 5 : 6-*dimethoxy*-2-(4′-*hydroxy*-3′-*methylphenyl*)*phthalide*, m. p. 185—186°, are also described.

When phenols are condensed as above with excess of opianic acid, diphthalidyl derivatives are obtained, of which the following are described: 4 : 6-*di*-(5′ : 6′-*dimethoxyphthalidyl*)-*phenol*, m. p. 204·5—206°; -*anisole*, m. p. 210—211°; -2-*methylphenol*, m. p. 205—207°; -3-*methylphenol*, m. p. 227·5—229·5°; and -2-*bromophenol*, m. p. 215—216°; and 3 : 5-*di*-(4′-*bromo*-5′ : 6′-*dimethoxyphthalidyl*)-o-*cresol*, m. p. 266—268° (decomp.). Reduction of the above phthalides with zinc and sodium hydroxide affords the corresponding benzylbenzoic acids, of which the following are described: 5 : 6-*dimethoxy*-2-(p-*hydroxybenzyl*)*benzoic acid*, m. p. 173—174°; -(o-*hydroxy*-m-*methylbenzyl*)-, m. p. 138·5—139·5°; -(p-*hydroxy*-m-*methylbenzyl*)-, m. p. 140—142°; -(p-*methoxybenzyl*)-; and -(o-*methoxy*-p-*methylbenzyl*)-*benzoic acid*, m. p. 124·5—126·5°; and 2-(o-*methoxybenzyl*)*benzoic acid*, m. p. 115—116°. Some of the latter were also obtained by catalytic reduction. F. G. Willson.

Constitution and physical properties of vulpinic acid. F. P. Mazza (Rend. Accad. Sci. fis. mat. Napoli, 1925, [iii], **31**, 182—193).—Spiegel (A., 1884, 841) ascribed to vulpinic acid (methyl pulvinate) the formula (I), $\begin{matrix}\mathrm{CPh{:}C(OH)\cdot C{:}CPh\cdot CO_2Me}\\ \mathrm{CO\text{———}O}\end{matrix}$, and Volherd (A., 1895, i, 99) the formula (II), $\mathrm{CO_2H\cdot CPh{:}C\text{—}C{:}CPh\cdot CO_2Me}$ (I) the acidic properties to the enolic hydroxyl group; it should thus be possible to prepare derivatives of the ketonic form (III), $\begin{matrix}\mathrm{CHPh\cdot CO\cdot C{:}CPh\cdot CO_2Me}\\ \mathrm{CO\text{———}O}\end{matrix}$ which must also be considered. The mol. wt. in benzene solution shows no polymerisation, indicating that a hydroxy-compound is not present; the dissociation constant, $K_{25}=4{\cdot}94\times10^{-6}$, is that of an extremely feebly acidic substance, and is of the order of that of a phenol. The increase in molecular conductivity of a solution of the sodium salt on dilution is abnormally great.

In an alkaline medium, a *benzoyl* derivative, m. p. 171°, is obtained which is absolutely neutral; phenylcarbimide does not react in the cold, but at 165° a neutral *phenylurethane*, m. p. 237°, is formed. These reactions exclude the structure (II), and suggest that the normal form is (III), converted in the presence of alkali or on heating into (I); correspondingly, in neutral media a *semicarbazone*, m. p. 175°, is obtained.

Values of $[R_L]_\alpha$, $[R_L]_D$, and $[R_L]_\beta$ in various solvents are given; although exalted, they are all inferior to the values calculated for the enolic form; the differential method of Brühl gives, however, high values in an alcoholic solution of sodium ethoxide; in water R_L increases, in agreement with increased enolisation. The absorption spectrum in alcoholic sodium ethoxide solution shows three absorption bands; that in chloroform two only. In water the third band appears on dilution. The dielectric constant is 3·79; the solid compound gives no anomalous electrical absorption, and thus contains no free hydroxyl group; the supercooled liquid shows a slight absorption. E. W. Wignall.

Hydroxyalkyl derivatives of vulpinic acid. A. Piutti and F. P. Mazza (Rend. Accad. Sci. fis. mat. Napoli, 1925, [iii], **31**, 148—155).—The lichen *Lepraria chlorina* contains 18% of its dry weight of vulpinic acid, with other substances containing a higher proportion of oxygen, suspected to be hydroxyalkyl derivatives. Some substances of the latter type are synthesised, but are not identical with any of the natural products.

The method of Volhard (A., 1895, i, 99) for synthesis of vulpinic acid by way of diphenylketipinodinitrile is extended. *o*-Methoxyphenylacetonitrile is condensed with ethyl oxalate and sodium ethoxide, and the product is acidified with acetic acid, giving *di*-o-*methoxyphenylketipinodinitrile*, m. p. 250° (decomp.) after turning brown at 190°. This is hydrolysed by sulphuric acid to the *dilactone*, $\mathrm{MeO\cdot C_6H_4\cdot C{:}C\cdot C{:}C\cdot C_6H_4\cdot OMe}$ (CO-O / O—CO) which on boiling with sodium carbonate solution yields *di*-o-*methoxypulvinic acid*, m. p. 195°, of which the *methyl* ester, *di*-o-*methoxyvulpinic acid*, m. p. 121° (*acetyl* derivative, m. p. 111°; *benzoyl* derivative, m. p. 151°), is obtained by dissolving in methyl-alcoholic potassium hydroxide solution and acidifying. An aqueous solution of this substance when heated with piperidine gives a *substance*, m. p. 98°.

Similarly are prepared: 3 : 4 : 3′ : 4′-*tetramethoxydiphenylketipinodinitrile*, m. p. 204° (decomp.); 3 : 4 : 3′ : 4′-*tetramethoxypulvinic acid*, m. p. 160°; *methyl* ester of the latter, *tetramethoxyvulpinic acid*, m. p. 97° (*acetyl* derivative, m. p. 103°; *benzoyl* derivative, m. p. 134°; *piperidine* salt, m. p. 93°).

3 : 4-*Methylenedioxyphenylacetonitrile*, b. p. 180—190° in a cathode-ray vacuum, is prepared from homopiperonyl chloride; it yields *di*-3 : 4-*methylenedioxyphenylketipinodinitrile*, m. p. 225° (decomp.), *di*-3 : 4-*methylenedioxypulvinic acid*, m. p. 167°, and its *methyl* ester, *di*-3 : 4-*methylenedioxyvulpinic acid*, m. p. 103° (*acetyl* derivative, m. p. 122°; *benzoyl* derivative, m. p. 141°; *piperidine* salt, m. p. 101°). E. W. Wignall.

Radical dissociation of derivatives of arylated succinic acids. III. 2 : 2′-Dihydroxytetra-arylsuccinodilactones. A. Lowenbein and H. Schmidt (Ber., 1927, **60**, [*B*], 1851—1861; cf. A., 1926, 168).—Bromo-2-hydroxydiphenylacetolactone is converted by boiling methyl alcohol into *methoxy*-2-*hydroxydiphenylacetolactone*, m. p. 116°, and by copper bronze in boiling benzene into 2 : 2′-*dihydroxytetraphenylsuccinodilactone*, $\left[\mathrm{O{<}\begin{matrix}C_6H_4\\ CO\end{matrix}{>}CPh\text{—}}\right]_2$, m. p. 166° (indef.). The latter substance is oxidised by free oxygen in boiling benzene to 2-*keto*-3-*phenylcoumaranyl*-3-*peroxide*, m. p. 212°. 2-Hydroxy-4′-methoxy-5-methyldiphenylacetolactone is similarly converted successively into *bromo*-2-*hydroxy*-4′-*methoxy*-5-*methyldiphenylacetolactone*, m. p. 108°, 2 : 2′-*dihydroxy*-4″ : 4‴-*dimethoxy*-5 : 5′-*dimethyltetraphenylsuccinodilactone*, m. p. 215—220°, and 2-*keto*-3-p-*anisyl*-5-*methylcoumaranyl*-3-*peroxide*, m. p. 192°. α-Bromo-

phenyl-2-hydroxy-1-naphthylacetolactone and copper bronze in boiling benzene afford *diphenyl*-2 : 2′-*dihydroxy*-1 : 1′-*dinaphthylsuccinodilactone*, m. p. 148—150°, which is converted by bromine in warm benzene into α-bromophenyl-2-hydroxy-1-naphthylacetolactone, by phenylhydrazine into phenyl-2-hydroxy-1-naphthylacetolactone and by free oxygen into 2-*keto*-3-*phenylbenzocoumaranyl*-3-*peroxide*, m. p. 233°. *α-Bromo*-4′-*methoxyphenyl*-2-*hydroxy*-1-*naphthylacetolactone*, m. p. 159°, yields analogously *α-methoxy*-α*p-dimethoxyphenyl*-2-*hydroxy*-1-*naphthylacetolactone*, m. p. 125°, *α-ethoxy*-p-*methoxyphenyl*-2-*hydroxy*-1-*naphthylacetolactone*, m. p. 106°, and pp′-*dimethoxydiphenyl*-2 : 2′-*dihydroxy*-1 : 1′-*dinaphthylsuccinodilactone*, m. p. 197—212°. A further method for the preparation of the dilactones is found in the action of sodium iodide on the bromolactones in acetone solution. All the succinodilactones dissociate into radicals when heated; the degree of dissociation has been determined for 2 : 2′-dihydroxytetraphenylsuccinodilactone, 2 : 2′-didihydroxy-4″ : 4‴-dimethoxy-5 : 5′-dimethyltetraphenylsuccinodilactone and diphenyl-2 : 2′-dihydroxy-1 : 1′-dinaphthylsuccinodilactone in boiling toluene and ethylene dibromide. Addition of concentrated aqueous hydrochloric acid to a boiling solution of the last-mentioned lactone in acetic anhydride causes the separation of intensely green crystals of the dilactone. The observation is explained by the hypothesis that, since crystallisation is induced at a temperature far above the association temperature, the product is a solid solution of the radical in the dilactone. When subjected to pressure the dilactones become more deeply coloured and the behaviour appears to extend to all ethanes capable of dissociation. The colour becomes less intense in course of time if the pressure is removed, but returns when the pressure is restored. Since in all cases the colour produced corresponds exactly with that of the free radical, it must be assumed that radical dissociation can be caused by high pressure on solid substances at the atmospheric temperature. It is probable that the aromatic nuclei become deformed by pressure or that the single ethane molecules are so modified in their structure by spatial proximity that liberation of radicals occurs locally and that solid solutions are thus produced which occupy a smaller volume than the original substance. H. WREN.

Oxidation products of aromatic aldehydehydrazones and their molecular transpositions. G. MINUNNI (Gazzetta, 1927, 57, 505—525).—A summary is given of previous work on the oxidation of the aromatic aldehydrazones and on the isomerisation and molecular transformations of the oxidation products. Oxidation of these phenylhydrazones yields various crystalline products, some of which, viz. the hydrotetrazones, dehydrohydrazones, and osazones of the α-diketones, arise by elimination of two atoms of hydrogen from two molecules of hydrazone. Other among these oxidation products result from the addition of one or two atoms of oxygen to a molecule of hydrazone. Under certain conditions benzaldehydephenylhydrazone gives compounds of analogous structure to the hydrotetrazones and dehydrohydrazones, but containing a benzoyl radical, these being formed by oxidation of the benzylidene group of one of the hydrazone molecules participating in the reaction. T. H. POPE.

Oxidation of hydrazine compounds. I. Behaviour of the *p*-tolylhydrazones of certain aromatic aldehydes with amyl nitrite. G. MINUNNI and S. D'URSO (Gazzetta, 1927, 57, 526—536; cf. preceding abstract).—When oxidised by treatment with amyl nitrite, *benzaldehyde*-p-*tolylhydrazone*, m. p. 114—115°, yields only *dibenzylidene-di*-p-*tolylhydrotetrazone*, $CHPh{:}N{\cdot}N(C_6H_4Me){\cdot}N(C_6H_4Me){\cdot}N{:}CHPh$, m. p. 174·5—175°, which cannot be transformed either into the dehydrohydrazone by heating or into benzil-*p*-tolylosazone by treatment with benzoyl chloride. Similarly, *piperonal*-p-*tolylhydrazone*, m. p. 116—117°, which turns red on prolonged exposure to light, yields only *dipiperonaldi*-p-*tolylhydrotetrazone*, $CH_2O_2{:}C_6H_3{\cdot}CH{:}N{\cdot}N(C_6H_4Me){\cdot}N(C_6H_4Me){\cdot}N{:}CH{\cdot}C_6H_3{:}CH_2O_2$, m. p. 155—156 (evolution of gas and browning); attempts to convert this into the dehydrotetrazone by heating proved unsuccessful, but treatment with benzoyl chloride gives *piperil*-β-p-*tolylosazone*, $CH_2O_2{:}C_6H_3{\cdot}C(:N{\cdot}NH{\cdot}C_6H_4Me){\cdot}C(:N{\cdot}NH{\cdot}C_6H_4Me){\cdot}C_6H_3{\cdot}CH_2O_2$, m. p. 214—215°. Salicylaldehyde-*p*-tolylhydrazone yields only *dehydro*-o-*hydroxybenzaldehyde*-p-*tolylhydrazone*, $OH{\cdot}C_6H_4{\cdot}CH{:}N{\cdot}N(C_6H_4Me){\cdot}C(C_6H_4{\cdot}OH){:}N{\cdot}NH{\cdot}C_6H_4Me$, m. p. 194—196° (decomp.) or 197—199° (decomp.) according to the rapidity of the heating. m-*Nitrobenzaldehyde*-p-*tolylhydrazone*, m. p. 150°, gives, as principal products: (1) *di*-m-*nitrobenzylidenedi*-p-*tolylhydrotetrazone*, m. p. 167·5—169·5° (decomp.), which is converted into iso*dehydro*-m-*nitrobenzaldehyde*-p-*tolylhydrazone*, $C_{28}H_{24}O_4N_6$, m. p. 230° (decomp.), when heated and into m-*nitrobenzil*-β-p-*tolylosazone*, m. p. 251°, when treated with benzoyl chloride; (2) *dehydro*-m-*nitrobenzaldehyde*-p-*tolylhydrazone*, $NO_2{\cdot}C_6H_4{\cdot}CH{:}N{\cdot}N(C_6H_4Me){\cdot}C(C_6H_4{\cdot}NO_2){:}N{\cdot}NH{\cdot}C_6H_4Me$, m. p. 193° (decomp.), which is converted into (1) by the action of nitrous acid. T. H. POPE.

Anhydro-compounds of *o*-aminobenzaldehyde. F. SEIDEL and W. DICK (Ber., 1927, 60, [*B*], 2018—2023; cf. A., 1926, 1140).—Anhydrotris-*o*-aminobenzaldehyde, dissolved in acetone, is converted by the prolonged action of nitrous fumes into *dinitrosoanhydrotris*-o-*aminobenzaldehyde*, m. p. 155—158° (decomp.), and by less prolonged action into the *mononitroso*-compound, m. p. 171° (or $+C_6H_6$, m. p. 172—173°); the monoacetyl derivative yields a *mononitroso*-compound, m. p. 165—167°. These observations are incompatible with the constitution assigned by Seidel (*loc. cit.*) to anhydrotris-*o*-aminobenzaldehyde and confirm the structure, $CH\leqslant^{C_6H_4{\cdot}NH}_{N\quad C_6H_4}>CH{\cdot}NH{\cdot}C_6H_4{\cdot}CHO$, proposed by Bamberger (this vol., 361). Similarly, anhydrotetrakis-*o*-aminobenzaldehyde affords a *dinitroso-*

derivative, m. p. 176° (or $+CH_3{\cdot}CO{\cdot}CH_3$, m. p. 125—155°, and (?) $+0{\cdot}5C_6H_6$, m. p. 170—193°), and a *mononitroso*-compound, m. p. 222—223°. *Mononitrosomonoacetylanhydrotetrakis-o-aminobenzaldehyde*, m. p. 193° after darkening at 185°, is described. The constitution

$CH\leqslant^{C_6H_4{\cdot}NH}_{N—C_6H_4}>CH{\cdot}NH{\cdot}C_6H_4{\cdot}CH{:}N{\cdot}C_6H_4{\cdot}CHO$ is

therefore assigned to the aldehyde. H. WREN.

***N*-Ethers of oximes.** H. LINDEMANN and K. T. TSCHANG (Ber., 1927, **60**, [*B*], 1725—1729).—In the hope of discriminating between the alternative constitutions $\begin{matrix}R\\H\end{matrix}>C<\begin{matrix}NR'\\O\end{matrix}$ and $\begin{matrix}R\\H\end{matrix}>C{:}NR'{:}O$ for the *N*-ethers of aldoximes the authors have examined the possibility of resolving *p*-dimethylaminobenzaldoxime *N*-methyl ether into optical antipodes (cf. Kuhn and Albrecht, this vol., 749). Failure to accomplish this is conditional evidence in favour of the nitrone structure.

Anisaldoxime *N*-methyl ether is hydrolysed by tartaric acid with production of N-*methylhydroxylamine tartrate*, m. p. 235°. p-*Dimethylaminobenzaldoxime* N-*methyl ether* ($+H_2O$), m. p. 110° (*hydrochloride*, m. p. 86°), is prepared from *p*-dimethylaminobenzaldehyde and *N*-methylhydroxylamine hydrochloride; the d-*tartrate*, m. p. 163°, *l*-tartrate, m. p. 166°, and d-*bromocamphorsulphonate*, m. p. 164°, are described. Optical activity could not be detected in the base isolated from the salts containing optically active acids. Anisaldehyde is transformed by hydroxylamine hydrochloride in alcoholic solution into the α-oxime, whereas protracted boiling causes formation of the β-compound. α-Anisaldoxime *O*-methyl ether, from the α-oxime, methyl alcohol, methyl iodide, and silver oxide, has m. p. 43°, b. p. 129°/15 mm., d_4° 1·0690, 1·53561, whereas the corresponding β-compound (prepared similarly at temperatures below 10°) has m. p. 36°, b. p. 129°/15 mm., $d^{84{\cdot}3}$ 1·0745, $n_\alpha^{84{\cdot}3}$ 1·53378. The β-compound is readily converted into the α-isomeride by hydrogen chloride. H. WREN.

Colour and chemical constitution. XXII. Dicyclic azomethines and their congeners. J. MOIR (Trans. Roy. Soc. S. Africa, 1927, **14**, 301—303).—The absorption band at λ 330 of *p*-hydroxybenzaldehyde and the stilbenes $CHPh{:}CH{\cdot}C_6H_4{\cdot}ONa$ and $[ONa{\cdot}C_6H_4{\cdot}CH{:}]_2$ (λλ 330 and 370) in alkaline solution is attributed to association of the (*para*) auxochrome ONa with the double linking. Replacement of CH by N produces a band near λ 400 as in $O{:}N{\cdot}C_6H_4{\cdot}ONa$ (λ 400), benzylidene-*p*-aminophenol (λλ 367 and 393), *p*-hydroxybenzylidene-*p*-aminophenol (434 and 406), and *p*-hydroxyazobenzene (433 and 395). The absorption of *p*-dimethylaminobenzylidene-*p*-aminophenol (433 and 405) and the stilbene, $NMe_2{\cdot}C_6H_4{\cdot}CH{:}CH{\cdot}C_6H_4{\cdot}ONa$ (λ 400), in alkaline solution, of the stilbenes,

$OH{\cdot}C_6H_4{\cdot}CH{:}CH{\cdot}C_6H_4{\cdot}NMe_2$ (360 and 400),

$CHPh{:}CH{\cdot}C_6H_4{\cdot}NMe_2$ (355), and

$NMe_2{\cdot}C_6H_4{\cdot}CH{:}CH{\cdot}C_6H_4{\cdot}NMe_2$ (430 and 461) and of *p*-dimethylamino-*p'*-hydroxyazobenzene (435 and 465), *p*-dimethylaminobenzylidene-*p'*-dimethylaminoaniline (496 and 464), *p*-hydroxybenzylidene-*p'*-dimethylaminoaniline (490 and 460), and *p*-dimethylaminobenzylideneaniline (430 and 460) in acetic acid indicate that substitution of the auxochrome NMe_2 for ONa shifts the band from 330 to 360. Since the colour of the stilbene derivatives is deeper than that of the hydroxy- and dimethylamino-benzaldehyde derivatives it is possible that the linking between C_6H_4 and CH and not the central double linking is concerned in these cases. The deep colour of *p*-dimethylaminoazobenzene (λλ 507 and 543), of bis-*pp'*-dimethylaminoazobenzene (λλ 505, 540, and 685), and of *p*-dimethylamino-*p'*-hydroxyazobenzene (λλ 507, 540, and 570) in acetic acid is attributed to a similar cause. In concentrated sulphuric acid *p*-dimethylamino-*p'*-hydroxyazobenzene shows a band (λ 692) similar to that of tetramethyldiaminoazobenzene in glacial acetic acid. *p*-Hydroxybenzylideneaniline has a band at λ 360, $NMe_2{\cdot}C_6H_4{\cdot}CHO$ (acetic acid) at λ 359, $NMe_2{\cdot}C_6H_4{\cdot}NO$ (acetic acid) at λ 458, *pp'*-dihydroxyazobenzene at λλ 487 and 455. Benzylidene-*p*-dimethylaminoaniline is exceptional in showing bands at λλ 482 and 514 in acetic acid. The twelve dihydroxybenzylideneanilines in alkaline solution show absorption bands as indicated: 2 : 2′, λ 450; 2 : 3′, 510; 2 : 4′ and 2 : 5′, 440; 2 : 6′ and 4 : 2′, 420; 3 : 2′; 430, 3 : 3′ and 3 : 5′, 470; 3 : 4′ and 4 : 3′, 410; 3 : 6′; 408 and 4 : 4′, 434 and 406. R. BRIGHTMAN.

Abnormal reaction of certain aromatic aldehydes with Schiff's reagent. J. B. SHOESMITH, C. E. SOSSON, and A. C. HETHERINGTON (J.C.S., 1927, 2221—2230).—On examination of a large number of aldehydes, it has been found that the abnormal reaction which consists in the production of yellow precipitates and colorations is dependent on the quantity of "free sulphur dioxide," *i.e.*, sulphur dioxide capable of reacting with iodine, present in the reagent. A large excess favours the aldehyde–hydrogen sulphite type of reaction, which is regarded by Wieland and Scheuing (A., 1922, i, 58) as being that which results in the production of colour. Certain of the aldehydes examined, notably *o*-hydroxy-aromatic aldehydes, undergo an entirely different reaction resulting in the formation of precipitates having the properties of sulphites of hydrated Schiff's bases of the general formula

$SO_3H{\cdot}C(C_6H_4{\cdot}NH{\cdot}CHR{\cdot}OH)_3$, in which R is an aromatic residue. The formation of these precipitates is retarded by a large excess of sulphurous acid, hence red precipitates (really yellow ones containing adsorbed red dye) result from reagents containing much free sulphur dioxide, and yellow ones from those deficient in free sulphur dioxide. Some of these aldehydes react abnormally with all types of reagent, others only under certain conditions. In order to ascertain the composition of the precipitates, that obtained from β-resorcylaldehyde was examined in detail. Since they cannot be separated as pure compounds owing to their insolubility in organic solvents or water and to their instability towards acids and alkalis, analytical results were only approximate, but a satisfactory clue to the constitution was obtained by comparison of the precipitates formed by interaction of the aldehyde with reagents made from other bases of the pararosaniline type.

The red colour developed by Schiff's reagent on heating disappears on cooling, provided that much sulphur dioxide is not allowed to leave the solution. *pp'*-Diaminotriphenylcarbinol undergoes a similar reaction, the solution being violet when hot, colourless when cold. W. J. Powell.

Preparation of nitrohydroxybenzaldehydes and colour relationships of their substituted phenylhydrazones. H. H. Hodgson and H. G. Beard (J.C.S., 1927, 2375—2384).—Nitration of 6-nitro-3-hydroxybenzaldehyde gives a mixture of 2 : 6-*dinitro*-3-*hydroxybenzaldehyde*, m. p. 94° [*sodium* and *ammonium* salts; p-*nitrophenylhydrazone*, exploding 240—242°; p-*bromophenylhydrazone*, m. p. 166—167° (decomp.)], and 4 : 6-*dinitro*-3-*hydroxybenzaldehyde*, m. p. 106° [*sodium* and *ammonium* salts; p-*nitrophenylhydrazone*, decomp. 282—283°; p-*bromophenylhydrazone*, m. p. 249—250° (decomp.)]. Nitration of 2- and 4-nitro-3-hydroxybenzaldehydes gives as single products the 2 : 6- and 4 : 6-dinitro-derivatives respectively. Further nitration of either compound yields 2 : 4 : 6-*trinitro*-3-*hydroxybenzaldehyde*, m. p. 161—162° (decomp.) [(*sodium* salt; p-*nitrophenylhydrazone*, exploding 228—230°; p-*bromophenylhydrazone*, exploding 218—220°; *azine*, exploding 150—160°)]. Nitration of 6-nitro-3-methoxybenzaldehyde yields in like manner a mixture of 2 : 6-dinitro-3-methoxybenzaldehyde, m. p. 157° [p-*nitrophenylhydrazone*, exploding 260°; p-*bromophenylhydrazone*, m. p. 196—197° (decomp.)], and 4 : 6-*dinitro*-3-*methoxybenzaldehyde*, m. p. 131° [p-*nitrophenylhydrazone*, m. p. above 300°; p-*bromophenylhydrazone*, m. p. 254—256° (decomp.)]. Tiemann and Ludwig's α-dinitro-*m*-methoxybenzaldehyde (cf. Ber., 1882, **15**, 2043) is thus the 2 : 6-dinitro-compound, whereas their β-isomeride is a mixture of the 2 : 6- and 4 : 6-dinitro-derivatives. Nitration of 3-nitro-4-hydroxybenzaldehyde with pure nitric acid gives 3 : 5-*dinitro*-4-*hydroxybenzaldehyde*, m. p. 102—103° [(*sodium* salt; p-*nitrophenylhydrazone*, decomp. 283—284°; p-*bromophenylhydrazone*, decomp. 242—244°; *phenylhydrazone*, m. p. 203°)], whereas if sulphuric acid is present only picric acid is formed. Nitration of 2 : 5-dichlorobenzaldehyde gives a mixture of 2 : 5-dichloro-6-nitrobenzaldehyde and, in lesser yield, 2 : 5-*dichloro*-3-*nitrobenzaldehyde* [*phenylhydrazone*, m. p. 171°; p-*nitrophenylhydrazone*, m. p. 290—292° (decomp.)]. 2 : 5-*Dichloro*-3-*nitrobenzoic acid* has m. p. 220°; 2 : 3 : 5-*trichlorobenzaldehyde* has m. p. 56°. The compounds described as 4-chloro-6-nitro-3-hydroxybenzaldehyde and 4-chloro-2-nitro-3-hydroxybenzaldehyde (A., 1926, 1040) are now shown to be 4-chloro-2-nitro-3-hydroxybenzaldehyde and 2-chloro-4-nitro-3-hydroxybenzaldehyde, respectively, the last-named compound being derived from 2-chloro-isomeride present as impurity in the 4-chloro-3-hydroxybenzaldehyde used in the preparation. The following are also described: p-*nitrophenylhydrazone*, m. p. 247—249° (decomp.), and p-*bromophenylhydrazone*, m. p. 192—193°, of 3-nitro-4-hydroxybenzaldehyde; 2 : 6-*dinitro*-3-*methoxybenzoic acid*, m. p. 199°.

The facility of decomposition of the *p*-nitrophenylhydrazones of the various nitrohydroxybenzaldehydes is shown to be dependent on the positions of the nitro-groups in the aldehyde residue. The colours of the nitro- and *p*-bromo-phenylhydrazones of these aldehydes, both as solids and in aqueous and alcoholic alkaline solution, are discussed in relation to positional influences. M. Clark.

Preparation of 2 : 5-dihydroxybenzaldehyde (gentisaldehyde). H. H. Hodgson and H. G. Beard (J.C.S., 1927, 2339—2340).—The method described gives an improved yield of a less crude product than that of Neubauer and Flatow (A., 1907, i, 771). *m*-Hydroxybenzaldehyde is treated at 30—35° with potassium persulphate in alkaline solution, and, after keeping, the mixture is rendered faintly acidic and the unchanged material extracted with ether. When the solution is strongly acidified, a dark brown, amorphous substance, which constitutes 40% of the yield, is precipitated. This substance chars above 330°, and contains an aldehyde group, since it yields a p-*nitrophenylhydrazone*, which gives the characteristic magenta colour with alkalis. 2 : 5-Dihydroxybenzaldehyde, m. p. 89—92°, is extracted from the filtrate with ether. The pure product has m. p. 98—99° (cf. Tiemann and Müller, A., 1882, 52). The p-*nitrophenylhydrazone*, brick-red, has m. p. 256—257° (decomp.); the *dibenzoate*, m. p. 106—107°, forms a p-*nitrophenylhydrazone*, orange, m. p. 272°; the dimethyl ether, m. p. 51° (cf. Tiemann and Müller, *loc. cit.*), forms a p-*nitrophenylhydrazone*, red, m. p. 216°; the monomethyl ether yields a p-*nitrophenylhydrazone*, orange, m. p. 206°. W. J. Powell.

Condensation of *cyclo*hexanones with aromatic aldehydes. Alkylation of *cyclo*hexanones. R. Cornubert and H. Le Bihan (Bull. Soc. chim., 1927, [iv], **41**, 1077—1087; cf. A., 1921, i, 422, 730).—Allylation of 2-methyl*cyclo*hexanone with sodamide and allyl chloride, bromide, and iodide gives a mixture of 2-allyl-2-methyl- and 2-allyl-6-methyl-*cyclo*hexanones (80 : 20 from chloride, 88 : 12 from bromide and iodide). Hydrogenation of these allyl compounds furnishes the corresponding *n*-propyl compounds, which condense with benzaldehyde in presence of hydrogen chloride, yielding *benzylidene*-2-*methyl*-6-*n*-*propyl*cyclo*hexanone*, m. p. 25°, and a "*tetrahydropyrone*," $C_{24}H_{30}O_2$, m. p. 136—137° (cf. A., 1926, 953), respectively. Allylation of 4-methyl*cyclo*hexanone with allyl chloride and bromide affords 2-allyl-4-methyl*cyclo*hexanone together with a mixture of 2 : 2-diallyl- and 2 : 6-diallyl-4-methyl*cyclo*hexanones (75 : 25 from chloride, 88 : 12 from bromide), all of which on hydrogenation yield the corresponding *n*-propyl compounds. 4-*Methyl*-2 : 6-*di*-n-*propyl*-cyclo*hexanone* thus obtained using allyl bromide had b. p. 129—129·5°/20 mm., 0·8925, n_D^{18} 1·4600, and yielded an *oxime*, m. p. 70°, b. p. 164—168°/26 mm., and a *semicarbazone*, m. p. 185·5—190°. The ketone on condensation with benzaldehyde in presence of hydrogen chloride yields a *benzylidene* derivative, b. p. 215—216°/16 mm., and the "*tetrahydropyrone*," $C_{27}H_{34}O_2$, m. p. 145°. Similar condensation of benzaldehyde with 4-methyl-2-*n*-propyl*cyclo*hexanone affords a *benzylidene* derivative, b. p. 194—196°/16 mm. (*semicarbazone*, m. p. 161°), whilst with sodium

methoxide as the condensing agent there are obtained the benzylidene derivative and a *compound*, $C_{17}H_{26}O_2$, m. p. 150° (*diacetyl* derivative, m. p. 86°), which has probably the formula $CH_2—CHMe—CH_2$ / $CHPr^{\alpha}·CH(OH)·CH·CHPh·OH$. 2-Allyl-4-methyl*cyclo*hexanone and benzaldehyde in presence of sodium methoxide yield an impure *benzylidene* derivative, b. p. 202—203°/17 mm. (*semicarbazone*, m. p. 141°), together with a small amount of a *compound*, $C_{17}H_{24}O_2$, m. p. 135°, analogous to that obtained from the propyl derivative. Hydrogenation of 6-benzylidene-4-methyl-2-*n*-propyl*cyclo*hexanone yields impure 6-*benzyl*-4-*methyl*-2-n-*propyl*-cyclo*hexanone*, b. p. 189·5°/14 mm., which condenses with benzaldehyde in presence of hydrogen chloride to yield a small amount of a "*tetrahydropyrone*," $C_{31}H_{34}O_2$, m. p. 172°. H. BURTON.

Semipinacolic and hydrobenzoinic transpositions in the alkylhydrobenzoin series. Alkylhydrobenzoins with branched chains. II. The *cyclo*hexane chain. A. OREKHOV and M. TIFFENEAU (Bull. Soc. chim., 1927, [iv], 41, 1174—1185).—α-*cyclo*Hexylhydrobenzoin, m. p. 159—160° (cf. Danilov, A., 1926, 519), undergoes a transposition of the semipinacolic type on dehydration with concentrated sulphuric acid forming *cyclo*hexyl benzhydryl ketone, m. p. 57—58°, its behaviour being therefore analogous to that of the corresponding benzyl and *iso*propyl derivatives of hydrobenzoin (cf. A., 1923, i, 333). Dehydration with hot dilute acid, however, leads to the formation of the three products theoretically possible, viz., *cyclo*hexyldiphenylacetaldehyde, m. p. 124°, by a semihydrobenzoinic change, *cyclo*hexyl benzhydryl ketone by a semipinacolic transposition, and *cyclo*hexyldeoxybenzoin, m. p. 120—121°, by dehydration followed by isomerisation without migration of the phenyl group. The last may be synthesised by the action of *cyclo*hexyl bromide on deoxybenzoin in presence of sodium ethoxide. The formation of a ketone rather than an aldehyde on dehydration is characteristic of hydrobenzoin derivatives in which the substituent is a radical of feeble affinity. Since the benzyl derivative with dilute acid undergoes exclusively the semipinacolic change, whilst the *iso*propyl like the *cyclo*hexyl derivative gives a mixture, the relative affinities are in the order $Bz < Pr^{\beta}$ and $C_6H_{11} < H$. *αγδ-Triphenylbutane-γδ-diol*, m. p. 147—148°, obtained from benzoin and magnesium β-phenylethyl bromide, yields, on oxidation with chromic acid, benzoic acid and phenyl β-phenylethyl ketone, m. p. 72—73°, and on dehydration with concentrated sulphuric acid affords an unsaturated *hydrocarbon*, $C_{22}H_{18}$, m. p. 85—86°, probably $C_6H_4<^{CH_2—CH}_{CHPh·CPh}$ or $C_6H_4<^{CH_2\ CH_2}_{CPh·CPh}$ *ααδ-Triphenylbutan-β-ol*, prepared from diphenylacetaldehyde and magnesium β-phenylethyl bromide, has m. p. 61—62° (yield 48%); *αδε-triphenylpentane-δε-diol*, from benzoin and magnesium γ-phenylpropyl bromide, has m. p. 100—101°, and yields on oxidation with chromic acid in acetic acid, *phenyl γ-phenylpropyl ketone*, m. p. 57—58°. Benzoin is reduced by magnesium *tert.*-butyl chloride and by magnesium *sec.*-butyl bromide, the chief product being hydrobenzoin. W. J. POWELL.

Pyrogenic decomposition of ketones under high pressures. V. N. IPATIEV and A. D. PETROV (Ber., 1927, 60, [*B*], 1956—1963).—Acetophenone, when heated under pressure at 270—300° in the presence of aluminium hydroxide, affords unchanged material, triphenylbenzene, 3 : 4-diphenylfuran, and a red resin; at 380—420° the reaction is complete and gives a mixture of benzene, toluene, ethylbenzene, and *o*-xylene (15% in all), the remainder being a resin which does not appear to contain diphenyl or *p*-diphenylbenzene and in which benzoic acid is present only in traces. The primary products of the change are therefore benzene and toluene, whereas ethylbenzene is formed by subsequent hydrogenation of acetophenone. Benzophenone remains unchanged at 430°, but suffers complete decomposition at 500—550°, yielding mainly carbon and gases; benzene and diphenylmethane, but not diphenyl or *p*-diphenylbenzene, are identified among the liquid products (12%). When heated with hydrogen in an iron tube at 400—430° in the presence of aluminium oxide, benzophenone affords diphenylmethane in very good yield; only about 20% of the ketone dissociates into benzene and resin. Acetone, under pressure in the presence of aluminium oxide at 350—400° yields mesityl oxide, *iso*phorone, xylitone, and mesitylene, reversible and irreversible reactions thus taking place. Increase of temperature to 500—550° favours the irreversible changes accompanied by maximal elimination of water whereby the unsaturated cyclic ketones (*iso*phorone and xylitone) are partly converted by loss of water into a mixture of aromatic compounds, mainly mesitylene, and partly by loss of methane into *s.*-*m*-xylenol. H. WREN.

Electrolytic reduction of ketoximes and aldoximes of the aromatic series. S. KAPLANSKY (Ber., 1927, 60, [*B*], 1842—1843; cf. Gulevitsch and others, A., 1924, i, 1285).—Aromatic ketoximes are considerably more smoothly reduced by Tafel's method than in the presence of colloidal palladium; the yields of primary amine vary from 50% to 70%. Tafel's process is applicable also to aldoximes. The electrolytic reduction of the oximes of benzophenone, acetophenone, dibenzyl ketone, benzaldehyde, and vanillin is described. H. WREN.

Oximes of *o*-amino-benzo- and -aceto-phenone. J. MEISENHEIMER, O. SENN, and P. ZIMMERMANN (Ber., 1927, 60, [*B*], 1736—1748; cf. Meisenheimer and Meis, A., 1924, i, 433; von Auwers and Jordan, *ibid.*, 743).—The mixture of *n*- and *h*-oximes of *o*-aminobenzophenone is transformed by boiling formic acid into the *n*-oxime and 4 : 5-*benzo*-3-*phenylhept*-1 : 2 : 6-*oxdiazine*, $C_6H_4<^{CP\ .N}_{N=CH}>O$, m. p. 173—174° (regarded by von Auwers and Jordan as the *N*-formyl derivative of the *n*-oxime). If the *n*-oxime dissolved in cold, dilute hydrochloric acid is treated with sodium nitrite, yellow 4 : 5-*benzo*-6-*phenyl*-1 : 2 : 3-*triazine*-1-*oxide*, $C_6H.<^{CPh.N.O}_{N—N}$, m. p. 154° (decomp.), is immediately precipitated. If, however, diazotisation is accomplished in warm solution, phenyl-

anthranil and benzenylphenyleneamidine, m. p. 285°, are produced. The *h*-oxime is almost quantitatively transformed by diazotisation into phenylindoxazene; if, however, the mixture is kept for some time before being heated and the small amount of resin is not immediately removed, 4 : 5-benzo-6-phenyl-1 : 2 : 3-triazine-1-oxide separates. The configurations $NH_2 \cdot C_6H_4 \cdot \overset{\displaystyle HO \cdot N}{\overset{\|}{C}}Ph$ and $NH_2 \cdot C_6H_4 \cdot \overset{\displaystyle N \cdot OH}{\overset{\|}{C}}Ph$ for the *h*- and *n*-oximes are therefore considered to be confirmed. The *N*-acyl derivatives of *o*-aminobenzophenoneoxime readily form seven-membered rings, the tendency being particularly marked in derivatives of the *h*-oxime. Evidence with regard to configuration cannot be deduced therefrom, since the precise mode of action is uncertain. Reopening of the ring occurs more uniformly and leads in all circumstances (in alkaline and hydrochloric acid solution and with superheated water) to the acyl-*N*-oxime whereby *trans* fission of the ring must be assumed.

Whereas aqueous sodium hydroxide causes transformation of benzophenone-*n*-oxime into the *h*-oxime, the homogeneous oximes are obtained by the action of concentrated alcoholic sodium hydroxide on the corresponding benzoyl derivatives. In dilute alcoholic solution the benzoyl-*h*-oxime is unchanged by sodium hydroxide, whereas the benzoyl-*n*-oxime is quantitatively transformed into the benzoyl-*h*-oxime.

o-Aminoacetophenoneoxime is converted by diazotisation and subsequent boiling of the solution into methylanthranil, 4 : 5-*benzo*-6-*methyl*-1 : 2 : 3-*triazine*-1-*oxide*, decomp. 185—188°, being formed intermediately. Attempts to reduce the oxide to the corresponding triazine resulted in the exclusive production of 3-methylindazole as defined product. Conversion of the triazine oxide into methylanthranil proceeds readily in cold, dilute sulphuric acid or boiling water, whereby *o*-azidoacetophenone is produced, identified as the *dinitrophenylhydrazone*, decomp. 182—183°; an additive *compound* of *o*-azidoacetophenone and mercuric chloride is described. The triazine oxide dissolves rapidly in aqueous or alcoholic alkali hydroxide and the dark red solution, if immediately acidified, affords *o-acetophenylazohydroxylamine* (or *o-acetanilinoazohydroxide*), decomp. 116—117° after softening, which with phenylcarbimide affords *N-phenyl*-N'-*o-acetophenylcarbamide*, m. p. 170° (decomp.) in a pre-heated bath. The carbamide derivative is also obtained from *o*-aminoacetophenone and phenylcarbimide. The conversion of *o*-aminobenzaldoxime into 4 : 5-*benzo*-1 : 2 : 3-*triazine*-1-*oxide* (Bamberger's "indiazoneoxime") occurs with very poor yield, but the corresponding change is easier with 3 : 5-dimethyl- and 3 : 6-dichloro-2-aminobenzaldoxime. The two latter oximes must certainly have the same configuration as *o*-aminoacetophenoneoxime, the hydrogen and hydroxyl groups being in the *cis*-position to one another. It appears probable that the more readily preparable and more stable forms of aromatic aldoximes have the aromatic nucleus and hydroxyl group in the *anti*-position (cf. Brady and Bishop, A., 1925, i, 930). H. WREN.

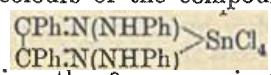
Indones. VIII. R. DE FAZI (Gazzetta, 1927, **57**, —550).—When heated for 2 hrs. with phosphoric anhydride in anhydrous benzene solution on a boiling water-bath, ethyl ββ-diphenyl-α-methyl-lactate is converted solely into ethyl β-phenyl-α-methylcinnamate, this being partly transformed into 3-phenyl-2-methylindone if the action is prolonged for about 8 hrs. Thus, although phosphoric anhydride readily removes the first molecule of water from the phenylmethyllactic ester, hydrolysis of this ester by phosphoric acid proceeds slowly. It is concluded that the formation of indones from the lactic esters proceeds by ring-closure of the cinnamic acid. 2 : 3-Diphenylindone, previously obtained in about 30% yield by the action of phosphoric anhydride on αβ-diphenyl-lactic acid (A., 1915, i, 542), may be prepared in almost theoretical yield by the action of concentrated sulphuric acid on αββ-triphenyl-lactic acid; the *phenylhydrazone* of this indone has m. p. 175—176° (cf. Garcia Banus and Medrano, A., 1924, i, 180).

T. H. POPE.

Indones. IX. Truxones. R. DE FAZI (Gazzetta, 1927, **57**, 551—554).—With reference to Brass' statement that the author assumes the bimolecular constitution of the aryl- and alkyl-truxones (A., 1926, 838, 839) the author points out that he showed by mol. wt. determinations that the products of the action of concentrated sulphuric acid on ethyl ββ-diphenyl-lactate include two diphenyltruxones (A., 1915, i, 1063; 1916, i, 151; 1920, i, 316). Not all truxones are obtainable by a single method. Thus the action of concentrated sulphuric acid on β-phenylindone yields two diphenyltruxones, whereas this acid does not act under similar conditions on 3-phenyl-2-methylindone. The latter is converted into dimethyldiphenyltruxones by the radiations from a quartz mercury vapour lamp, and these also transform into two other isomerides the two diphenyltruxones formed by the action of sulphuric acid on β-phenylindone.

T. H. POPE.

Ring-closure in additive compounds. III. Determination of configuration of stereoisomeric hydrazones. W. HIEBER and F. SONNEHALB (Annalen, 1927, **456**, 86—110; cf. A., 1925, i, 1325).—The configurations of stereoisomeric compounds may be determined from a consideration of their cyclic co-ordinated additive compounds with metallic salts. Benzil-α-osazone in chloroform combines with 0·5 mol. of stannic chloride to form a yellow *compound*, decomp. above 145°, and with 1 mol. of stannic chloride to give a red *compound*, m. p. 120° (decomp.). The β-osazone, on the other hand, forms only a single (equimolecular) additive *compound*, m. p. 60°. No isomerisation takes place, for the corresponding osazones are regenerated by treatment with water. In similar manner stannic chloride combines with 2 mols. of benzaldehydephenylhydrazone, giving a yellowish-brown *compound*, m. p. 70—75° (decomp.); with 2 mols. of benzophenonephenylhydrazone (red *compound*, m. p. 190°); with 2 mols. of benzylidenecaniline [yellow *compound*, m. p. 200° (decomp.)]; with 1 mol. of benzophenoneanil (yellow *compound*, m. p. 180°); with 1 mol. of benzildianil [yellow *compound*, m. p. 225° (decomp.); also a red *compound* containing more stannic chloride]; with 1 mol. and 1·5 mols. of benzilmonoanil (orange and red *compounds*, m. p. 175° and 90°, respectively);

with 1 mol. of benzilmonophenylhydrazone (brownish-red *compound*, m. p. 165°). The evolution of heat during the reaction with benzylideneaniline and benzophenoneanil and the great stability of these products indicate that in all the compounds the tin is attached to doubly-linked nitrogen atoms. This is confirmed by the colours of the compounds, and leads to the formula  for the β-osazone product; *i.e.*, the β-osazone is the *anti*-compound, the α-osazone the *syn*-compound. The only known benzilmonophenylhydrazone has an *anti*-configuration.

2 : 3 : 5 : 6-Tetraphenylpyrazine gives with 1 mol. of stannic chloride a yellow *compound*, decomp. 135°; with 2 mols. a red *compound*, m. p. 100°. 5 : 6-Diphenyl-2 : 3-dihydropyrazine is more closely analogous with the osazones in constitution, and gives a yellow *compound*, sintering at 75°, with 0·5 mol. of stannic chloride, and an orange equimolecular *compound*, m. p. 115—120° (decomp.); this confirms the *syn*-configuration for the α-osazone. Mol. wt. determinations in benzene and in ethylene dibromide give values (allowing for dissociation) in accord with these views. C. Hollins.

Absorption spectra of derivatives of acetophenone. T. Tasaki (Acta Phytochim., 1927, **3**, 259—315; cf. A., 1925, i, 1444, 1445; ii, 838).—The absorption spectra of acetophenone, deoxybenzoin, benzylacetophenone (hydrochalkone), benzoylacetone, propionylacetophenone, dibenzoylmethane, benzyl phenacyl ketone, and of 49 methyl, hydroxy-, alkoxy-, and acetoxy-derivatives of these were examined. Acetophenone and phenyl benzyl ketone in *M*/1000 alcoholic solution give indications of a band at 3600 Å., the latter compound being markedly hypochromic compared with phenyl styryl ketone. All the diketones show in *M*/10,000 alcoholic solution a single band, which lies at 3200 Å. for benzoylacetone, propionylacetophenone, and benzyl phenacyl ketone, but is displaced to 2900 Å. in dibenzoylmethane; as in the monoketones, replacement of methyl by benzyl has little effect. Introduction of hydroxyl or alkoxyl exerts both bathochromic and hyperchromic effects, the increased effect due to *o*- or *p*-position of the hydroxyl group being less marked in diketones than in monoketones, owing probably to the overwhelming influence of the two carbonyl groups. Acetylation of hydroxyl groups is without effect. Methyl groups have not the auxochromic effect here which they show in the benzophenone series.

The following new compounds are described: 2 : 4 : 5-*trimethylphenyl* β-*phenylethyl ketone*, m. p. 37—38°; *phenyl* β-p-*tolylethyl ketone*, m. p. 48—50°; o-, m-, and p-*hydroxyphenyl* β-*phenylethyl ketones*, m. p. 36—37°, 40—42°, and 62—64°, respectively; *phenyl* β-m-*hydroxyphenylethyl ketone*, m. p. 73—74°; *phenyl* β-3-*methoxy*-4-*ethoxyphenylethyl ketone*, m. p. 54—55°; p-*anisyl* β-o-*hydroxyphenylethyl ketone*, m. p. 59—60°; p-*phenetyl* β-3-*methoxy*-4-*ethoxyphenylethyl ketone*, m. p. 70—71°; 3 : 4-*dimethoxyphenyl* β-p-*anisylethyl ketone*, m. p. 65—66°; 2-*hydroxy*-4-*ethoxyphenyl* β-3-*methoxy*-4-*ethoxyphenylethyl ketone*, m. p. 77—79°; 2-*hydroxy*-4-*ethoxyphenyl* β-3 : 4-*methylenedioxyphenylethyl ketone*, m. p. 117° (this and all the preceding ketones are prepared by reduction of the corresponding chalkones); 3 : 4-*dimethoxybenzoylacetone*, m. p. 71—72°; 4-*methoxy*-2′-*ethoxydibenzoylmethane*, m. p. 90—91°; *dianisoylmethane*, m. p. 114°; α-*anisoyl*-γ-*phenylacetone*, m. p. 75—76° (the last four compounds are prepared by Claisen condensations).

The author's conclusion, from absorption spectra, that rutin is of the hydroxypyroneglucoside type (A., 1925, i, 1445) has since been confirmed chemically by Atree and Perkin (this vol., 231). Rutin compared with quercetin is appreciably hypso- and hypochromic. C. Hollins.

Synthesis of 4-hydroxy-3-methoxystyryl *n*-butyl ketone. H. Nomura and S. Tsurumi (Sci. Rep. Tôhoku Imp. Univ., 1927, **16**, 563—564; cf. A., 1925, i, 1156).—Vanillin and methyl *n*-butyl ketone, when heated for 6 hrs. under a reflux condenser with alcohol and potassium hydroxide, condense to form 4-hydroxy-3-methoxystyryl *n*-butyl ketone, m. p. 39—40° ($1H_2O$, m. p. 66—100°). B. W. Anderson.

Homologues of zingerone. II. H. Nomura and S. Tsurumi (Sci. Rep. Tôhoku Imp. Univ., 1927, **16**, 565—579).—Vanillin was condensed with methyl *n*-nonyl ketone to form 4-*hydroxy*-3-*methoxystyryl* n-*nonyl ketone*, m. p. 55·5—56·5° ($+1H_2O$, m. p. 68—100°), and this was reduced to 4-*hydroxy*-3-*methoxyphenylethyl* n-*nonyl ketone*, m. p. 42·5—43·5° (*benzoyl* derivative, m. p. 51—52°; *methyl ether*, m. p. 33·5—35°; *oxime* of the latter, m. p. 73·5—74·5°). The preparation of the *n*-hexyl, *n*-heptyl, and *n*-octyl homologues of the above is also described (cf. A., 1926, 1145). B. W. Anderson.

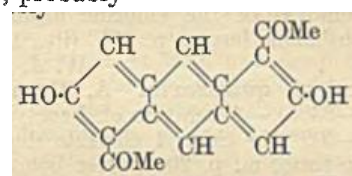
Nuclear condensation of phenols and phenolic ethers with nitriles to ketimines and ketones of phenols and phenolic ethers. II. Syntheses with anisole, *o*-bromoanisole, phenetole, *o*-, *m*-, and *p*-tolyl ethers, veratrole, and resorcinol ethers. J. Houben and W. Fischer (Ber., 1927, **60**, [*B*], 1759—1778; cf. this vol., 143).—The extension of Gattermann's synthesis to mononuclear phenolic ethers and various nitriles is reported. α-Naphthol yields nuclear substituted products with acetonitrile, chloro- and trichloro-acetonitrile, benzonitrile, and phenylacetonitrile even in the absence of zinc chloride, whilst considerably enhanced yields are obtained in its presence. With benzene derivatives, the presence of halogen in the *ortho*-position to the alkoxyl group greatly diminishes the yield without entirely inhibiting the change. A methyl group in the *ortho*-position facilitates the reaction, whilst in the *meta*-position it diminishes the yield somewhat. The methoxy-group facilitates the reaction if in the *meta*-position. If the *para*-position to the alkoxy-group is replaced by methyl, condensation is still possible to a limited extent, but not if the alkoxy-group is here present. *o*-Nitro- and *o*-acetamido-groups inhibit reaction completely. *o*-Carboxy-groups introduce complications, since they react with the nitrile. Ether is the most suitable solvent. Methyl acetate may be used, but gives a less pure

product, whilst small amounts of ketones are obtained when ethyl bromide is employed. Acetyl chloride, acetic anhydride, glacial acetic acid, and dioxan are quite unsuitable. It is frequently possible to improve the yield of ketone to a considerable extent by use of an excess of nitrile. The following substituted acetophenones are described; ωωω-*trichloro*-4-*ethoxy*-, m. p. 63—64° (*sulphonic acid*; *compound* of corresponding ketimine hydrochloride and zinc chloride); ωωω-*trichloro*-4-*methoxy*-, m. p. 33—34·5°; ωωω-*trichloro*-4-*ethoxy*-3-*methyl*-, m. p. 67—68°; ωωω-*trichloro*-4-*methoxy*-2-*methyl*-, b. p. 130°/0·8 mm.; ωωω-trichloro-2-methoxy-5-methyl-, b. p. 150—155°/12 mm. (accompanied by p-*tolyl trichloroacetate*, m. p. 67—68°); ωωω-*trichloro*-3 : 4-*dimethoxy*-, m. p. 101—102°; ωωω-*trichloro*-2 : 4-*dimethoxy*-, b. p. 153°/0·5—0·6 mm. (quinol monoethyl ether affords p-*ethoxyphenyl trichloroacetate*, m. p. 49—50°); ωωω-*trichloro*-3-*bromo*-4-*methoxy*- (N-*trichloroacet*-o-*methoxybenzamide*, $OMe{\cdot}C_6H_4{\cdot}CO{\cdot}NH{\cdot}CO{\cdot}CCl_3$, m. p. 184—185°, from *o*-methoxybenzoic acid); ωωω-*trichloro*-4-*phenoxy*-; ω-*chloro*-4-*ethoxy*-, m. p. 65—66·5°; ω-*bromo*-4-*ethoxy*-, m. p. 59—60° [accompanied by dibromodiacetamide, m. p. 195° (decomp.) after darkening at 190°]. α-Naphthyl ethyl ether is converted by trichloroacetonitrile, zinc chloride, and hydrogen chloride into ωωω-*trichloro*-4-*ethoxyacetonaphthone* [4-*ethoxy*-α-*naphthyl trichloromethyl ketone*], m. p. 74—74·5°, and by chloroacetonitrile into ω-*chloro*-4-*ethoxyacetonaphthone*, m. p. 132—132·5°. ω-*Bromo*-4-*ethoxyacetonaphthone*, m. p. 120—121°, and the corresponding *ketimine hydrochloride*, decomp. about 150°, are described. 4-Ethoxyacetonaphthone has m. p. 77—79°. α-Naphthol, hydrogen chloride, and trichloroacetonitrile in the absence of zinc chloride give an almost immediate precipitate of cinnabar-red *ketimine hydrochloride*, which becomes converted into a colourless substance, probably the imino-ether hydrochloride; in the presence of zinc chloride similar phenomena are observed and the semi-solid product affords ωωω-*trichloro*-4-*hydroxyacetonaphthone*, m. p. 100—101°, when decomposed by water. Benzonitrile and α-naphthol give the corresponding *ketimine hydrochloride* and 4-hydroxybenzonaphthone, m. p. 164—165°. 4-*Hydroxynaphthyl benzyl ketone*, m. p. 185—187°, is derived from α-naphthol and phenylacetonitrile. β-Naphthol, trichloroacetonitrile, and hydrogen chloride give *trichloroacetimino*-β-*naphthyl ether hydrochloride*, $C_{10}H_7{\cdot}O{\cdot}C(CCl_3){:}NH,HCl$, and β-*naphthyltrichloroacetate*, m. p. 86—87°. Phenyl 2-hydroxynaphthyl ketone, m. p. 141°, is derived from β-naphthol, benzonitrile, hydrogen chloride, and zinc chloride at 60°.

Unsuccessful attempts to induce isomerisation of trichloroacetiminophenyl ether hydrochloride by heat in the presence or absence of zinc chloride are recorded. H. WREN.

Quinonedisulphones. A. RECSEI (Ber., 1927, 60, [*B*], 1836—1840).—The term "quinonedisulphones" is applied to compounds, $O{:}Ar{:}(SO_2R)_2$, which contain two sulphonyl groups in place of a quinonoid oxygen. *p*-Benzoquinone dissolved in glacial acetic acid condenses with ethyl mercaptan in the presence of concentrated sulphuric acid and hydrogen chloride, giving a compound which is oxidised by permanganate to p-*benzoquinonedisulphone* [1 : 1 - *diethanesulphonyl* - $\Delta^{2\cdot5}$ - cyclo*hexadiene* - 4 - *one*], m. p. 84°, black-violet crystals, giving brownish-red solutions in organic solvents. The compound does not yield an oxime, semicarbazone, or phenylhydrazone; it is readily reduced to a colourless compound which becomes oxidised when exposed to air. It is converted by cold bromine into 2 : 3 : 5 : 6-*tetrabromo*-1 : 1-*diethanesulphonyl*-$\Delta^{2\cdot5}$-cyclo*hexadiene*-4-*one*, m. p. 286° (closed capillary), and by warm bromine into 2 : 2 : 3 : 3 : 5 : 5 : 6 : 6-*octabromo*-1 : 1-*diethanesulphonyl*cyclo*hexan*-4-*one*, m. p. 276° after softening at 230°. α-Naphthaquinone affords similarly 4 : 4-*diethanesulphonyl*-α-*naphthaquinone*, m. p. 86°, reduced by zinc dust to 1-*hydroxy*-4 : 4-*diethanesulphonyl*-1 : 4-*dihydronaphthalene*, m. p. 91°. 2-*Ethylthiol*-1 : 4-*naphthaquinone*, m. p. 142°, is obtained as by-product during the preparation of the naphthaquinonedisulphone. H. WREN.

Action of substances containing an active methylene group on quinones. M. V. IONESCU (Bull. Soc. chim., 1927, [iv], **41**, 1094—1096).—Acetylacetone reacts with *p*-benzoquinone in pyridine solution forming a dark green *compound*, m. p. above 300°, probably



H. BURTON.

Formation of 1 : 2- and 2 : 3-dichloroanthraquinones from *o*-dichlorobenzene. H. E. FIERZ-DAVID (J. Amer. Chem. Soc., 1927, **49**, 2334).—Treatment of *o*-3 : 4-dichlorobenzoylbenzoic acid with concentrated sulphuric acid at 150° yields, in addition to 2 : 3-dichloroanthraquinone (cf. Phillips, this vol., 362), a small proportion of the 1 : 2-dichloro-derivative, m. p. 196·5° (lit., 207°) (cf. Senn, Diss., Swiss Tech. High School, 1923). F. G. WILLSON.

Formation of 1 : 2- and 2 : 3-dichloroanthraquinones from *o*-dichlorobenzene. M. PHILLIPS (J. Amer. Chem. Soc., 1927, **49**, 2335; cf. preceding abstract).—Acknowledgment of Fierz-David's correction. F. G. WILLSON.

Determination of the structure of α-hydroxyanthranols. A. GREEN (J.C.S., 1927, 2341—2345).—The reduction of an α-hydroxyanthraquinone to the anthranol may occur in two ways, viz., 1-hydroxyanthraquinone may yield either 1 : 9- or 1 : 10-dihydroxyanthracene or a mixture of the two. Structures may be assigned to these compounds by observing the differences in the resistance of the derived benzanthrones to methylation (Miller and Perkin, A., 1926, 174), but this method is tedious and the yields are low (cf., however, Cross and Perkin, this vol., 771). The reaction of the dihydroxyanthracene with thionyl chloride at the ordinary temperature may also be used for this purpose, since only those phenols possessing two hydroxy-groups in the *o*- or *peri*-position to each other yield thionyl

derivatives (cf. this vol., 354, 457). 1 : 8-Dihydroxynaphthalene, when treated with thionyl chloride in carbon disulphide–pyridine solution, yields 1 : 8-*thionyldihydroxynaphthalene*, m. p. 97°, in quantitative yield, whereas, in the case of the 1 : 5-dihydroxy-compound, the product is a complex mixture which contains chlorine. The reduction product of 1-hydroxyanthraquinone yields a *thionyl* derivative, m. p. 115° (decomp.), and is therefore 1 : 9-dihydroxyanthracene, whilst that of 4-chloro-1-hydroxyanthraquinone is 4-*chloro*-1 : 9-*dihydroxyanthracene*, m. p. 170—171° (*diacetyl* derivative, m. p. 157°), since with thionyl chloride it yields 4-*chloro*-1 : 9-*thionyldihydroxyanthracene*, m. p. 123—124° (decomp.). Anthragallolanthranol yields with thionyl chloride only complex chlorine-containing mixtures, indicating that this anthranol is not 1 : 2 : 3 : 9-tetrahydroxyanthracene, since this would be expected to yield a thionyl derivative (cf. J.C.S., 1926, 2202) but 1 : 2 : 3 : 10-tetrahydroxyanthracene (cf. Cross and Perkin, *loc. cit.*). Liebermann and Mamlock's method (A., 1905, i, 521) for the preparation of anthranols from anthraquinones yields products which are more readily purified than that of Breare and Perkin (J.C.S., 1923, **123**, 2606), but the reduction of 4-chloro-1-hydroxyanthraquinone must be carefully controlled to avoid removal of the chlorine atom. 1 : 8-Diacetoxynaphthalene has m. p. 155° (lit., 147—148°).

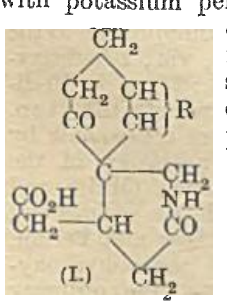
W. J. Powell.

Structure of quinizarin. A. Green (J.C.S., 1927, 2384—2385).—A solution of diacetylquinizarin, m. p. 207—208°, in thionyl chloride deposited the polymorphic form, m. p. 200°, after being boiled for 2 hrs. This lack of reactivity of a quinizarin derivative in which the hydroxyl hydrogens are replaced, renders improbable the second mechanism suggested (J.C.S., 1926, 1430) for the conversion of quinizarin into 10-chloro-1-hydroxy-4 : 9-anthraquinone by treatment with thionyl chloride. It is therefore probable that quinizarin assumes an *ortho*-quinonoid state (1 : 10-dihydroxy-4 : 9-anthraquinone) in this reaction (cf. Perkin, J.C.S., 1899, **75**, 433).

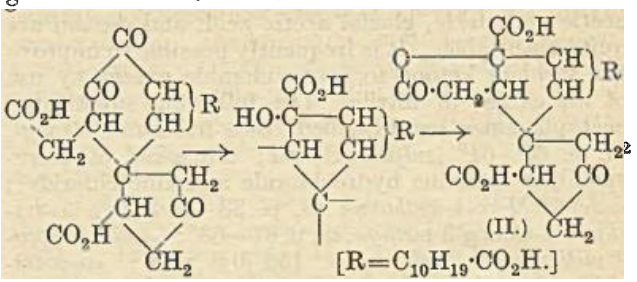
M. Clark.

Derivatives of the anthraquinone series. I. G. Farbenind. A.-G.—See B., 1927, 743.

Bile acids. XVII. M. Schenck and H. Kirchof (Z. physiol. Chem., 1927, **169**, 164—176; cf. this vol., 665).—Oxidation of the ketolactam-carboxylic acid, $C_{23}H_{35}O_4N$, m. p. 218—220° (this vol., 666), with potassium permanganate gives a *ketolactamdicarboxylic acid*, $C_{23}H_{35}O_6N$ (I), m. p. 277° (decomp.), a reaction similar to the preparation of the diketodicarboxylic acid from pyrodeoxybilianic acid (Wieland and Kulenkampff, A., 1921, i, 112).



When bil*iso*idanic acid (Schenck, A., 1924, i, 179, 1318), is heated with sodium hydroxide solution it undergoes a benzilic acid rearrangement, and the product isolated is a *lactonic acid*, $C_{24}H_{32}O_9,2H_2O$ (II), which on heating shrinks at about 155°, becomes a frothy mass at 165°, assumes a white turbidity at 235—245°, and at 275—277° gives a clear brown-coloured melt.



The lactonic acid is formed through the intermediate hydroxytetracarboxylic acid, which cannot be isolated, but its presence is proved definitely by titration values.

H. Burton.

New derivatives of caoutchouc. G. Bruni and E. Geiger (Atti R. Accad. Lincei, 1927, [vi], **5**, 823—828).—In benzene solution, nitrosobenzene (3 mols.) and caoutchouc ($1C_5H_8$) readily react (cf. Angeli, Alessandri, and Pegna, A., 1910, i, 552; Alessandri, A., 1915, i, 555), giving azoxybenzene, together with a 94—98% yield of a yellow iso*caoutchouc nitrone*, ·CH:CMe·C(:NPh:O)·CH_2· or ·CH_2·C(:CH_2)·C(:NPh:O)·CH_2·. The formation of this compound, which is obtained also when the latex of *Hevea brasiliensis* and nitrosobenzene react in pyridine solution, serves well for the determination of crude caoutchouc. It unites with bromine to form the *compound* $(:C_5H_6Br_2{\cdot}NOPh)_x$.

Treatment of caoutchouc ($1C_5H_8$) with ethyl *o*-nitrosobenzoate gives azoxybenzene and a colloidal *acid*, $(:C_5H_6:NO{\cdot}C_6H_4{\cdot}CO_2H)_x$, decomp. about 100°. Caoutchouc reacts also with the *p*-nitroso-derivatives of dimethylaniline, methylaniline, diphenylamine, and *o*-toluidine. Gutta percha reacts with nitroso-compounds in the same way as caoutchouc.

These nitrones do not react with hydroxylamine, but with phenylhydrazine the nitrone of *iso*caoutchouc yields the phenylhydrazone of a ketone which contains the carbonyl in the caoutchouc chain and is termed *cauccione*: ·CH:CMe·C(:NPh:O)·CH_2· + NH_2·NHPh ⟶ ·CH:CMe·C(:NO·NHPh)·CH_2· + NHPh·OH.

T. H. Pope.

Formation and decomposition of ketonecyanohydrins. Some compounds recently classified as such. A. Lapworth, R. H. F. Manske, and E. B. Robinson (J.C.S., 1927, 2052—2056).—The formation of the cyanohydrin of menthone, as with other ketones, is a reversible reaction, and equilibrium is attained in a few min. or sec. in strongly alkaline solution. The extraordinary stability of the "menthonecyanohydrin" obtained from the nitroimine by Houben and Pfankuch (this vol., 364) is probably due to a Wagner transformation during the preparation. True menthonecyanohydrin has been prepared and shown to have a higher dissociation constant than *cyclo*hexanone cyanohydrin. The stability of the two supposed "camphorcyanohydrins" (*ibid.*) is similarly explained.

C. Hollins.

Menthone series. V. *d*-*neoiso*Menthylamine. J. Read and G. J. Robertson (J.C.S., 1927, 2168—2174).—Of the 12 menthylamines all but the 3-*neo*-

*iso*menthylamines have previously been described. d-neoiso*Menthylamine* is now isolated from the mixture of formylated bases obtained by heating *l*-menthone with ammonium formate. The free base has $[\alpha]_D$ +9° and gives the following derivatives: *hydrochloride*, not melted at 250°, $[\alpha]_D^{15}$ +20·9°; *formyl* derivative, $[\alpha]_D^{i}$ +3·9°; *acetyl* derivative, m. p. 99—100°, $[\alpha]_D^{15}$ −2·6°; *benzoyl* derivative, m. p. 151°, $[\alpha]_D^{15}$ −10·4°; β-*naphthalenesulphonyl* derivative, m. p. 120°, $[\alpha]_D^{15}$ −10·7°; *carbamide*, m. p. 115—116°, $[\alpha]_D$ −3·1°; *phenylcarbamide*, m. p. 149—150°, $[\alpha]_D^{15}$ −12·1°; *phenylthiocarbamide*, m. p. 99°, $[\alpha]_D^{15}$ −6·7°; *benzylidene* derivative, m. p. 68—69°, $[\alpha]_D$ −34·2°; *salicylidene* derivative, m. p. 98—100°, $[\alpha]_D^{15}$ −17·9°. The hydrochloride is converted by nitrous acid mainly into partly racemised *d*-Δ^3-menthene, and a little *d-iso*menthol. The salicylidene derivatives of *neo-* and *d-neoiso*menthylamines are non-phototropic, whilst those of menthylamines and *iso*menthylamines are distinctly so. The molecular configuration of *neoiso*menthylamine is discussed and numerical powers of derivatives of the four stereoisomeric types of menthylamines are pointed out. C. HOLLINS.

Mononitriles of camphoric acid. F. SALMON-LEGAGNEUR (Ann. Chim., 1927, [x], 7, 385—407; 8, 5—70).—The action of Grignard reagents on the esters of camphoric semi-nitrile (*i.e.*, of α-camphornitrilic acid) is in general more complex than in the case of cyanocampholic esters, and may take either course (A) or, in addition, course (B), according to the nature and proportion of Grignard reagent and solvent used. It is, however, only slightly affected by variation of the ester group:

·CMe(CO$_2$R)·CMe$_2$·CH(CN)· ——
·CMe(CR$_2$OH)·CMe$_2$·CH(CN)· ——
·CMe(CR$_2$OH)·CMe$_2$·CH(CO·R)·.

Thus with 5 mols. of magnesium methyl iodide in ether course (A) is followed, the yield of product varying from 43% with the methyl to 32% with the *o*-tolyl ester; in the latter case rather more of a compound, m. p. 164° (below), is produced. In boiling benzene or toluene solution course (B) is also followed. With magnesium phenyl bromide course (B) is followed even in ethereal solution, the intermediately-formed ketimine being isolable, together with an amide. Course (A) is followed when magnesium ethyl bromide is used, but other products are also formed (below).

When either the *syn-* or the *anti*-form of *iso*nitrosocamphor is treated in benzene solution with thionyl chloride and the product formed is treated with an alcohol or a phenoxide, the corresponding α-camphornitrilic ester is formed in the yield indicated: methyl, m. p. 40° (85%); ethyl, m. p. 25—28°, b. p. 162°/18 mm., *phenyl*, m. p. 76—77°, b. p. 215—225°/18 mm., $[\alpha]_D^{22}$ +30° 27′; *o-tolyl* (70%), m. p. 99—100°, b. p. 228—233°/18 mm., $[\alpha]_D^{23}$ +25° 7′; *p-tolyl*, m. p. 96—97°, b. p. 228—233°/18 mm., $[\alpha]_D^{23}$ +28° 52′; *benzyl* (86%; a little camphorimide is also formed), b. p. 223—224°/17 mm., $[\alpha]^{20}$ +59° 24′ (in alcohol), $[\alpha]_D^{2}$ +56° 3′ (in benzene). The chloride of α-camphornitrilic acid obtained in 86% yield by the action of thionyl chloride on the pure acid (Borsche and Sander, A., 1915, i, 148) has m. p. 93—95°, b. p. 152—154°/15 mm. Attempts to alkylate the tolyl ester with sodamide in ether or in benzene were unsuccessful, and even in toluene and xylene only 25% and 50%, respectively, of the theoretical amount of ammonia was liberated, and no substitution product was obtained with butyl iodide. Similarly the methyl ester could not be benzylated. Possibly the ester group is attacked affording an amide, converted by the alkyl halide into a substituted amide (cf. Ramart and Haller, A., 1924, i, 732). β-Camphornitrilic acid, m. p. 108—109°, obtained in 67% yield from camphorimide (Rupe and Splittgerber, A., 1907, i, 1016), is converted by thionyl chloride into the *chloride* (yield 80%), b. p. 148—149°/17 mm., from which the *o-tolyl* ester, m. p. 68—69°, b. p. 219—221°/15 mm., $[\alpha]_D^{i}$ −105° 39′, is obtained in the usual way.

o-Tolyl α-camphornitrilate and 5 mols. of magnesium methyl iodide in ethereal solution afford 3-*cyano*-1-α-*hydroxy*i*sopropyl*-1 : 2 : 2-*trimethyl*cyclo*pentane* (2 : 2 : 3-*trimethyl*-3-α-*hydroxy*i*sopropyl*cyclo*pentane*-1-*carboxylonitrile*), m. p. 93—94°, $[\alpha]_D^{22}$ +78° 15′ (*phenylurethane*, m. p. 169—170°), together with a *compound*, $C_{11}H_{17}ON$, m. p. 164°, which gives iodoform when treated with potassium hydroxide and alcoholic iodine and forms no oxime or semicarbazone. With bromine in chloroform it gives a *monobromo*-compound, m. p. 161—162°, does not react with phenylcarbimide, whilst with potassium permanganate it yields only the above compound, $C_{11}H_{17}ON$. Substitution of ether by toluene is accompanied by the formation of 3-*acetyl*-1-α-*hydroxy*i*sopropyl*-1 : 2 : 2-*trimethyl*cyclo*pentane*, m. p. 95—96° (*semicarbazone*, m. p. 221—222°), giving, when distilled at 144—145°/15 mm., 3-*acetyl*-1-α-*methylethenyl*-1 : 2 : 2-*trimethyl*-cyclo*pentane* (yield 47%), m. p. 164°, $[\alpha]_D^{21}$ +40° 44′ (*oxime*, m. p. 103—104°; *semicarbazone*, m. p. 229—230°), which yields indefinite products with bromine in chloroform, and is oxidised by potassium permanganate to 1 : 3-*diacetyl*-1 : 2 : 2-*trimethyl*cyclo*pentane*, b. p. 154—156°/19 mm. [*disemicarbazone*, m. p. 305—307° (decomp.)].

When the product of interaction, in ether, of magnesium phenyl bromide (4 mols.) and the methyl ester of α-camphornitrilic acid is acidified with hydrobromic acid there is formed the *ketimine hydrobromide*, COPh·C$_8$H$_{14}$·CPh:NH,HBr, m. p. 211—213°, $[\alpha]_D^{i}$ −53° 16′, converted by boiling alcoholic, hydrochloric, or hydrobromic acid into 1 : 3-*dibenzoyl*-1 : 2 : 2-*trimethyl*cyclo*pentane*, m. p. 118°, $[\alpha]^{20}$ −60° 10′ (α-*monoxime*, m. p. 199—200°), together with the *amide*, m. p. 172—175°, $[\alpha]_D^{i}$ +44° 51′ (*oxime*, 194—196°), of 3-*benzoyl*-1 : 2 : 2-*trimethyl*cyclo*pentane*-1-*carboxylic acid*, m. p. 169—170° (*silver* salt). The structure of the amide follows from its formation by hydrolysing 3-*benzoyl*-1 : 2 : 2-*trimethyl*cyclo*pentane*-1-*carboxylonitrile*, m. p. 58—59° (*oxime*, 152—153°), formed from the chloride of β-camphornitrilic acid, benzene, and aluminium chloride. The chloride of α-camphornitrilic acid, however, under similar conditions, affords in 75% yield a *nitrile*, $C_{15}H_{19}N$, b. p. 153—155°/3·5 mm., $[\alpha]_D^{i}$ +21° 12′, slowly hydrolysed at 125—130° by acetic–hydrochloric acid to an *acid*, $C_{15}H_{20}O_2$, m. p. 140°, identical with that obtained from benzene and camphoric anhydride by Bürcker

(A., 1896, i, 179) and Blanc (A., 1899, i, 925) ("phenyldihydro*iso*lauronolic" acid). Ethereal magnesium *p*-tolyl bromide similarly affords 1 : 3-*di*-p-*toluoyl*-1 : 2 : 2-*trimethylcyclopentane*, m. p. 143—144°. Ethereal magnesium ethyl bromide and the methyl ester of α-camphornitrilic acid afford camphorimide, 3-*cyano*-1-α-*hydroxyisopropyl*-1 : 2 : 2-*trimethylcyclopentane*, m. p. 79—80°, b. p. 185—187°/18 mm., $[\alpha]_D^{18}$ +63° 54′ (*o-nitrobenzoate*, m. p. 112—113°), together with an oil, $[\alpha]^{21\cdot5}$ +40° 48′, which is probably a mixture of *isomerides*, $C_{10}H_{21}ON$, and α-*ethylidene campholidene*, $C_8H_{14}\langle \overset{C(:CHMe)}{CO} \rangle NH$, m. p. 206°, b. p. 200°/18 mm., $[\alpha]_D^{16}$ +11° 16′ (yield 30%) [*hydrochloride*, $C_{12}H_{20}ONCl$, m. p. 230—235°, *hydrobromide*, $(C_{12}H_{19}ON)_2,HBr(?)$, m. p. 245—248°], which is very stable both to acids and alkali but which affords a *dibromide*, softening at 140—145° (decomp.). Decomposed with cold water the latter affords a *substance*, $C_{12}H_{18}ONBr$, m. p. 126—127°, boiling water giving an *isomeride*, m. p. 67—68°. These isomerides probably possess the structures $C_8H_{14}\langle \overset{C(:CMeBr)}{CO} \rangle NH$ or $C_8H_{14}\langle \overset{C\cdot CHMeBr}{CO} \rangle N$, the structure $CH_2\cdot C{=\!=}C\cdot CHMeBr$ / CMe_2 NH / $CH_2\cdot CMe—CO$ being less probable.

Oxidation of α-ethylidenecampholidone with chromic–sulphuric acid yields camphoric and acetic acids, whilst sodamide and benzyl chloride in toluene convert it into α-*ethylidene*-N-*benzylcampholidone*, m. p. 140—141°, $[\alpha]_D^{18}$ +43° 46′, oxidised by chromic–sulphuric acid to camphoric acid, a little camphoric anhydride, acetic acid, and benzylamine; this reaction establishes the structure of α-ethylidenecampholidone. α-*Ethylidene*-N-*allylcampholidone*, m. p. 125—126°, $[\alpha]_D^{21}$ +67° 34′, is prepared similarly. Reduction of the benzyl or *p*-tolyl ester of α-camphornitrilic acid with sodium and absolute alcohol at 150—160° affords α-campholidone, α-aminocampholic acid, and α-*aminocampholic alcohol* (yield 36%), b. p. 163—165°/9 mm., $[\alpha]_D$ −14° 39′ (*hydrochloride*, m. p. 190—200°; *chloroplatinate*; *phenylcarbamide-urethane*, NHPh·CO·CH_2·C_8H_{14}·CH_2·O·CO·NHPh).

R. Brightman.

[Camphorchloroanilic] acids and camphorochlorophenylimides. M. Singh and R. Singh (J.C.S., 1927, 1994—1997; cf. Wootton, *ibid.*, 1910, **97**, 405).—Camphoric anhydride is condensed with the three chloroanilines to give mixtures of the chloroanilic acids and the chloroanils, separable by means of sodium carbonate. The chloroanilic acids have increasing mol. rotatory power in the order *o*-, *m*-, *p*-, and melt at 165° (*o*-), 216—217° (*m*-), and 197° (*p*-). The chlorophenylimides have m. p. 128° (*o*-), 176° (*m*-), and 165° (*p*-). Rotatory powers of the six compounds in various solvents are given.

C. Hollins.

Hydration of nopinene. III. Comparison of the hydration of pinene and nopinene. G. Austerweil (Bull. Soc. chim., 1927, [iv], **41**, 1088—1094; cf. this vol., 60, 156).—The reaction between pinene and organic acids forming bornyl esters is bimolecular as for nopmene, and it is accompanied by a unimolecular reaction affording limonene. The reaction velocities are smaller than those for nopinene. In the production of limonene from nopinene it appears improbable that pinene is the intermediate product, and alternative mechanisms for the formation of limonene from pinene and nopinene, through the intermediate *iso*pinene, are formulated.

H. Burton.

δ-*d*-Bornylsemicarbazide and δ-*d*-*neo*bornylsemicarbazide. J. A. Goodson (J.C.S., 1927, 1997—2000).—Acetonesemicarbazone, when heated with anhydrous *d*-bornylamine at 175° gives *acetone*-δ-d-*bornylsemicarbazone*, m. p. 141—148°, $[\alpha]^{20}$ +25·5°, which is hydrolysed with 10% hydrochloric acid to δ-d-*bornylsemicarbazide*, m. p. 75°, $[\alpha]_D^{20}$ +17° (*hydrochloride*, m. p. 190—198°, $[\alpha]_D^{0}$ +2·6°). δ-d-*Bornylsemicarbazones* of the following ketones are described: *iso*pulegone, m. p. 224—226°, $[\alpha]^{20}$ +9·2°; 4-methyl*cyclo*hexanone, m. p. 154°, $[\alpha]_D^{20}$ +27·2°; 3-methyl*cyclo*hexanone, m. p. 172—177°, $[\alpha]_D^{20}$ +27·4°; *d*-3-methyl*cyclo*hexanone, m. p. 173—179°, $[\alpha]_D^{0}$ +7·4°.

Acetone-δ-d-neo*bornylsemicarbazone*, m. p. 175—179°, $[\alpha]_D^{20}$ −92·1°, similarly prepared, gives on hydrolysis δ-d-neo*bornylsemicarbazide hydrochloride*, m. p. 198—202°, $[\alpha]^{20}$ −50·8°. 4-*Methyl*cyclo*hexanone*-δ-d-neo*bornylsemicarbazone*, m. p. 151—155°, $[\alpha]^{20}$ −91·3°, and the 3-*methyl isomeride*, m. p. 157—161°, $[\alpha]_D^{0}$ −91·2°, are described. All m. p. are corrected.

No resolution into optical enantiomorphs could be achieved by means of the active semicarbazides.

C. Hollins.

Action of bromine on dimethylpyrone. J. N. Collie and L. Klein (J.C.S., 1927, 2162—2164).—Bromination of dimethylpyrone in chloroform with 1 mol. of bromine yields dimethylpyrone hydrobromide perbromide, $C_{14}H_{17}O_4Br_3$, m. p. 136° (Hantzsch and Denstorff, A., 1906, i, 745). Excess of bromine gives Feist and Baum's dibromodimethylpyrone, m. p. 163° (A., 1905, i, 914), and in the absence of a solvent *tetrabromodimethylpyrone*, m. p. 229°. When bromine is added to an aqueous suspension of the barium salt of dimethylpyrone there is formed a *compound*, $C_7H_7O_3Br$, m. p. 106°, b. p. about 310° [decomp.; *monobenzoyl* derivative, m. p. 112°; *phenylhydrazine* compound, m. p. 142° (decomp.)], similar in all respects to the iodine compound obtained by Collie (J.C.S., 1921, **119**, 1550).

C. Hollins.

Coumarin series. I. Action of the Grignard reagent on substituted coumarins. I. M. Heilbron and D. W. Hill (J.C.S., 1927, 2005—2013).—Magnesium phenyl bromide reacts with 4-hydroxycoumarin and its methyl ether to give 4-*hydroxy*-2 : 2-*diphenyl*-Δ^3-*chromen*, m. p. 230—231°, and the 4-*methoxy*-compound, m. p. 135°, respectively. The constitution of the latter follows from its conversion by boiling concentrated alkali, into benzophenone. 4-*Methoxy*-2 : 2-*di*-p-*anisyl*-Δ^3-*chromen* melts at 155°. 2 : 2-*Diphenyl*-4-*methyl*-Δ^3-*chromen*, m. p. 89°, prepared from 4-methylcoumarin and magnesium phenyl bromide, gives on hydrolysis phenyl benzhydryl ether, $CHPh_2$·OPh, m. p. 56°. 2 : 2-*Diphenyl*-4 : 6-*dimethyl*-Δ^3-*chromen*, m. p. 126°, similarly prepared, is hydrolysed to p-*tolyl benzhydryl ether*, m. p. 96°. By the action of magnesium phenyl bromide on

4 : 7-dimethylcoumarin the ring is opened, with formation of *diphenyl-o-hydroxy-β-p-dimethylstyrylcarbinol*, m. p. 146°; the main product is 2 : 2-*diphenyl*-4 : 7-*dimethyl*-Δ^3-*chromen*, m. p. 87° (also obtainable by heating the carbinol in acetic acid), which is hydrolysed to m-*tolyl benzhydryl ether*, m. p. 125°, and lactaldehyde, m. p. 103—105°.

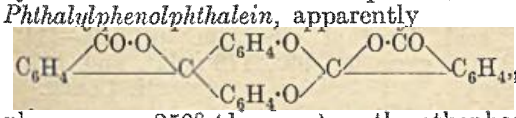
On the other hand when 3-methylcoumarin is treated with magnesium phenyl bromide the product is 2 : 4-*diphenyl*-3-*methylchroman*-4-*ol*, m. p. 149°, which is converted into 2 : 2-*diphenyl*-3-*methyl*-Δ^2-*chromen*, m. p. 91°, by boiling with acetic acid. 3-Phenylcoumarin behaves similarly (Löwenbein, A., 1924, i, 1221; Löwenbein and Rosenbaum, A., 1926, 955).

These reactions are explained on the assumption that the initial reaction with either 3- or 4-substituted coumarins is ring scission with formation of β-unsaturated ketones, the subsequent reactions of which follow the Kohler rule (A., 1907, i, 535). C. Hollins.

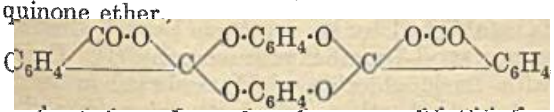
Constitution of gentisin. J. Shinoda (J.C.S., 1927, 1983—1985).—Since 1 : 3-*dihydroxy*-7-*methoxyanthrone* ("*iso*gentisin"), m. p. 241° (*acetyl* derivative, m. p. 211—212°), synthesised by condensing 2-*hydroxy*-5-*methoxybenzonitrile*, m. p. 136°, with phloroglucinol in ether in presence of zinc chloride and hydrogen chloride and hydrolysis of the resulting *ketimine hydrochloride*, differs from gentisin, the latter must have the structure of 1 : 7-dihydroxy-3-methoxyxanthone as indicated by Perkin (J.C.S., 1898, **73**, 1028). The nitrile is prepared by dehydration of 2-*hydroxy*-6-*methoxybenzaldoxime*, m. p. 118°. *iso*-Gentisin gives on demethylation gentisein, m. p. 318°.

C. Hollins.

Synthetic medicinals. II. Theory of laxatives. H. P. Kaufmann [with H. Haas] (Z. angew. Chem., 1927, 40, 831—836, 858—863).—Laxatives can be differentiated from, and stand between, drastic purgatives and mild aperients, although the classification is not precise. The copious literature of this subject is reviewed, and attention is drawn to the anomalous position of phenolphthalein and its analogues, which are usually classed with the anthraquinone derivatives and other substances the action of which is chiefly on the lower bowel. *Succinylphenolphthalein*, prepared by heating together phenolphthalein and succinyl chloride at 120° for 5 hrs., is amorphous and has m. p. 170°; it is readily hydrolysed by alkali and is also a mild aperient, acting slowly. *Phthalylphenolphthalein*, apparently



amorphous, m. p. 250° (decomp.), on the other hand, resists hydrolysis and is inactive as a purgative. It is prepared by heating phenolphthalein and phthalyl chloride at 120—130°; the preparation of the latter is described and its b. p. at various pressures are recorded, thus, 147°/13 mm., 150·5°/15 mm., 153—154°/21 mm. In passing it is noted that Pawlewsky's compound (A., 1895, i, 219; 1896, i, 50) is a bisphthalidenehydroquinone ether,



as the mol. wt. in molten phenol agrees with this formula.

The above results, taken in conjunction with other data, suggest that purgative properties depend on the presence, or formation by hydrolysis, of free hydroxy-groups. That the two phenyl groups must also be free in other respects is shown by the fact that fluorescein, thiofluorescein, and similar compounds, have no purgative action. *Phenolhomophthalein*, however, is a powerful purgative. This compound, m. p. 227°, is obtained by heating together, at 125°, homophthalic anhydride, phenol, and zinc chloride. It dissolves readily in alkalis, but the solutions exhibit only a yellow colour, like that of 4-hydroxycoumarin; this indicates that a quinonoid modification is not formed, and if this is so, the hypothesis that purgative properties are associated with a quinonoid arrangement is disproved.

The (di?)-*acetyl* derivative, m. p. 161°, is weakly purgative; the *tribenzoyl* derivative, m. p. 185°, is inactive. Homophthalic acid does not yield its chloride when it is heated with phosphorus pentachloride; the product is 4-*chloroisocoumarin*, m. p. 96—97°. Bis-(4-hydroxyphenyl)isatin (Baeyer and Lazarus, A., 1886, 154) is also an active purgative, but its acetyl derivative is weak and its *phthalyl* derivative, m. p. about 280°, is inactive. Phenolnaphthalein is more active than phenolphthalein; its *diacetyl* derivative, m. p. 198°, acts mildly, whilst its *phthalyl* derivative, m. p. 175° (decomp.), which is not readily hydrolysed, is inactive. These results demonstrate that the important grouping in respect to purgative properties is the 4 : 4′-dihydroxydiphenylmethylene radical. In accordance with this conclusion it is found that 4 : 4′-dihydroxybenzophenone is an active purgative; its acetyl derivative is mildly active, its *phthalyl* derivative, m. p. 125° (decomp.), is more stable and inactive; and 4 : 4′-dihydroxydiphenyldimethylmethane and 4 : 4′-dihydroxytetraphenylmethane both also possess laxative properties.

W. A. Silvester.

Synthesis of pyrylium salts of anthocyanidin type. XII. D. D. Pratt, A. Robertson, and R. Robinson (J.C.S., 1927, 1975—1983; cf. this vol., 974).—Benzoylacetaldehyde condenses with phloroglucinol in formic acid to give *trianhydrobisbenzoylacetaldehydephloroglucinol*, $C_{30}H_{22}O_7$, which chars without melting above 280°, and is converted by boiling hydrochloric-acetic acid into chrysinidin chloride (5 : 7-dihydroxyflavylium chloride), obtained also by condensing the components in ether or glacial acetic acid in presence of hydrogen chloride. *O*-Benzoylphloroglucinaldehyde and acetophenone in ethyl acetate saturated with hydrogen chloride yield *O*-benzoylchrysinidin chloride, from which chrysinidin chloride is obtained by treatment with methylalcoholic ammonia and addition of hydrochloric acid. Chrysinidin perchlorate melts at 244° (decomp.). From *p*-methoxyacetophenone *O*-*benzoylacacetinidin chloride* and acacetinidin chloride [dimorphic perchlorate, m. p. 278—280° (decomp.); picrate, m. p. 231—233° (decomp.)]. Demethylation of acacetinidin chloride with hydriodic acid and phenol gives a purer apigenidin iodide (chloride, *mercurichloride*, *perchlorate*, and *periodide* prepared) than previously obtained.

Hydroxymethyleneacetoveratrone (*copper* compound,

decomp. 188°) condenses with phloroglucinol in ether in presence of hydrogen chloride to form 5 : 7-*dihydroxy*-3′ : 4′-*dimethoxyflavylium chloride*, decomp. 272°, which gives on demethylation a luteolinidin chloride monomethyl ether (probably 5 : 7 : 4′-*dihydroxy*-3′-*methoxyflavylium chloride*), decomp. 282°, and eventually luteolinidin chloride. 7-*Hydroxy*-3 : 2′ : 4-*trimethoxyflavylium chloride*, decomp. 185°, from ω : 2 : 4-trimethoxyacetophenone and β-resorcylaldehyde, and its demethylation product, *resomorindin chloride*, decomp. 216°, are described. The *copper* compound of hydroxymethylene-2 : 4-dimethoxyacetophenone has m. p. 190°. Phloroacetophenone trimethyl ether condenses with ethyl oxalate to give *ethyl* 2 : 4 : 6-*trimethoxybenzoylpyruvate*, m. p. 84°.

C. HOLLINS.

Synthesis of pyrylium salts of anthocyanidin type. XIII. Some monohydroxyflavylium salts. F. M. IRVINE and R. ROBINSON (J.C.S., 1927, 2086—2094).—Attempts to demethylate 8-methoxyflavylium chloride, m. p. 190° (decomp.), prepared from *o*-vanillin and acetophenone, or *iodide*, m. p. 134°, were unsuccessful. Condensation of 5-methoxysalicylaldehyde with acetophenone in aqueous-alcoholic potassium hydroxide gives 40% of 5-*methoxysalicylidenediacetophenone* [αγ-dibenzoyl-β-2-hydroxy-5-methoxyphenylpropane], m. p. 125°, and 50% of *phenyl*-2-*hydroxy*-5-*methoxystyryl ketone*, m. p. 104°, which is converted by hydrochloric–acetic acid into 6-*methoxyflavylium chloride*, m. p. 97° [$+2H_2O$; *ferrichloride*, m. p. 203°; *iodide*, m. p. 143°; *periodide*, m. p. 86—87°; *perchlorate*, m. p. about 200° (decomp.)]. Careful demethylation with phenol and hydriodic acid gives 6-*hydroxyflavylium chloride* (*ferrichloride*, m. p. 198°; *chloroaurate*). 4′-*Hydroxyflavylium iodide* yields on demethylation 4′-*hydroxyflavylium periodide*, m. p. 208—209° [*chloride*, m. p. 142° ($+2H_2O$); *chloroaurate*, m. p. 177°]. The corresponding 4′-*hydroxyflavanhydrone*, m. p. 200°, gives no methiodide.

p-Hydroxyacetophenone, m. p. 110° (*acetate*, m. p. 54°), obtained in 33% yield by a modification of Nencki and Stoeber's method (A., 1897, i, 521), condenses with *o*-vanillin in formic acid to form 4′-*hydroxy*-8-*methoxyflavylium chloride*, m. p. 190° [decomp.; *ferrichloride*, m. p. 217°; *periodide*, m. p. 170—173° (decomp.)]; 4′-*hydroxy*-8-*methoxyflavanhydrone* decomposes at 206°.

o-Hydroxyacetophenone gives with salicylaldehyde a scarlet *solid*, which is not a flavylium salt. 2′-*Hydroxyflavylium ferrichloride*, m. p. 125°, is obtained by using *o*-acetoxyacetophenone. For the condensation with *o*-vanillin, *o*-hydroxyacetophenone is more suitable than the acetate, and yields 2′-*hydroxy*-8-*methoxyflavylium chloride*, m. p. 188° (decomp.).

6-*Methoxy*-4-*phenacylideneflavene*, m. p. 146°, obtained with acetophenone and *phenyl* β-2-*hydroxy*-5-*methoxyphenylethyl ketone* (*semicarbazone*, m. p. 184°; *p-nitrophenylhydrazone*, m. p. 163—165°), from 5-methoxysalicylidenediacetophenone, resembles the pyrones in that the ketone group is unattacked by magnesium phenyl bromide, and the flavene yields a *ferrichloride*, m. p. 170° (decomp.), readily hydrolysed by water. In this flavene the pyrone system ·O·C:C·C:O is extended to ·O·C:C·C:C·C:O.

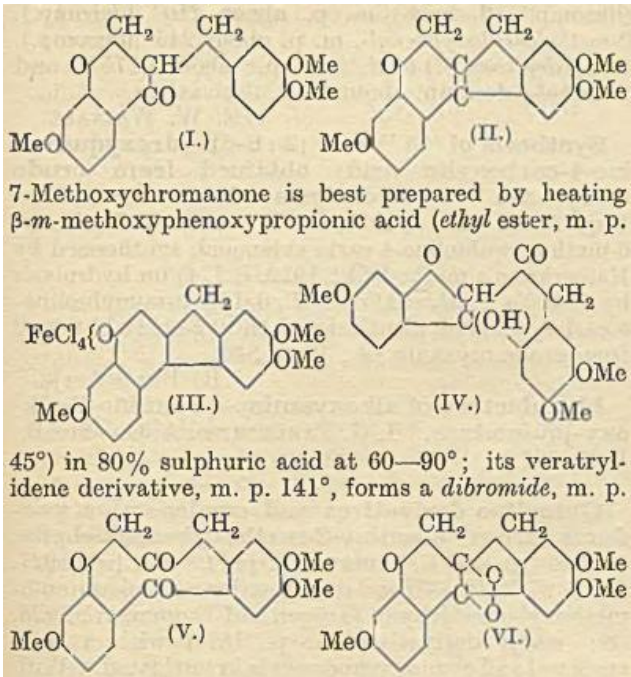
C. HOLLINS.

Pyrylium salts of anthocyanidin type. XIV. A. ROBERTSON and R. ROBINSON (J.C.S., 1927, 2196—2206).—Flavylium salts containing free hydroxyl groups in positions 3, 5, 3′, and 4′ have been prepared. Their colour reactions with alkalis are described and compared with those of cyanin and mecocyanin. 2 : 6-*Dimethoxy*-4-*methylbenzoyl chloride*, m. p. 84—85°, obtained by the action of phosphorus pentachloride on *p*-orsellinic acid dimethyl ether, yields a corresponding p-*toluidide*, m. p. 168—169°, *iminochloride*, *amide*, m. p. 199°, and *nitrile*, m. p. 138—139°. Reduction of the last-named compound by Stephen's method (A., 1925, i, 1131) gives 2 : 6-*dimethoxy*-4-*methylbenzaldehyde*, m. p. 90—91° (p-*nitrophenylhydrazone*), which could not be condensed with ω-methoxyacetoveratrone. Application of the Gattermann synthesis to *m*-xylorcin yields m-*xylorcylaldehyde*, a bright yellow substance, m. p. 155—156°, which condenses with ω-4-dimethoxyacetophenone in formic acid solution under the influence of hydrogen chloride giving 5-*hydroxy*-3 : 4′-*dimethoxy*-6 : 8-*dimethylflavylium chloride* (*ferrichloride*, m. p. 211—212°). Demethylation yields 3 : 5 : 4′-*trihydroxy*-6 : 8-*dimethylflavylium chloride* (*iodide*). Similar condensation of *m*-xylorcylaldehyde with ω-methoxyacetoveratrone yields 5-*hydroxy*-3 : 3′ : 4′-*trimethoxy*-6 : 8-*dimethylflavylium chloride* (*ferrichloride*, m. p. 200—203°). Demethylation gives 3 : 5 : 3′ : 4′-*tetrahydroxy*-6 : 8-*dimethylflavylium chloride* (*iodide*). Rhamnetin was acetylated and reduced by zinc dust in boiling acetic anhydride solution. The product was hydrolysed with aqueous-alcoholic hydrogen chloride, giving *rhamnetidin chloride* and insoluble by-products. Salicylaldehyde condenses with ω-4-dimethoxyacetophenone in presence of hydrogen chloride giving 3 : 4′-*dimethoxyflavylium chloride* (ferrichloride, m. p. 151—152° dimorphic [?]; lit. 135°). Demethylation yields 3 : 4′-*dihydroxyflavylium chloride* (*iodide*). Comparison of the colour of alkaline solutions of this salt with those of 7 : 3′ : 4′-trihydroxyflavylium chloride and the representative of the 5 : 3′ : 4′-hydroxylated series described above, demonstrates the relatively feeble hypsochromic character of the hydroxyl groups in positions 7 and 5. An improved method for the preparation of *p*-orsellinic acid is described. The following are mentioned: methyl *p*-orsellinate, m. p. 93—94°; 3 : 5-dimethoxy-*p*-toluic acid, m. p. 180—182° (decomp.); 2 : 4-dimethoxy-6-methylbenzaldehyde, m. p. 64—65°; orsellinic acid dimethyl ether, m. p. 143—144° (decomp.) [lit. gives 98—99°, 178°, 62°, and 140°, respectively].

M. CLARK.

Synthesis of brazilin and hæmatoxylin and their derivatives. II. Synthesis of deoxytrimethylbrazilone and of *iso*brazilein ferrichloride trimethyl ether. W. H. PERKIN, jun., J. N. RÂY, and R. ROBINSON (J.C.S., 1927, 2094—2100).—The constitution of deoxytrimethylbrazilone (II), originally obtained by reduction of trimethylbrazilone with phenylhydrazine (Gilbody and Perkin, *ibid.*, 1902, **81**, 1046), is established by its synthesis by dehydration of 3-homoveratryl-7-methoxychromanone (I). Oxidation with ferric chloride yields *iso*brazilein ferrichloride trimethyl ether, which therefore has the

structure (III). Trimethylbrazilone is probably best represented by V in equilibrium with (IV) and (VI).



7-Methoxychromanone is best prepared by heating β-*m*-methoxyphenoxypropionic acid (*ethyl* ester, m. p. 45°) in 80% sulphuric acid at 60—90°; its veratrylidene derivative, m. p. 141°, forms a *dibromide*, m. p. 137—138°, and an *oxamino-oxime*. The 3-mp-*dihydroxybenzylidene* derivative, m. p. 212°, is reduced smoothly by hydrogen and palladium to 3-mp-*dihydroxybenzyl*-7-*methoxychromanone*, m. p. 138°, and a *substance*, m. p. 139°. The benzyl compound is methylated with methyl sulphate to give 3-*homoveratryl*-7-*methoxychromanone* (I), m. p. 92°, obtainable, although in poor yield, by reduction of 3-veratrylidene-7-methoxychromanone. The dehydration of 3-homoveratryl-7-methoxychromanone to deoxytrimethylbrazilone, m. p. 166—171°, is accomplished by boiling in benzene with phosphorus pentoxide.

C. Hollins.

Manufacture of vat dyes containing sulphur [*peri*naphthathioindoxyls]. I. G. Farbenind. A.-G.—See B., 1927, 809.

[Transformations of ethyl isatin-*N*-carboxylate.] N. Putochin (Ber., 1927, **60**, [*B*], 2033; cf. this vol., 885).—The course of the reaction between sodioisatin and ethyl chloroformate has been elucidated previously by Heller and Lauth (A., 1926, 957; cf. also Heller, A., 1918, i, 309). H. Wren.

5 : 6-Dimethoxy-2-methyl-1 : 2 : 3 : 4-tetrahydro*iso*quinoline and its derivatives. R. D. Haworth (J.C.S., 1927, 2281—2284).—Treatment of the *amide*, m. p. 99—100°, of β-2 : 3-dimethoxyphenylpropionic acid with sodium hypochlorite yields β-2 : 3-*dimethoxyphenylethylamine*, b. p. 190°/70 mm. (*hydrochloride*; *picrate*, m. p. 174—176°). The N-*formyl* derivative of the amine reacts with phosphorus oxychloride to give 5 : 6-*dimethoxy*-3 : 4-*dihydro*isoquinoline. Reduction of the *methiodide*, m. p. 174—175°, of this base with zinc and dilute sulphuric acid gives 5 : 6-*dimethoxy*-2-*methyl*-1 : 2 : 3 : 4-*tetrahydro*isoquinoline [*hydrochloride*; *hydriodide*, m. p. 201°; *picrate*, m. p. 164° (decomp.)]. Nitration of the tetrahydro-base in glacial acetic acid gives 8-*nitro*-5 : 6-*dimethoxy*-2-*methyl*-1 : 2 : 3 : 4-*tetrahydro*isoquinoline, m. p. 104—105°, which fails to condense with piperonal or veratraldehyde in presence of either piperidine or methyl-alcoholic potassium hydroxide. It is inferred that the effect of the nitro-group on the 1-methylene group is neutralised by the methylimino-grouping. Reaction of β-2 : 3-dimethoxyphenylethylamine with 6-bromohomopiperonylic acid at 180° yields 6′-*bromo*-3′ : 4′-*methylenedioxyphenylaceto*-β-2 : 3-*dimethoxyphenylethylamide*, m. p. 131°, which is converted by treatment with phosphorus oxychloride into 6′-*bromo*-5 : 6-*dimethoxy*-3′ : 4′-*methylenedioxy*-1-*benzyl*-3 : 4-*dihydro*isoquinoline, m. p. 134—135°. The last-named compound is oxidised by the air to 6′-*bromo*-5 : 6-*dimethoxy*-3′ : 4′-*methylenedioxy*-1-*benzoyl*-3 : 4-*dihydro*isoquinoline, m. p. 168°. M. Clark.

Resolution of racemic *N*-ethyltetrahydroquinoline oxide. J. Dodonow (J. pr. Chem., 1927, [ii], **117**, 154—160).—Oxidation of *N*-ethyltetrahydroquinoline for 74 hrs. with 3% hydrogen peroxide at 60—70° yields N-*ethyltetrahydroquinoline oxide*, an unstable syrup (dl-*picrate*, m. p. 124·5°; dl-*hydrochloride*, m. p. 125—126°). Treatment of an aqueous solution of the *dl*-hydrochloride with silver *d*-bromocamphorsulphonate and concentration of the solution in a vacuum yields d-N-*ethyltetrahydroquinoline oxide* d-α-*bromocamphor*-π-*sulphonate*, m. p. 165—166°, $[\alpha]_D$ +69·4°, in practically quantitative yield; whilst further evaporation of the mother-liquor yields l-N-*ethyltetrahydroquinoline oxide bromocamphorsulphonate* ($+H_2O$), m. p. 85—87°; anhydrous, m. p. 137—138°, $[\alpha]_D$ +45°, mixed with a little of the *dl*-salt. From these salts in the usual manner are obtained the d-*picrate*, m. p. 97—98°; l-*picrate*, m. p. 98—104°; d-*hydrochloride*, m. p. 139—140°, $[\alpha]_D$ +30·6°; and l-*hydrochloride*, m. p. 138—139°, $[\alpha]_D$ −29·4°. Although the active bases themselves could not be isolated the optical rotations of the *d*- and *l*-forms were found to be $[\alpha]_D$ +41° and $[\alpha]_D$ −40° respectively by exact neutralisation of solutions of the active chlorides with barium hydroxide. J. W. Baker.

Dimeride of 4 : 6-dichloro-5-cyano-2-styrylpyridine. G. Koller (Ber., 1927, **60**, [*B*], 1920—1922; cf. Spath and Koller, A., 1925, i, 1446).—The dimeric substance formed by the action of light on 4 : 6-dichloro-5-cyano-2-styrylpyridine probably owes its production to the disappearance of the ethylenic linking and consequent transformation into a *cyclo*butane derivative. In favour of this view it is noted that the dimeride is colourless, whereas the monomeride is yellow and that the former is stable to potassium permanganate in the presence of acetone whereas the latter is not. Under certain conditions, depolymerisation of the dimeride to monomeride can be effected by distillation. Photopolymerisation is not a general property of stilbazoles. 4-*Chloro*-2-*hydroxy*-6-*styrylpyridine*, m. p. 234—235° after softening at 233°, 4 : 6-*dichloro*-5-*cyano*-2-m-*nitrostyrylpyridine*, m. p. 263—264°, and 4 : 6-*dichloro*-5-*cyano*-2-m-*chlorostyrylpyridine*, m. p. 182—183°, are incidentally described. H. Wren.

Action of sulphuryl azide on *p*-cymene. A. Bertho, T. Curtius, and F. Schmidt (Ber., 1927, **60**,

[*B*], 1717—1720).—*p*-Cymene is converted by sulphurylazide at 180° into nitrogen, sulphur dioxide, and a non-acetylable base, $C_9N_{13}N$, isolated as the *picrate*, m. p. 146°, and *chloroplatinate*, m. p. 163—164° (decomp.). Since the base does not lose ammonia when repeatedly evaporated with hydrochloric acid, the presence in it of a seven-membered ring appears excluded. It and the isomeric base derived from *p*-xylene and carbonyl azide (A., 1926, 509) are therefore considered to be the two possible methyl*iso*propylpyridines containing the alkyl groups in the 2 : 5-position. In addition, a neutral *substance*, (?) $C_{10}H_{10}NCl$, m. p. 79°, is obtained in small amount owing to the presence of chloride in the azide solution, whilst the mother-liquors from the picrate, m. p. 146°, yield a second *picrate*, m. p. 149°. H. WREN.

Manufacture of quinoline derivatives [zinci-chlorides]. BRITISH DYESTUFFS CORP., LTD., etc. —See B., 1927, 809.

Condensation of acetaldehyde and paracetaldehyde with aniline in the presence of aluminium oxide as contact substance. A. E. TSCHITSCHIBABIN and M. P. OPARINA (Ber., 1927, **60**, [*B*], 1873—1876; cf. A., 1924, i, 709, 766).—Condensation is effected between aldehydes and aniline in much the same manner as between aldehydes and ammonia (*loc. cit.*), but the use of considerably higher temperatures is advantageous for the production of quinoline bases in general and of 4-methylquinoline in particular. The production of 2- and 4-methylquinolines from acetaldehyde and aniline is precisely analogous to that of 2- and 4-methylpyridines from acetaldehyde and ammonia. Probably crotonaldehyde is intermediately formed. Skraup's reaction appears therefore as a special case of the reactions of Dobner and von Miller (production of 2-substituted quinoline homologues) and Tschitschibabin (production of 4-substituted quinoline homologues). H. WREN.

Condensation of crotonaldehyde with ammonia in the presence of aluminium oxide. A. E. TSCHITSCHIBABIN and M. P. OPARINA (Ber., 1927, **60**, [*B*], 1877—1879).—Substitution of crotonaldehyde for acetaldehyde in the synthesis of pyridine bases from aldehydes and ammonia in the presence of aluminium oxide causes a very marked reduction in the amount of the picoline fraction (the formation of these is due to the partial depolymerisation of crotonaldehyde to acetaldehyde) and a great increase in the proportion of collidines of which the main component is β-collidine. The yield of the latter substance amounts to 20% of the crude bases. The isolation of a *collidine picrate*, m. p. 163—164°, is recorded. H. WREN.

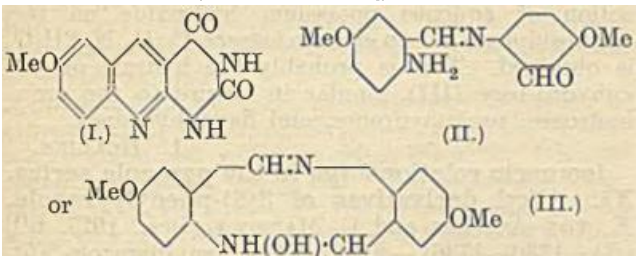
Synthesis of quinoline-4-carboxylic acids. S. BERLINGOZZI and A. TURCO (Rend. Accad. Sci. fis. mat. Napoli, 1927, [iii], **33**, 50—52).—Substituted derivatives of 2-phenylcinchoninic acid (" atophan "), shown by Nicolajer and Dorn (Det. Arch. klin. Med., 1908, **93**, 331) to increase excretion of uric acid in the urine, are prepared by condensing pyruvic acid and acetylbenzidine with various aldehydes by the method of Knorr (A., 1884, 1198). The following are described: 6-p-*acetamidophenyl*-2-*phenylquinoline*-4-*carboxylic acid*, decomp. about 250°, and the corresponding 2-(?)*methoxyphenyl*-, m. p. about 199° (decomp.), 2-*styryl*-, m. p. about 210° (decomp.), 2-*methylenedioxyphenyl*-, m. p. about 245° (decomp.), 2-(?)*dihydroxy*-(?)-*tolyl*, m. p. about 175°, and 2-*methyl*-, decomp. about 260°, derivatives. E. W. WIGNALL.

Synthesis of " β " acid (2 : 6-dihydroxyquinoline-4-carboxylic acid) obtained from crude " cryzanin " by hydrolysis. Y. SAHASHI (Proc. Imp. Acad. Tokyo, 1927, **3**, 437—438).—2-Hydroxy-6-methoxyquinoline-4-carboxylic acid, synthesised by Halberkann's method (A., 1922, i, 174) on hydrolysis by Zeisel's method affords 2 : 6-dihydroxyquinoline-4-carboxylic acid, identical with the " β-acid " obtained from crude oryzanin (A., 1926, 846). R. BRIGHTMAN.

Manufacture of alkoxyamino- [8-amino-6-alkoxy-]quinolines. I. G. FARBENIND. A.-G.—See B., 1927, 797.

Quinoline derivatives and condensation products from 6-amino-3-methoxybenzaldehyde. J. TROGER and C. COHAUS (J. pr. Chem., [ii], 1927, **117**, 97—116).—The condensation of 6-amino-3-methoxybenzaldehyde (Troger and Fromm, A., 1926, 68; *acetyl* derivative, m. p. 187°) with various carbonyl and cyano-compounds is investigated. With ethyl acetoacetate and ethyl benzoylacetate in hot alcoholic solution in presence of a few drops of sodium hydroxide it yields respectively *ethyl* 6-*methoxy*-2-*methylquinoline*-3-*carboxylate*, an oil (*chloroplatinate*), and *ethyl* 6-*methoxy*-2-*phenylquinoline*-3-*carboxylate*, m. p. 115° (*acid*, m. p. 232°; *chloroplatinate* and *silver* salt of the acid), whilst when heated together in a sealed tube at 160° for 4 hrs. without solvent or catalyst the products are respectively 2-*hydroxy*-6-*methoxy*-3-*acetylquinoline*, m. p. 297° (*phenylhydrazone*, m. p. 252°), and 2-*hydroxy*-6-*methoxy*-3-*benzoylquinoline*, m. p. 293° (*phenylhydrazone*, m. p. 229°). Condensation with compounds of the type $R{\cdot}CH_2{\cdot}CN$ in alcoholic solution with sodium hydroxide as a catalyst yields 2-aminoquinoline derivatives: thus *p*-bromobenzenesulphonacetonitrile, phenylacetonitrile, and malononitrile yield, respectively, 2-*amino*-6-*methoxy*-3-p-*bromobenzenesulphonyl*-, m. p. 89—90°; -3-*phenyl*-, m. p. 143° (*hydrochloride*; yields 2-*hydroxy*-6-*methoxy*-3-*phenylquinoline*, m. p. 109°, on treatment with nitrous acid), and -3-*cyano-quinoline*, m. p. 243—244° [which, on treatment with nitrous acid, yields 2-*hydroxy*-6-*methoxy*-3-*cyanoquinoline*, m. p. 263°, and, on hydrolysis, 2-*amino*-6-*methoxyquinoline*-3-*carboxylic acid*, m. p. above 300° (*silver* salt; *chloroplatinate*) whilst subsequent treatment with nitrous acid yields 2-*hydroxy*-6-*methoxyquinoline*-3-*carboxylic acid*, m. p. 283° (*disilver* salt)]. In all three cases the 2-amino-group is eliminated as ammonia on reduction with tin and hydrochloric acid. Condensation with ethyl cyanoacetate yields 2-hydroxy-6-methoxy-3-cyanoquinoline (above) whilst the corresponding -3-carboxylic acid is also obtained by condensation with malonic acid. Condensation with phenacyl cyanide yields 6-*methoxy*-3-*cyano*-2-*phenylquinoline*, m. p. 170 (*chloroplatinate*), irrespective of the method of con-

densation employed. Condensation with barbituric acid in the presence of alkali yields 2 : 4-*diketo*-1 : 2 : 3 : 4-*tetrahydro*-9-*methoxyquinoline*-1 : 3-*diazine*



(I), m. p. 273° (*sodium* and *silver* salts). 6-Amino-3-methoxybenzaldehyde itself is unstable and readily condenses to a yellow solid *substance*, possibly (II) or (III). J. W. Baker.

β-Substituted derivatives of "atophan" [2-phenylquinoline-4-carboxylic acid]. S. Berlingozzi and A. Turco (Rend. Accad. Sci. fis. mat. Napoli, 1925, [iii], **31**, 191—193).—On condensing a solution of isatin in potassium hydroxide solution with ω-phenoxyacetophenone in alcohol, there is obtained, on acidification, 3-*phenoxy*-2-*phenylquinoline*-4-*carboxylic acid*, m. p. 232° (heavy metal salts insoluble, but *barium* salt soluble in water), which when heated yields 3-*phenoxy*-2-*phenylquinoline*, m. p. 130—131°. E. W. Wignall.

3-Substituted quinolines. S. Berlingozzi and W. E. Burg (Rend. Accad. Sci. fis. mat. Napoli, 1927, [iii], **33**, 39—40).—By condensing *N*-*p*-hydroxyphenacylphthalimide (obtained from *p*-chloroacetylanisole and potassium phthalimide) with *o*-aminobenzaldehyde, and hydrolysing, 3-*amino*-2-p-*methoxyphenylquinoline*, m. p. 138° (*acetyl* derivative, m. p. 165°), is obtained, which on diazotisation yields 3-hydroxy-2-*p*-methoxyphenylquinoline.

Using isatoic acid, 3-*amino*-2-p-*methoxyphenylquinoline*-4-*carboxylic acid*, decomp. about 150° (*acetyl* derivative, m. p. 212°), is obtained, which on diazotisation yields the corresponding 3-hydroxy-compound (Berlingozzi and Capuano, A., 1924, i, 1345). E. W. Wignall.

[Nitro- and amino-acridines.] H. Jensen (Ber., 1927, **60**, [*B*], 2033).—The constitution of the nitroacridines established by Lehmstedt by oxidation to the known nitroacridones (this vol., 776) has been confirmed by synthesis by Jenson and Friedrich (this vol., 575). 4-Aminoacridine has been described previously by Clemo, Perkin, and Robinson (A., 1924, i, 1339). H. Wren.

4-Amino-1-phenyl-5-pyrazolone-3-carboxylic acid. F. D. Chattaway and W. G. Humphrey (J.C.S., 1927, 2133—2139).—4-*Amino*-1-*phenyl*-5-*pyrazolone*-3-*carboxylic acid*, m. p. 225° [decomp.; *hydrochloride*, decomp. 160°; *acetyl* derivative, m. p. 216°; ON-*dibenzoyl* derivative, m. p. 205°], is obtained by reduction with sodium amalgam of 1-phenyl-4 : 5-diketopyrazoline-3-carboxylic acid 4-phenylhydrazone, or of the 4-*oxime*, m. p. 209° (decomp.), prepared by nitrosation of 1-phenyl-5-pyrazolone-3-carboxylic acid. Anhydrodiketosuccinic acid phenylosazone is reduced with sodium amalgam first to sodium amino-oxalacetate phenylhydrazone, which on acidification gives 4-amino-1-phenyl-5-pyrazolone-3-carboxylic acid, and finally to the two stereoisomeric diaminosuccinic acids.

When 1-phenyl-4 : 5-diketopyrazoline-3-carboxylic acid 4-phenylhydrazone is brominated in glacial acetic acid the product is the 4-p-*bromophenylhydrazone*, m. p. 258° (decomp.), which is synthesised from 1-phenyl-5-pyrazolone-3-carboxylic acid and *p*-bromodiazobenzene.

The following esters of 1-phenyl-4 : 5-diketopyrazolone-3-carboxylic acid 4-phenylhydrazone are prepared by action of alcohols and hydrogen chloride on anhydrodiketosuccinic acid phenylosazone: *methyl*, m. p. 138°; ethyl, m. p. 153°; n-*propyl*, m. p. 116·5°; n-*butyl*, m. p. 117°. C. Hollins.

Condensation of dimethylbarbituric acid with aldehydes. Colour reaction of furfuraldehydes. S. Akabori (Proc. Imp. Acad. Tokyo, 1927, **3**, 342—344).—Dimethylbarbituric acid condenses readily in aqueous or alcoholic solution with benzaldehyde, vanillin, furfuraldehyde, methylfurfuraldehyde, hydroxymethylfurfuraldehyde, β-indolealdehyde, cinnamaldehyde, and citral, forming crystalline *products*, m. p. 159—159·5°, 222·5—223·5°, 194·5—195°, 172—172·5°, 181—182°, 291—292° (decomp.), 195·5—196°, and 101—101·5°, respectively. Barbituric and dimethylbarbituric acid derivatives of furfuraldehyde, methylfurfuraldehyde, and hydroxymethylfurfuraldehyde give intense colorations with aniline and aniline acetate, recognisable up to dilutions of 1 in 10^6. B. W. Anderson.

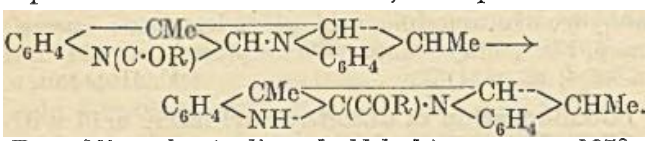
Barbituric acid derivative. E. H. Volwiler.—See B., 1927, 797.

Action of the Grignard reagent on alkylbarbituric acids. A. W. Dox (J. Amer. Chem. Soc., 1927, **49**, 2275—2279).—Treatment of 5 : 5′-dialkylbarbituric acids with Grignard reagents results in reaction of two carbonyl groups, with subsequent elimination of 1 mol. of water. The products are highly resistant to hydrolytic agents, and are therefore regarded as *endo*-*ethers* of 4 : 6-*dihydroxy*-2-*keto*-4 : 5 : 5 : 6-*tetra*-*alkylhexahydropyrimidines* (I).



Derivatives of this type were prepared from magnesium ethyl bromide and 5 : 5′-diethyl-, 5-ethyl-5′-phenyl-, 5-ethyl-5′-*iso*amyl-, and 5 : 5′-diallyl-barbituric acids; from magnesium phenyl bromide and 5 : 5′-diethylbarbituric acid; from magnesium propyl bromide and 5 : 5′-diethylbarbituric acid; from magnesium propyl bromide and 5 : 5′-diethylbarbituric acid; from magnesium *n*-butyl bromide and 5 : 5′-diethylbarbituric acid, and from magnesium *iso*amyl bromide and 5 : 5′-diallylbarbituric acid. They all have m. p. not below 250°, whilst some can be sublimed. 1 : 3-*Diphenyl*-5 : 5′-*dipropylbarbituric acid*, m. p. 104—105°, obtained by condensing dipropylmalonic acid with carbanilide in chloroform in presence of phosphoryl chloride, yields, when treated with magnesium ethyl bromide, the *endo*-*ether* of 2 : 4 : 6-*trihydroxy*-1 : 3-*diphenyl*-2 : 4 : 6-*triethyl*-5 : 5′-*dipropylhexahydropyrimidine*, m. p. 102° (cf. Béis, A., 1904, i, 503, 671; Sachs and Ludwig, A., 1904, i, 266). F. G. Willson.

Transpositions in discatole. B. Oddo and Q. Mingoia (Gazzetta, 1927, **57**, 480—485).—*Acetyldiscatole*, $C_{20}H_{20}ON_2$, m. p. 180°, and *benzoyldiscatole*, m. p. 207°, are resistant to hot aqueous alkali, and form silver compounds with the silver atom attached to the imino-nitrogen atom. These derivatives are hence carbon-substituted compounds, and it must be assumed that the mobility of the imino-hydrogen atom of the tetrolic nucleus remains unaltered in the discatole molecule and that transposition of the substituent group to the only available carbon atom, that in the α-position of the tetrolic nucleus, takes place :

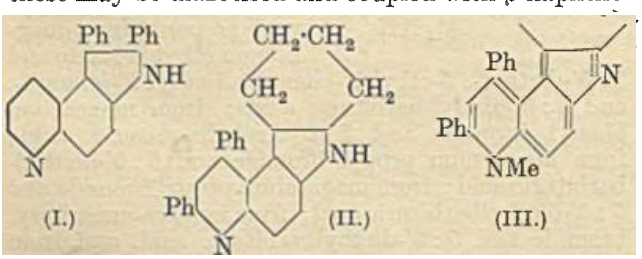


Formyldiscatole (*α-discatolealdehyde*), m. p. 187°, and *ethyldiscatole*, m. p. 157°, have similar structures. Scatole picrate, m. p. 170—171°, undergoes transformation into a *compound*, m. p. 216—217°, when exposed to the air (cf. A., 1924, i, 427).

T. H. Pope.

Polynuclear heterocyclic aromatic types. III. Pyrroloquinoline derivatives. R. C. Fawcett and R. Robinson (J.C.S., 1927, 2254—2261).—Condensation of 6-aminoquinoline with benzoin gives 5 : 6-(2′ : 3′-*diphenyl*-4′ : 5′-*pyrrolo*)*quinoline* (I), m. p. 167—168° [+H_2O; *hydrogen sulphate*, *hydrochloride*, and *picrate*, m. p. 218° (decomp.), described; crystallographic data for the base by H. E. Buckley]. The yellow *methosulphate*, m. p. 218—219°, does not give an anhydro-base (cf. Armit and Robinson, A., 1925, i, 1170), but is converted by alkaline ferricyanide into 2-*keto*-1-*methyl*-5 : 6-(2′ : 3′-*diphenyl*-4′ : 5′-*pyrrolo*)-1 : 2-*dihydroquinoline*, m. p. 195·5°.

Dibenzoylmethane gives with *p*-aminoacetanilide an anil, which is converted by sulphuric acid into a *substance*, m. p. 237·5—238·5°, probably the sodium salt of a sulphonic acid of the desired quinoline. From dibenzoylmethane and *m*-phenylenediamine, heated at 140° and then cyclised with zinc chloride at 175—180°, are obtained 5-*amino*- and 7-*amino*-2 : 4 *diphenylquinolines*, m. p. 168·5° and 187°, respectively : these may be diazotised and coupled with β-naphthol.



6-Nitro-1 : 2 : 3 : 4-tetrahydrocarbazole (Borsche, Witte, and Bothe, A., 1908, i, 365) is best reduced with iron powder and alcoholic hydrochloric acid. The 6-amino-compound condenses with dibenzoylmethane to form *phenyl* 1 : 2 : 3 : 4-*tetrahydro*-6-*carbazyl*-α-*aminostyryl ketone*, m. p. 229·5—230°, which is converted by phosphoryl chloride into 2 : 4-*diphenyl*-5 : 6-(4′ : 5′ : 6′ : 7′-*tetrahydro*-2′ : 3′-*indoloquinoline* (II) m. p. 235° [*picrate*, m. p. 241° (decomp. 243°); *methosulphate*; *methopicrate*, m. p. 252—254° (decomp.)]. The base is yellow, gives red salts, and absorbs oxygen from the air, forming a *dioxy*-derivative, $C_{27}H_{22}O_2N_2$, decomposing at 168° with incandescence. By the action of aqueous potassium hydroxide on the methosulphate a deep green *substance*, $C_{28}H_{24}N_2,2H_2O$, is obtained. This is probably the hydrate of the anhydro-base (III), similar in nature to the quinhydrones, pyranhydrones, and flavanhydrones.

C. Hollins.

Isomeric relationships in the pyrazole series. XI. Alkyl derivatives of 3(5)-phenylpyrazole. K. von Auwers and C. Mausolf (Ber., 1927, **60**, [*B*], 1730—1736).—Ethyl 5(3)-phenylpyrazole-3(5)-carboxylate, m. p. 140°, prepared from ethyl benzoylpyruvate and hydrazine hydrate, is hydrolysed to 5(3)-*phenylpyrazole*-3(5)-*carboxylic acid*, m. p. 234° after softening (*methyl* ester, m. p. 182°). Treatment of the esters with methyl iodide and methyl-alcoholic sodium methoxide followed by hydrolysis of the product affords a mixture of 5-*phenyl*-1-*methylpyrazole*-3-*carboxylic acid*, m. p. 143—144°, and the isomeric 3-*phenyl*-1-*methylpyrazole*-5-*carboxylic acid*, m. p. 183—184°. Bromination of the acid of m. p. 143—144° in glacial acetic acid affords the *bromo*-derivative, $C_{11}H_9O_2N_2Br$, m. p. 205°, which is converted by methyl-alcoholic hydrogen chloride into the *methyl* ester, $C_{12}H_{11}O_2N_2Br$, m. p. 114—115°, whereas the *bromo*-derivative, m. p. 208°, of the acid, m. p. 183—184°, cannot be esterified in this manner. The position of the substituents is thus established (cf. von Auwers and Hollmann, A., 1926, 623, 847). The acid of m. p. 143—144° when decarboxylated affords 5-phenyl-1-methylpyrazole, b. p. 118°/12 mm. (picrate, m. p. 143°), whereas similar treatment of the acid of m. p. 183—184° yields 3-phenyl-1-methylpyrazole, m. p. 56° (picrate, m. p. 132°), thus confirming the constitution of the phenylmethylpyrazoles obtained by von Auwers and Schmidt (A., 1925, i, 585). The bromo-acid, m. p. 205°, gives a bromo-*base*, m. p. 53—54°. Ethylation of ethyl 5(3)-phenylpyrazole-3(5)-carboxylate gives a mixture of esters which can be roughly separated by fractional distillation. Hydrolysis of the separate fractions leads to the isolation of 3-*phenyl*-1-*ethylpyrazole*-5-*carboxylic acid*, m. p. 162—163°, and 5-*phenyl*-1-*ethylpyrazole*-3-*carboxylic acid*, m. p. 137—138°, which afford respectively 4-*bromo*-3-*phenyl*-1-*ethylpyrazole*-5-*carboxylic acid*, m. p. 154—155°, and 4-*bromo*-5-*phenyl*-1-*ethylpyrazole*-3-*carboxylic acid*, m. p. 179—180° after softening (converted by methyl-alcoholic hydrogen chloride into the *methyl* ester, m. p. 111°). Decarboxylation of the corresponding acids yields 3-phenyl-1-ethylpyrazole. b. p. 146°/12 mm., m. p. 34—36° (picrate, m. p. 104—106°) (cf. A., 1925, i, 586), and 5-*phenyl*-1-*ethylpyrazole*, b. p. 129°/12 mm., $d_4^{17\cdot4}$ 1·0595, n_{H_α} 1·57077 (*picrate*, m. p. 106·5—107°). During the direct ethylation of 3(5)-phenylpyrazole with ethyl bromide 5-phenyl-1-ethylpyrazole is produced in relatively very small amount (cf. A., 1925, i, 585).

H. Wren.

Porphyrin syntheses. X. Synthesis of *iso*-uroporphyrin and carboxyhæmatic acid. H. Fischer and P. Heisel (Annalen, 1927, **457**, 83—102; cf. this vol., 469).—In uroporphyrin, the octa-

carboxylic acid corresponding with coproporphyrin, the four additional carboxyl groups are most probably attached to the same carbon atoms as the remaining four; *i.e.*, uroporphyrin contains four malonic acid groupings. This view is confirmed by the synthesis of *iso*uroporphyrin.

Bromination of ethyl 2 : 4-dimethyl-3-ββ-dicarbethoxyethylpyrrole-1-carboxylate (Fischer and Andersag, unpublished work) in ether gives the 4-*bromomethyl* compound, m. p. 90° (4-*anilinomethyl* compound, m. p. 100°), which is converted by boiling with water or methyl alcohol, with loss of formaldehyde and hydrogen bromide, into *bis*(1-*carbethoxy*-2-*methyl*-3-ββ-*dicarbethoxyethyl*-4-*pyrryl*)*methane*, m. p. 126°; when methyl alcohol is used there is also formed, by exchange of alkyl groups, *bis*(1-*carbethoxy*-2-*methyl*-3-ββ-*dicarbomethoxyethyl*-4-*pyrryl*)*methane*, m. p. 168°. The *hexasodium* salt (free *acid*, m. p. 176°), obtained by alkaline hydrolysis, is converted, when heated in formic or acetic acid, into a mixture of copro- and *iso*copro-porphyrins, separable by means of their tetramethyl esters. This loss of four "malonic" carboxyl groups is prevented, however, by aerating a solution of the hexasodium salt in 95% formic acid maintained at 40°. Under these conditions *isouroporphyrin* separates after 24—48 hrs. The *octamethyl* ester, m. p. 263° (cf. uroporphyrin octamethyl ester, m. p. 292°), gives complex *iron* and *copper* salts. *iso*Uroporphyrin loses $4CO_2$ at 150—170°, forming *iso*coproporphyrin, and is reduced by sodium amalgam to a *leuco*-compound, readily re-oxidised to the porphyrin. Oxidation of *iso*uroporphyrin with chromic acid gives a carboxyhæmatic acid, α-methyl-β(ββ-dicarboxyethyl)maleinimide, m. p. 178°, which sublimes in a vacuum at 115—120° and is identical with the oxidation product from natural uroporphyrin [crystallographic data by STEINMETZ]. *iso*Uroporphyrin strikingly resembles uroporphyrin in physiological action, but is more poisonous.

Reduction of ethyl 2 : 4-dimethyl-3-ββ-dicarbethoxyethylpyrrole-1-carboxylate with hydriodic acid gives cryptopyrrolecarboxylic acid, m. p. 138° (picrate, m. p. 153°). Fischer and Nenitzescu's bis-(2 : 4-dimethyl-3-ββ-dicarbomethoxyethyl-5-pyrryl)-methene (A., 1926, 178) forms a complex *copper* salt, $C_{50}H_{62}O_{16}N_4Cu$. C. HOLLINS.

Action of diacetyl on magnesylpyrrole. N. A. NARYSCHKIN (Ber., 1927, **60**, [*B*], 1928—1930; cf. A., 1926, 183; this vol., 162).—Diacetyl is converted by magnesium pyrryl iodide into a *compound*, $C_{12}H_{16}O_2N_2$, converted by hydrochloric acid into an unstable, coloured *hydrochloride*. H. WREN.

1 : 8-Naphthyridine. G. KOLLER (Ber., 1927, **60**, [*B*], 1918—1920; cf. this vol., 367, 886).—1 : 8-*Naphthyridine*, m. p. 98—99° after softening at 95° (in an evacuated tube), is isolated from the products of the catalytic reduction of 2 : 4-dichloro-1 : 8-naphthyridine by cautious fractional distillation in a vacuum. Its sensitiveness towards hydrogenation and oxidation is remarkable. The *picrate*, m. p. 207—208° after softening at 200°, and *methiodide*, $C_9H_9N_2I$, m. p. 180—181°, are described; the latter substance regenerates 1 : 8-naphthyridine when heated. H. WREN.

Derivatives of 2 : 3 : 5 : 6-dibenzo-1 : 8-naphthyridine. R. D. HAWORTH and H. S. PINK (J.C.S., 1927, 2345—2349).—Homophthalimide condenses with *o*-nitrobenzaldehyde in pyridine solution in presence of a trace of piperidine, giving o-*nitrobenzylidenehomophthalimide*, m. p. 236°, which is reduced with stannous chloride in alcoholic solution to 7-*keto*-2 : 3 : 5 : 6-*dibenzo*-7 : 8-*dihydro*-1 : 8-*naphthyridine* (I), m. p. 246—247° (*potassium* salt; *sodium* salt). Further reduction with zinc dust in glacial acetic acid saturated with hydrogen chloride gives 7-*keto*-2 : 3 : 5 : 6-*dibenzo*-1 : 4 : 7 : 8 : 9 : 10-*hexahydro*-1 : 8-*naphthyridine* (II), m. p. 250° (*monohydrochloride*, decomp. 270°; *nitrosoamine*; *picrate*, m. p. 270°). The corresponding derivatives from *N*-β-phenylethyl- and *N*-β-piperonylethylhomophthalimide were also prepared: o-*nitrobenzylidene*-N-β-*phenylethylhomophthalimide*, m. p. 146°; 7-*keto*-8-β-*phenylethyl*-2 : 3 : 5 : 6-*dibenzo*-7 : 8-*dihydro*-1 : 8-*naphthyridine*, m. p. 220°; 7-*keto*-8-β-*phenylethyl*-2 : 3 : 5 : 6-*dibenzo*-1 : 4 : 7 : 8 : 9 : 10-*hexahydro*-1 : 8-*naphthyridine*, m. p. 217°; o-*nitrobenzylidene*-N-β-*piperonylethylhomophthalimide*, m. p. 176°; 7-*keto*-8-β-*piperonylethyl*-2 : 3 : 5 : 6-*dibenzo*-7 : 8-*dihydro*-1 : 8-*naphthyridine*, m. p. 217°; 7-*keto*-8-β-*piperonylethyl*-2 : 3 : 5 : 6-*dibenzo*-1 : 4 : 7 : 8 : 9 : 10-*hexahydro*-1 : 8-*naphthyridine*, m. p. 211°. When (I) is heated with phosphorus oxychloride and phosphorus pentachloride at 180° and the resulting unstable chloro-compound is reduced with phosphorus and hydriodic acid at 160—170°, a *base*, 2 : 3 : 5 : 6-*dibenzo*-4 : 9-*dihydro*-1 : 8-*naphthyridine* (?), m. p. 232° (*monohydrochloride*; *hydriodide*), is obtained, in addition to (II). M. CLARK.

Cyanine dyestuffs. I. Synthesis of pinacyanol. II. Synthesis of pinacyanol using trioxymethylene. T. OGATA (Proc. Imp. Acad. Tokyo, 1927, **3**, 334—338).—2-Methylquinoline ethiodide reacts with 2-β-*hydroxyethylenequinoline ethiodide*, decomp. 214—218° (obtained from 2-β-hydroxyethylenequinoline), in presence of sodium ethoxide to form pinacyanol iodide. 6-Ethoxy-2-methylquinoline when heated with formaldehyde and alcohol, yields 6-*ethoxy*-2-β-*hydroxyethenylquinoline*, m. p. 85—86° (*platinum* derivative, m. p. 135—140° [decomp.]), the *ethiodide*, decomp. 193—195°, of which combines with 6-ethoxy-2-methylquinoline ethiodide, yielding 6 : 6′-*diethoxy*-1 : 1′-*diethyl*-2 : 2′-*carbocyanine iodide* (*diethoxypinacyanol iodide*), m. p. 290—291°. Similarly 6-ethoxy-2-methylquinoline ethiodide combines with 2-β-hydroxyethenylquinoline ethiodide to form 6-*ethoxy*-1 : 1′-*diethyl*-2 : 2′-*carbocyanine iodide*, m. p. 278—279° (decomp.).

2-Methylquinoline ethiodide (2 mols.) reacts with trioxymethylene (1/3 mol.) in presence of sodium (2 mols.) to give a 75% yield of pinacyanol iodide. B. W. ANDERSON.

Condensation of 2-amino-3-methoxybenzaldehyde, its acyl derivatives and quinazolines derived from them. J. TROGER and V. SABEWA (J. pr. Chem., 1927, [ii], **117**, 117—141).—2-Amino-3-methoxybenzaldehyde readily condenses with itself, the best yield of crystalline *anhydrobis*-2-*amino*-3-*methoxybenzaldehyde*, m. p. 265°, possibly

$OMe\cdot C_6H_3<\begin{matrix}CHO\\N{:}CH\cdot C_6H_3(OMe)\cdot NH_2\end{matrix}$ or

$OMe\cdot C_6H_3\cdot N{:}CH\cdot C_6H_3(OMe)$ / $CH(OH)\text{—}NH$ being by keeping its solution in acetic acid for 12—15 hrs. The same product is obtained in an amorphous form in the preparation of various of the acyl derivatives described below. When the aldehyde is heated for a long time in benzene solution with ethyl chloroformate, *anhydrotris-2-amino-3-methoxybenzaldehyde*, m. p. 259°, possibly

$OMe\cdot C_6H_3<^{CHO}_{N{:}CH\cdot C_6H_3(OMe)N{:}CH\cdot C_6H_3(OMe)\cdot NH_2}$

$OMe\cdot C_6H_3\cdot N{:}CH\text{—}C_6H_3\cdot OMe$ / $CH[NH\cdot C_6H_3(OMe)(CHO)\cdot NH$ i b-

tained as a dark yellow powder. Either product is reconverted into the original aldehyde (isolated as its chloroplatinate) by hot concentrated hydrochloric acid, but subsequent treatment with phenylhydrazine yields a *phenylhydrazone*, m. p. 190°, of the bis- or tris-compound. A series of acyl derivatives of 2-amino-3-methoxybenzaldehyde has been prepared, the method varying somewhat from case to case. By the action of acetic anhydride in ether is obtained 2-*acetamido*-, m. p. 156° (*phenylhydrazone*, m. p. 214°); the action of butyric anhydride for 2 hrs. at 100° yields 2-*butyramido*-, m. p. 100° (*phenylhydrazone*, m. p. 165°); 2-*benzamido*-, m. p. 115° (*phenylhydrazone*, m. p. 166°), is obtained by the action of benzoyl chloride on a suspension of the aldehyde in potassium hydrogen carbonate solution, whilst by the Schotten–Baumann method using the appropriate acid chloride are obtained 2-*phenylacetamido*-, m. p. 98° (*phenylhydrazone*, m. p. 194°) [which on treatment with alcoholic potassium hydroxide solution yields 2-hydroxy-8-methoxy-3-phenylquinoline (Troger and Gero, A., 1926, 1045)]; 2-*toluoylamido*-, m. p. 150° (*phenylhydrazone*, m. p. 180°); 2-o-*chlorobenzamido*-, m. p. 140° (*phenylhydrazone*, m. p. 212°); 2-(2 : 4)-*dichlorobenzamido*-, m. p. 161° (*phenylhydrazone*, m. p. 225°); and 2-p-*bromobenzamido*-, m. p. 134° (*phenylhydrazone*, m. p. 192°) -3-*methoxybenzaldehyde*. It was not found possible to prepare the 2-*p*-nitrobenzamido-compound, the only product obtained by the action of *p*-nitrobenzoyl chloride being the condensation product of the aldehyde, m. p. 265°. These acyl derivatives, on treatment with alcoholic ammonia, yield 8-methoxyquinazoline derivatives in accordance with the scheme $OMe\cdot C_6H_3(CHO)\cdot NH\cdot COR+NH_3=$

$OMe\cdot C_6H_3<^{CH.N}_{N\text{—}CR}+2H_2O$, and thus from the appropriate acyl derivative are obtained 2-*methyl*-, m. p. 128° (*chloroplatinate*; *chloromercurate*, m. p. 140°; picrate, m. p. 118°); 2-n-*propyl*-, m. p. 60° (*chloroaurate*, m. p. 116°; *picrate* $+2H_2O$, m. p. 140°); 2-*phenyl*-, m. p. 99° (*chloroplatinate* $+1{\cdot}5H_2O$; *picrate*, m. p. 178°; *perchlorate*); 2-*benzyl*-, m. p. 88°; 2-p-*tolyl*-, m. p. 70° (*chloroplatinate* $+4H_2O$; *picrate*, m. p. 169°); 2-o-*chlorophenyl*-, m. p. 118° (*chloroplatinate*; *chloromercurate*); 2-(2 : 4-)-*dichlorophenyl*-, m. p. 132° (*picrate*, m. p. 105°); 2-p-*bromophenyl*-, m. p. 127° (*picrate*, m. p. 129°; *chloromercurate*) -8-*methoxyquinazolines*. J. W. Baker.

Triazoles. VII. Substituted 1-phenyl-3 : 5-dimethyl-1 : 2 : 4-triazoles. F. Hernler (Monatsh., 1927, **48**, 391—403).—1-*p*-Bromophenyl-3 : 5-dimethyl-1 : 2 : 4-triazole, m. p. 93—94° (picrate, m. p. 166—167°) (cf. Hernler and Matthes, this vol., 468), is prepared in good yield from 3 mols. of diacetamide and 1 mol. of *p*-bromophenylhydrazine. It is also obtained by the usual method from the corresponding amino-compound, which in turn is prepared from the bromo-derivative by the action of ammonia in presence of copper bronze. 1-p-*Cyanophenyl*-3 : 5-*dimethyl*-1 : 2 : 4-*triazole*, m. p. 68—70° (*picrate*, m. p. 143·5—144°), is hydrolysed by alcoholic potassium hydroxide to 1-*phenyl*-3 : 5-*dimethyl*-1 : 2 : 4-*triazole*-4′-*carboxylic acid*, m. p. 293—294°. This acid is also obtained from the bromo-compound by the action of cuprous potassium cyanides (cf. Rosenmund and Struck, A., 1920, i, 44), but not by the action of magnesium and carbon dioxide.

H. Burton.

7 : 9-Dimethyl-[$\Delta^{3:4}$-]*iso*uric acid. H. Biltz and H. Bulow (Annalen, 1927, **457**, 103—131).—8-Thio-7 : 9-dimethyl-*ψ*-uric acid (Biltz and Bulow, A., 1922, i, 381) dissolves in sodium hydrogen carbonate solution with evolution of carbon dioxide; after cooling with ice, iodine is added, whereupon carbon dioxide is again evolved, and 7 : 9-*dimethyl*-$\Delta^{3:4}$-*isouric acid*, decomp. 262—263°, separates. This gives a strong murexide reaction. The *dihydrate*, *monohydrate*, *anhydride* (all of the above decomp. temperature), *hydrochloride* (darkens from 270°, decomp. 350—360°, easily hydrolysed by water), *nitrate* (decomp. 130°), *perchlorate* (probably $C_7H_8O_3N_4,HClO_4,2H_2O$), and *hydrogen sulphate* (sinters at about 190°), *potassium* salt ($C_7H_7O_3N_4K,H_2O$), *sodium*, *ammonium*, and *lead* salts are described.

Attempts to determine the position of the replaceable hydrogen atom by the action of methyl sulphate or of methyl iodide on the salts give no crystallisable product, whilst diazomethane has no action on the free dimethyl*iso*uric acid. Oxidation by chromic acid yields dimethylparabanic acid: the methylated glyoxaline ring is more resistant than the unsaturated pyrimidine ring. 7 : 9-Dimethyluric acid yields the same product.

Dimethyl*iso*uric acid is not reduced by ordinary reducing agents even at high temperatures. Zinc and hydrochloric acid give oily products. Chlorine and water cause oxidation to 7 : 9-dimethyluric acid glycol, or, in presence of alcohol, to the dimethyl ether of the glycol.

A boiling solution of sodium 7 : 9-dimethyl*iso*urate with hydrochloric acid yields 7 : 9-dimethyluric acid; this transformation does not occur when acetic acid is used, nor when the solution is well cooled during acidification. Treatment of the acid with hydrochloric acid in a sealed tube has the same action; on boiling with water, however, only one fifth of the theoretical yield of dimethyluric acid is obtained, the rest decomposing.

The action of organic acids on 7 : 9-dimethyl*iso*uric acid causes a new condensation. The hydrocarbon radical of the acid becomes attached to the 4-carbon atom, and hydrogen to the 3-nitrogen atom, carbon dioxide being evolved. It is suggested that the first product is a 4-hydroxy-3-acyl derivative, which then inverts thus: $\cdot N{:}C< \longrightarrow \cdot N(COR)\cdot C(OH)< \longrightarrow \cdot NH\cdot CR<+CO_2$. This is thought to be more probable

than the intermediate formation of ·NH(CO_2R):C· (cf. the formation of 8-alkylxanthines by the action of acid anhydrides on uric acid; Biltz and Schmidt, A., 1923, i, 489).

When formic acid is used, the group R becomes hydrogen and the acid is reduced. Thus on boiling the dihydrate with 80% formic acid, 7 : 9-*dimethyl*-4 : 5-*dihydrouric acid*, sintering from 250°, decomp. 268°, is obtained. A *sodium* salt is prepared; although the substance is soluble in hydrochloric acid, no hydrochloride can be isolated, in agreement with the absence of an unsaturated tertiary nitrogen atom. Oxidation by chromic acid yields a substance which may be *formylmethylbiuret*, CHO·NH·CO·NH·CO·NHMe, m. p. 250° (decomp.), and dimethylparabanic acid; by chlorine water, amorphous products are obtained.

Dimethyl*iso*uric acid dihydrate in hot acetic acid gives, with evolution of carbon dioxide, 4 : 7 : 9-*trimethyl*-4 : 5-*dihydro*i*souric acid*, decomp. 250°, soluble in alkali without change on acidification, soluble in hydrochloric acid. As the murexide reaction is not given, a methyl group is considered to be present in the 4-position; chromic acid oxidation yields the same products as 7 : 9-dimethyl-4 : 5-dihydro*iso*uric acid.

Dimethyl*iso*uric acid when heated with benzoic acid at 150—160° gives, with another substance, m. p. 241—244°, 4-*phenyl*-7 : 9-*dimethyl*-4 : 5-*dihydrouric acid*, m. p. 244° (decomp.), which is only slightly soluble in sodium hydroxide solution, gives no murexide reaction, and is not reduced by hydriodic acid. In accordance with the formulation, dimethylparabanic acid cannot be obtained by oxidation.

The above dimethyldihydrouric acids on heating with sodium hydroxide solution evolve ammonia, and by fission of the pyrimidine ring are converted into glyoxalonecarboxylic acids. Thus 7 : 9-dimethyl-4 : 5-dihydrouric acid gives 1 : 3-*dimethylglyoxalone*-5-*carboxylic acid*, sintering from 205°, decomp. 220° (*silver* salt, from which the *methyl* ester, m. p. 127°, is obtained, although unobtainable from the acid by the action of methyl alcohol and hydrogen chloride). This is oxidised by chromic acid to dimethylparabanic acid, and on distillation gives 1 : 3-*dimethylglyoxalone*, m. p. about 100°, which becomes oily in contact with water, and forms a hygroscopic hydrochloride. Heating the o-carboxylic acid with hydrochloric acid gives, however, other decomposition products.

1 : 3-Dimethylglyoxalone in water, alcohol, or acetic acid gives with bromine a dark violet coloration, turning red and then yellow on further addition of bromine. Chromic acid oxidation yields dimethylparabanic acid. Attempted catalytic hydrogenation was unsuccessful, as was an attempt to isolate s-diformyldimethylcarbamide from the products of nitric acid oxidation.

4 : 7 : 9-Trimethyl-4 : 5-dihydrouric acid yields 1 : 3 : 4-*trimethylglyoxalone*-5-*carboxylic acid*, decomp. 179° (*silver* salt, decomp. 182°, yielding a *methyl* ester, m. p. 88—89°, unobtainable from the acid). The acid easily loses carbon dioxide in water at 100° to give 1 : 3 : 4-*trimethylglyoxalone*, b. p. about 210°. Attempted catalytic hydrogenation failed, as did oxidation by nitric acid, which gave syrupy products.

4-Phenyl-7 : 9-dimethyl-4 : 5-dihydrouric acid yields with sodium hydroxide 4-*phenyl*-1 : 3-*dimethylglyoxalone*-5-*carboxylic acid*, decomp. 217—218° (*silver* salt, decomp. 195°, giving a *methyl* ester, m. p. 124°), which when heated with aqueous or alcoholic hydrochloric acid gives 4-*phenyl*-1 : 3-*dimethylglyoxalone*, m. p. 92° (*hydrochloride*, m. p. 93—94°). This is oxidised by nitric acid in acetic acid to N-*formyl*-N′-*benzoyl*-NN′-*dimethylcarbamide*, m. p. 115° (decomp.), and is converted by chromic acid into 5-*hydroxy*-5-*phenyl*-1 : 3-*dimethylhydantoin*, m. p. 115—118°. The latter is reduced by hydriodic acid to 5-phenyl-1 : 3-dimethylhydantoin, m. p. 105—106° (cf. Gabriel, A., 1907, i, 91). E. W. WIGNALL.

3 : 9-Dimethyl-$\Delta^{5:7}$-*iso*uric acid, its chlorination products and degradation. H. BILTZ and H. KRZIKALLA [in part with K. SLOTTA] (Annalen, 1927, 457, 131—139).—Experiments on the chlorination of 3 : 9-dimethyluric acid (Biltz and Krzikalla, A., 1921, i, 614) gave under very similar conditions varied products. Continuing this work, a 3 : 9-*dimethyl*-$\Delta^{5:7}$-iso*uric acid* has been prepared by reduction of the chloro-derivatives, the structure of which has been established. By degradation, hydantoins are obtained, including one with a new fused ring system, a hydantoinohydantoin.

The preparation of 3 : 9-dimethyluric acid by methylation of dipotassium urate is improved at all stages. For the methylation, methyl toluene-*p*-sulphonate is now employed, at atmospheric pressure in *o*-dichlorobenzene at 145—155°, and much of the decomposition caused by methyl sulphate is thus avoided, improved yields being obtained.

There are three main products of chlorination, according to the conditions.

(1) Chlorination in acetic acid, followed by removal of chlorine in a current of air and precipitation by ether, gives 4-*chloro*-3 : 9-*dimethyl*-$\Delta^{5:7}$-iso*uric acid*, (I), which (+0·5AcOH) sinters from 70° to 80°, and then decomposes, and gives a strong murexide reaction. This on treatment with water yields 3 : 9-dimethyluric acid glycol, and in methyl and ethyl alcohols the corresponding dialkyl ethers (*loc. cit.*). By reduction with hydriodic acid, the original 3 : 9-dimethyluric acid is obtained. Other reducing agents yield a different product (see below). By the action of hydrogen chloride in acetic acid, 1 : 7-dimethyl*spiro*dihydantoin (*loc. cit.*) is formed.

Similarly 1-acetyl-3 : 9-dimethyluric acid (*loc. cit.* : the method of preparation has been improved) chlorinates to the 4-*chloro*-derivative, decomp. 205°. This, which is remarkably stable to water and to alcohol, liberates iodine from potassium iodide solution, and gives on reduction 3 : 9-dimethyluric acid. The formulation is confirmed by the production of methylamine on heating with sodium hydroxide solution, and of 4-*hydroxy*-3 : 9-*dimethyl*-$\Delta^{5:7}$-iso*uric acid*, m. p. 265—267°, by hydrolysis with 30% acetic acid. The hydroxy-compound is converted by diazomethane into tetramethyl*spiro*dihydantoin, with the probable intermediate formation of the 5 : 7-glycol.

That the acetyl group in acetyldimethyluric acid is in the 1-position is confirmed by implication in the above reaction, for the shifting of the double linking from

the 4 : 5- to the 5 : 7-position is probably due to addition of chlorine at the 5- as well as at the 4-position (see also II, below), followed by loss of hydrogen chloride by removal of the 7-hydrogen atom, which would not be possible if acetyl were present at the 7- instead of at the 1-position. A definite proof is, however, given by methylation: by the action of methyl sulphate and sodium hydroxide solution, followed by removal of the acetyl group by heating in absence of methyl sulphate, 3 : 7 : 9-trimethyluric acid is obtained.

(2) Chlorination of 3 : 9-dimethyl-$\Delta^{5:7}$-*iso*uric acid in a similar manner, using carefully dried materials, gives on slow crystallisation, instead of precipitation by ether, 4 : ɔ-*dichloro*-3 : 9-*dimethyl*-4 : 5-*dihydrouric acid* (II), decomp. (+0·5AcOH) from 210° to 230°, with some 1 : 7-dimethyl*spiro*dihydantoin. The dichloro-compound does not react with cooled methyl alcohol, and gives no murexide reaction. It is reduced by zinc and acetic acid to 3 : 9-dimethyluric acid; attempted removal of hydrogen chloride to give an *iso*uric acid gave no crystalline product. The substance was at first thought to be 4 : 7-dichloro-3 : 9-dimethyl-4 : 5-dihydrouric acid, which formulation would make the formation of a hydantoin derivative (see later) more easily understood; this formula was, however, discarded.

(3) Chlorination in acetic anhydride, or in an equal mixture of the anhydride and the acid, gives 4-*chloro*-5-*acetoxy*-4 : 9-*dimethyl*-4 : 5-*dihydrouric acid* (III) (sintering from 190° to 200°, followed by decomposition), also obtainable by the action of acetic anhydride on I. The new substance reacts with alcohol, but no product has been isolated; it gives no murexide reaction. Reduction by zinc and acetic acid yields 3 : 9-dimethyluric acid.

Similarly 1-acetyl-3 : 9-dimethyluric acid yields its 4-*chloro*-5-*acetoxy*-derivative, decomp. 168—170°, also obtainable from the 4-chloro-derivative.

All chlorination products in the above three groups (the usual starting material being the dichloride) are reduced by potassium iodide and sodium thiosulphate to 3 : 9-*dimethyl*-$\Delta^{5:7}$-iso*uric acid*, $\begin{matrix}\mathrm{NH{\cdot}CO{-}C{:}N{\cdot}CO}\\ \mathrm{CO{\cdot}NMe{\cdot}CH{-}NMe}\end{matrix}$ (IV), decomp. 418—420°, the same temperature as that of 3 : 9-dimethyluric acid, into which it inverts. The new acid is distinguished from the latter by giving no murexide reaction, whether treated with nitric acid or with chlorine water. By hydrolysis with barium hydroxide solution, or with dilute mineral acids (in which its solubility is a characteristic), methylamine is produced, and a substance described below. Diazomethane causes no methylation, although nitrogen is evolved (cf. acetylcarbamide, which behaves similarly). Unlike 3 : 9-dimethyluric acid, the *iso*-acid crystallises without water; it reduces ammoniacal silver nitrate solution. The solid has d_4^{23} 1·591 (L. Klemm); the mol. vol. is thus 123·2 c.c., 1·6 c.c. greater than that of the stable 3 : 9-dimethyluric acid (Klemm and Klemm, this vol., 498).

Reduction of 4-chloro-5-acetoxy-3 : 9-dimethyl-4 : 5-dihydrouric acid gives an acetoxycarbamylmethylhydantoin (see below).

3 : 9-Dimethyl-$\Delta^{5:7}$-*iso*uric acid forms a loosely combined *hydrochloride*, a *hydrotri-iodide*, $C_7H_8O_3N_4,HI_3$, decomp. 107°, and a *perchlorate*, in agreement with its possession of the $-C{:}N{\cdot}C-$ grouping.

3 : 9-Dimethyl-$\Delta^{5:7}$-*iso*uric acid is oxidised by hydrogen peroxide on the water-bath to ammonium methyloxalurate (Slotta, A., 1925, i, 1189). At the ordinary temperature, an intermediate substance, regarded as 4 : 5-*dihydroxy*-4-α-*methylcarbamido*-3-*methyl*-2-*glyoxalidone*, decomp. 175—180°, is formed; this on heating with acetic anhydride yields an *isomeride* (?), m. p. 226°.

The inversion of the *iso*-acid to 3 : 9-dimethyluric acid, which occurs on melting, is produced on heating at 310—320°, or on heating with acetic or formic acid. The inversion in presence of acetic acid explains the formation of dimethyluric acid when the above chloro-derivatives are reduced by zinc and acetic acid. The action of chlorine upon the *iso*-acid in methyl alcohol yields 4 : 5-dichloro-3 : 9-dimethyldihydrouric acid, free from acetic acid, darkening from 200°, decomp. about 310°.

Degradation of the above chloro-derivatives yields a substance $C_5H_7O_4N_3$, possibly as the result of inversion with rupture of the pyrimidine ring, to give a carbamylhydantoin (cf. following abstract for synthesis). Thus 4 : 5-dichloro-3 : 9-dimethyldihydrouric acid dissolves slowly in boiling water, with the evolution of carbon dioxide and separation of methylamine hydrochloride to form 5-*hydroxy*-1-*carbamyl*-3-*methylhydantoin*, $\begin{matrix}\mathrm{CH(OH){\cdot}N{\cdot}CO{\cdot}NH_2}\\ \mathrm{CO{\cdot}NMe{\cdot}CO}\end{matrix}$ (V), decomp. 216—217°, resolidifying at 230°, decomp. 235°, b. p. about 200°/20 mm. (?), which crystallises out on cooling. The same substance is obtained from 4-chloro-3 : 9-dimethyl*iso*uric acid, or from 3 : 9-dimethyl*iso*uric acid itself by passing chlorine into a suspension in water. This substance gives no murexide reaction; it is unaltered by boiling water, by hydrochloric acid, by concentrated sulphuric acid, by boiling aniline or nitrobenzene, by gentle heating with hydriodic acid or hydrochlorostannic acid, by diazomethane or by nitrous acid; it is oxidised, however, by ammoniacal silver nitrate solution. Attempts to prepare a derivative by action of benzoic anhydride or benzoyl chloride were unsuccessful, as were those to induce reaction with phenyl- or methyl-carbimide.

The hydantoin (V) on heating in a flame gives the acrid odour of cyanic acid; it is oxidised by chromic acid to methylparabanic acid, and reduced by fuming hydriodic acid in presence of phosphonium iodide at 100° to 1-carbamyl-3-methylhydantoin (see below), and 3-methylhydantoin.

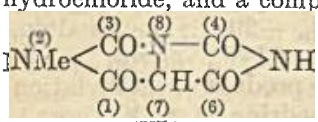
5-*Acetoxy*-1-*carbamyl*-3-*methylhydantoin*, m. p. 212—215° (slight decomp.), is obtained by acetylation of the hydroxy-compound in boiling acetic anhydride, or by treating 4-chloro-5-acetoxy-3 : 9-dimethyl-4 : 5-dihydrouric acid (in the reduction of which, above, it is formed as a by-product) with boiling water, or, better, with 50% acetic acid. The acetoxy-compound is hydrolysed by concentrated sulphuric acid, is oxidised to methylparabanic acid, and reduced to 1-carbamyl-3-methylhydantoin.

The compound (V) is nitrated by fuming nitric acid to ɔ-*hydroxy*-1-*nitrocarbamyl*-3-*methylhydantoin*, m. p.

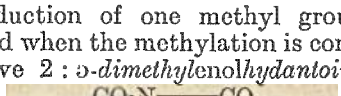
180°, reduced to 3-methylhydantoin more easily than the parent substance.

Degradation of (V) by treatment with barium hydroxide solution gives a *barium* salt, which on dissolving in hydrochloric acid and precipitating the barium as sulphate, yields oxalic acid; whilst treatment with sodium hydroxide solution, followed by acidification and addition of phenylhydrazine, gives glyoxylic acid phenylhydrazone. The filtrate from the above barium salt yields ω-methylbiuret (cf. Biltz and Jeltsch, A., 1923, i, 1074). The hydantoin ring has thus been broken between the 3- and the 4-, and between the 5- and the 1-positions.

Degradation of 3 : 9-dimethyl-$\Delta^{5:7}$-*iso*uric acid by dilute acids yields, as mentioned above, methylamine hydrochloride, and a compound $C_6H_5O_4N_3$. This, to which is ascribed formula (VI), and the name 2-*methylhydantoinohydantoin*, decomp. 262°, is considered to be formed by rupture of the linking between the 3- and 4-positions, to give NHMe·CO·NH·C:N·CO / OH·CH–NMe, which then loses methylamine, hydrogen being lost from the 4-position in the hydantoin ring, the 2-carbonyl group of the original *iso*uric acid becoming attached to the 1-nitrogen of the hydantoin ring. The product thus consists of two hydantoin rings fused in the 1 : 5-positions. The substance in aqueous solution is neutral to indicators; when, however, it is treated with sodium hydroxide solution, and the excess is titrated, it behaves as a dibasic acid. This is attributed to the opening of the rings to give N-*carbamyl*-N-*methylcarbamylaminomalonic acid*, NHMe·CO·N(CO·NH_2)·$CH(CO_2H)_2$.



(VI.)

The methylhydantoinohydantoin is oxidised by hydrogen peroxide to 5-hydroxy-1-carbamyl-3-methylhydantoin. The action of diazomethane causes the introduction of one methyl group, followed by a second when the methylation is continued for 10 days, to give 2 : 5-*dimethylenolhydantoinohydantoin methyl ether*,  (VII), m. 198—200°, changing after resolidification to a substance, $C_7H_{11}O_3N_3$ (?), m. p. 232—234°.

Demethylation of (VII) by hydriodic acid not giving isolable products, hydrochloric acid was employed. This gives, in very small yield, a substance which is probably the *methyl ether* of the *enol* form of 1-methylcarbamyl-3-methylhydantoin, OMe·C:CH·N·CO·NHMe / NMe–CO m. p. 128—138° (see following abstract); or, in two experiments, the desired 2 : 5-*dimethylhydantoinohydantoin*, m. p. 272°. This is also obtained, very slowly, by hydrolysis by boiling water: the rate of evolution of carbon dioxide and of methylamine in this case is shown graphically, and in one experiment is stopped at the stage of 1-methylcarbamyl-3-methylhydantoin.

Similar hydrolysis of 2-methylhydantoinohydantoin by boiling water yields 1-*carbamyl*-3-*methylhydantoin*, m. p. 250°, or after purification by heating with hydriodic acid, 258—260°. This substance is also obtained directly by the action of boiling 2*N*-hydrochloric acid on 3 : 9-dimethyl*iso*uric acid, or by the action of fuming hydriodic acid to which a small quantity of water and some phosphonium iodide are added, or from 5-hydroxy-1-carbamyl-3-methylhydantoin, in which case some 3-methylhydantoin is formed as a by-product. Chromic acid prepared from potassium dichromate and sulphuric acid has no action, but when chromium trioxide dissolved in acetic acid is used, methylparabanic acid is obtained. Reduction by fuming hydriodic acid yields 3-methylhydantoin.

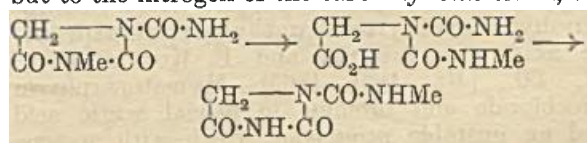
The product of the nitration of 1-carbamyl-3-methylhydantoin by fuming nitric acid is the 1-*nitrocarbamyl* derivative, m. p. 170°, reduced more readily to 3-methylhydantoin by hydriodic acid than is the parent substance.

The action of barium hydroxide solution gives a *barium* salt; that of 2*N*-sodium hydroxide solution gives, however, the *sodium* salt of an isomeride, $C_5H_6O_3N_3Na,2H_2O$, decomp. 278—280°, converted by hydrochloric acid into a substance, $C_5H_7O_3N_3$ (1-*methylcarbamylhydantoin*, cf. following abstract), m. p. 255° (decomp.), giving with barium hydroxide solution a *barium* salt. The isomeride cannot be reconverted into 1-carbamyl-3-methylhydantoin by acids. E. W. Wignall.

Carbamyl derivatives of hydantoins and their inversion. H. Biltz and (Frl.) D. Heidrich (Annalen, 1927, 457, 190—208).—The 1-carbamyl-3-methylhydantoin described by Biltz and Krzikalla (preceding abstract) is synthesised by the action of carbamyl chloride on 3-methylhydantoin. The former is prepared from cyanuric acid, the latter from 9-methyluric acid glycol by reduction, or from allantoin by methylation and reduction, or from hydantoin and methyl sulphate (Biltz and Slotta, A., 1926, 1045). The reaction does not take place in presence of solvents, but on heating the 3-methylhydantoin with carbamyl chloride prepared *in situ*, in a U-tube, hydrogen chloride is evolved and the 1-carbamyl derivative, m. p. 250—252°, or, after purification by hydriodic acid, 258—260°, is obtained. This has the same reactions as the sample prepared from 2-methylhydantoinohydantoin (preceding abstract).

On treatment with 2*N*-sodium hydroxide solution, the isomeride (1-methylcarbamylhydantoin), m. p. 255° (decomp.), previously described, is obtained. This is oxidised by chromium trioxide in acetic acid to parabanic acid, showing that the methyl group is no longer in the 3-position.

This suggested that the inversion might be due to opening of the hydantoin ring by hydrolysis, followed by lactam formation, not to the original 2-nitrogen, but to the nitrogen of the carbamyl side-chain, thus:



(cf. the inversion of 2-imino-1 : 3-diphenylparabanic acid under the action of sodium alkoxide to give 2-anilo-1-phenylparabanic acid, Dieckmann and Kämmerer, A., 1907, i, 979).

Reduction was not brought about by hydriodic acid, whilst the fuming acid gave no isolable product.

In the hope that a nitro-derivative would, as before, be more easily reduced, nitration was attempted, but without success. Methylation of the sodium salt by methyl sulphate yields 1-*methylcarbamyl*-3-*methylhydantoin*, m. p. 128—130°, also, and better, obtainable by the action of an ethereal diazomethane solution; the product is oxidised by chromium trioxide in acetic acid to methylparabanic acid, showing that the 3-position is again substituted by methyl. Attempted synthesis by heating 3-methylhydantoin with methylcarbimide was unsuccessful. When, however, hydantoin itself is heated in a sealed tube with methylcarbimide, 1-methylcarbamylhydantoin is obtained.

1-*Carbamyl*-3-*ethylhydantoin*, m. p. 205—208°, is obtained by the action of carbamyl chloride on 3-ethylhydantoin, prepared from 9-ethyluric acid glycol. The product gives with fuming nitric acid 1-*nitrocarbamyl*-3-*ethylhydantoin*, m. p. 99°. On treatment with 2*N*-sodium hydroxide solution, the *sodium* salt, m. p. 125°, of 1-*ethylcarbamylhydantoin*, m. p. 185—187°, is obtained; this is oxidised to parabanic acid, is synthesised by the action of ethylcarbamyl chloride (prepared from *s*-diethylcarbamide) on hydantoin, and is methylated by diazomethane to 1-*ethylcarbamyl*-3-*methylhydantoin*, m. p. 93—94°. The isomeric 1-*methylcarbamyl*-3-*ethylhydantoin*, m. p. 91—92°, is obtained by heating 3-ethylhydantoin with methylcarbimide, and gives a *sodium* salt, decomp. from 40°; by the action of fuming nitric acid, a *nitro*-derivative, $C_7H_{10}O_5N_4$ (?), m. p. 91—92°, is obtained. E. W. WIGNALL.

Synthesis of a substance resembling porphyrin. W. KÜSTER and G. KOPPENHÖFER (Ber., 1927, **60**, [*B*], 1778—1781).—Ethyl 3 : 5-dimethylpyrrole-2 : 4-dicarboxylate is converted by hydrogen peroxide and hydrochloric acid in presence of glacial acetic acid into a *substance*, $C_{12}H_{13}O_4NCl_4$, m. p. 166° after softening at 150°, decomp. 170°; the analogous *bromo*-derivative, $C_{12}H_{15}O_4NBr_2$, m. p. 131°, decomp. 180°, is similarly prepared. 4-Carbethoxy-3 : 5-dimethylpyrrole-2-carboxylic acid, hydrobromic acid, and hydrogen peroxide yield the *compound* $C_{36}H_{34}O_8N_4Br_4$, m. p. 137° (possibly 1 : 3 : 5 : 7-tetracarbethoxy-2 : 4 : 6 : 8-tetrabromomethylporphyrin, but differing in optical properties from known porphyrins). If the dye remains in the solution in which it was prepared for several days, the colour gradually disappears and *carbethoxybromomethylmaleinimide*, m. p. 130° (decomp.), is produced. The production of a bromine-free *substance*, $C_{36}H_{38}O_8N_4$, m. p. 208° after softening at 190°, is occasionally observed during the synthesis. H. WREN.

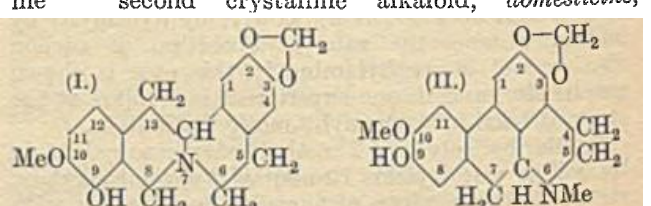
Degradation of hæmatoporphyrin to bromobromohydroxyethyltetramethylporphindipropionic acid. H. FISCHER and F. KOTTER (Ber., 1927, **60**, [*B*], 1861—1865).—Hæmatoporphyrin hydrochloride and bromine in glacial acetic acid afford an unstable *perbromide* which with acetone yields bromoacetone and *bromobromohydroxyethyltetramethylporphindipropionic acid* (*bromoporphyrin* I), $C_{32}H_{30}O_5N_4Br_2$ or $C_{32}H_{32}O_5N_4Br_2$; the *iron*, *cobalt*, *copper*, *nickel*, and *zinc* complex salts are described. It is converted by methyl-alcoholic hydrogen chloride into the *dimethyl* ester, $C_{34}H_{34}O_5N_4Br_2$, m. p. 273°, and oxidised by chromic acid to bromocitraconimide, m. p. 174°. H. WREN.

Manufacture of vat dyes of the 1-thionaphthen-2'-indoleindigo series. I. G. FARBENIND. A.-G.—See B., 1927, 743.

Preparation of arecoline. F. CHEMNITIUS (J. pr. Chem., 1927, [ii], **117**, 147—150).—Details are given for the extraction of arecoline from betel nuts in 500 kg. quantities. The yield of pure hydrobromide is 0·35—0·4%. J. W. BAKER.

***l*-Methylephedrine, an alkaloid from *Ephedra* species.** S. SMITH (J.C.S., 1927, 2056—2059).—The Chinese drug Ma Huang contains, in addition to *d*-ψ- and *l*-ephedrines, a third alkaloid, *l*-methylephedrine, m. p. 87—88° (corr.), $[\alpha]_D$ −29·2° [*hydrochloride*, m. p. 188—189°, $[\alpha]_D$ −29·8°; *methiodide*, m. p. 212—213° (corr.), $[\alpha]_D$ −21·8°; *picrate*, m. p. 144° (corr.)], identical with the product of methylation of *l*-ephedrine. *d*-ψ-Methylephedrine, m. p. 30° (corr.), $[\alpha]_D$ +48·1° [*methiodide*, m. p. 216—217° (corr.); *picrate*, m. p. 152—153° (corr.); *hydrogen tartrate*, m. p. 84° (corr., $+2H_2O$), or 152° (corr., anhyd.)], is obtained by methylation of *d*-ψ-ephedrine. C. HOLLINS.

***iso*Quinoline alkaloids. I. Constitution of nandinine. II. Constitution of domesticine; *iso*domesticine. III. Constitution of coptisine. IV. Worenine. V. Synthesis of some new *iso*quinoline alkaloids. VI. Spectrographic researches.** Z. KITASATO (Acta Phytochim., 1927, **3**, 175—258).—By an improved method of extraction, nandinine, $C_{19}H_{19}O_4N$, (I), the amorphous alkaloid isolated from *Nandani domestica*, Thunb., by Eijkmann (A., 1885, 565), is obtained crystalline, m. p. 145—146°, $[\alpha]_D$ +63·2° in alcohol. It contains one phenolic hydroxyl and one methoxyl group, and gives with diazomethane a racemised methyl ether, m. p. 166°, identical with *dl*-tetrahydroberberine. Under special conditions, *d*-nandinine methyl ether, m. p. 139°, $[\alpha]_D$ +246·73°, identical with *d*-canadine, is obtained. The d-*ethyl ether*, m. p. 109°, obtained by the action of diazoethane on nandinine, is converted, by oxidation with iodine followed by reduction, into the dl-*ethyl ether*, m. p. 128°. Reduction of berberrubine (Frerichs, A., 1910, i, 500) with zinc and sulphuric acid gives *dl*-tetrahydroberberrubine, m. p. 168°, which is resolved by means of its *d*-bromocamphorsulphonate into *d*-tetrahydroberberrubine, m. p. 144°, $[\alpha]_D$ +62·9°, identical with nandinine, and a little impure *l*-isomeride; *dl*-tetrahydroberberrubine ethyl ether, m. p. 128°, is identical with *dl*-nandinine ethyl ether. The positions of the hydroxyl and methoxyl groups in nandinine must therefore be as in (I). From the residues after extraction of nandinine second crystalline alkaloid, *domesticine*,



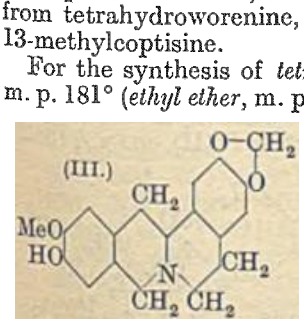
$C_{19}H_{19}O_4N$, m. p. 115—117°, $[\alpha]_D$ +60·51° (*hydrochloride* and *chloroplatinate* described), is isolated,

which also contains a phenolic hydroxyl, a methoxyl, and a methylenedioxy-group, but has the absorption spectrum of a phenanthraquinoline alkaloid (see below). The *methyl ether*, m. p. 139°, $[\alpha]_D$ +101·7° in chloroform, differs from bulbocapnine methyl ether, dicentrine, and synthetic *d-epi*dicentrine, and has probably the *iso*dicentrine structure (II). For the synthesis of dl-epi*dicentrine*, m. p. 119° (*hydrochloride*, m. p. about 147°), *homopiperonylhomoveratrylamine*, m. p. 130—131°, obtained from homopiperonyl chloride and homoveratrylamine, is converted by phosphoryl chloride in toluene into 6 : 7-*dimethoxy*-1-(3′ : 4′-*methylenedioxybenzyl*)-3 : 4-*dihydro*isoquinoline (*methiodide*, m. p. 135—138°), and thence, by reduction of the methochloride, into 6 : 7-*dimethoxy*-1-(3′ : 4′-*methylenedioxybenzyl*)-2-*methyl*-1 : 2 : 3 : 4-*tetrahydro*isoquinoline, m. p. 116° (*sulphate*, m. p. 110°). This is nitrated, giving the 6′-*nitro*-compound, m. p. 151°, and a *substance*, m. p. 198°; the 6′-*amino*-compound, m. p. 110°, by diazotisation and treatment with copper, yields *dl-epi*dicentrine, which is resolved by means of *d*-tartaric acid to give the *d*-compound, m. p. about 110°. Oxidation of domesticine with alkaline permanganate yields 4 : 5-*methylenedioxybenzene*-1 : 2 : 3-*tricarboxylic acid*, m. p. about 170°, thus confirming the structure (II).

The acid mother-liquor, after removal of nandinine and domesticine, contains a third alkaloid, iso-*domesticine*, m. p. 85°, which gives the same methyl ether as domesticine, but a different *ethyl ether*, m. p. 82°. The m. p. of the alkaloids indicate that domesticine is the 9-hydroxy-10-methoxy-compound, *iso*-domesticine the 10-hydroxy-9-methoxy-compound (see II).

Coptis japonica, Mak., contains, in addition to berberine and the yellow alkaloid coptisine already reported (A., 1926, 1160), a new, crystalline alkaloid *worenine*, $C_{20}H_{17}O_5N$ (*hydrochloride*, m. p. 295°), isolated as *tetrahydro*-derivative, m. p. 212—213°, from which it is regenerated by the action of iodine. *Coptisine iodide* decomposes above 280° : the *chloride* is not melted at 300°. Tetrahydrocoptisine, m. p. 217—218° (previously given as 215°), is different from tetrahydro-*ψ*-coptisine (2 : 3 : 10 : 11-bismethylenedioxytetrahydroprotoberberine; Buck, Perkin, and Stevens, A., 1925, i, 958), m. p. 214°, which is synthesised independently by the method of these authors. Tetrahydroworenine yields a N-*methyl* derivative (*hydrochloride*, m. p. 281°; *hydriodide*, m. p. 263°). Since 8-*methyltetrahydrocoptisine*, m. p. 215°, obtained by the action of magnesium methyl iodide on coptisine chloride, followed by reduction, differs from tetrahydroworenine, worenine is most probably 13-methylcoptisine.

For the synthesis of *tetrahydro-ψ-berberrubine* (III), m. p. 181° (*ethyl ether*, m. p. 131°), vanillin is converted by way of the azlactone, m. p. 191° (which on hydrolysis yields α-benzamido-4-hydroxy-3-methoxycinnamic acid, m. p. 210°; cf. Sugii, A., 1921, i, 346), into 4-hydroxy-3-methoxyphenylpyruvic acid, which by condensation with ethyl chloroformate and oxidation with hydrogen peroxide gives *ethylcarbonatohomovanillic acid*, m. p. 138—139°, also prepared by the action of ethyl chloroformate on homovanillic acid, m. p. 140—141°, obtained by oxidation of eugenyl acetate, m. p. 30°, with permanganate in acetone. The acid at 200°, or the corresponding *acid chloride* in benzene, is condensed with homopiperonylamine, and the resulting *homopiperonylamide* is cyclised by means of phosphoryl chloride in toluene to a *dihydro*isoquinoline derivative, which is reduced and hydrolysed to the oily 6 : 7-*methylenedioxy*-1-p-*hydroxy*-m-*methoxybenzyl*-1 : 2 : 3 : 4-*tetrahydro*isoquinoline (*ethyl ether*, m. p. 99°). Condensation of this compound with formaldehyde gives tetrahydro-*ψ*-berberrubine, which on methylation with diazomethane yields tetrahydro-*ψ*-berberine, m. p. 177° (Haworth, Perkin, and Rankine, A., 1924, i, 1098).



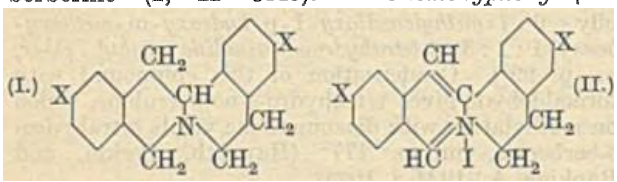
Tetrahydroprotoberberine, m. p. 254—260°, is synthesised by condensing formaldehyde with *tetrahydroprotopapaverine* (*sulphate*, m. p. 174—175°) obtained from dihydroprotopapaverine (Pictet and Gams, A., 1909, i, 671; cf. Rügheimer, A., 1900, i, 522). For the synthesis of its 2 : 3-*methylenedioxy*-derivative, m. p. 169°, phenylacethomopiperonylamide, m. p. 97—98°, is converted into the *dihydro*isoquinoline, reduced to 6 : 7-*methylenedioxytetrahydroprotopapaverine*, m. p. 57°, and condensed with formaldehyde.

Homoveratroyl-β-phenylethylamine, m. p. 105—106°, is described.

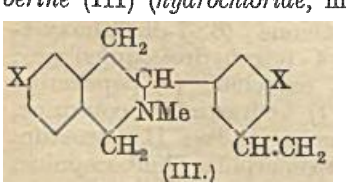
The absorption spectra of 42 alkaloids are examined. Alkaloids of the tetrahydro*iso*quinoline series containing methylenedioxy- or methoxyl groups show a single band at about 3500 Å. Those of the *apo*morphine type in the phenanthraquinoline series show two bands at 3200 and 3650 Å., the former being due to methylenedioxy- or two methoxyl groups in positions 1 : 2, the latter in positions 10 : 11; absence of 1 : 2-substituents results in a flat curve at 3200 Å., whilst 9 : 10-substitution in place of 10 : 11 has a bathochromic effect on the second band. The methylenedioxy-group is rather more bathochromic than two *o*-methoxyl groups. Change from tervalent to quinquevalent nitrogen, especially from carbinol form to ammonium form, exerts a hyper- and bathochromic effect. Absorption spectra curves are given for the following substances: Class I (structure analogous with I): (*a*) Hydrohydrastinine, 6 : 7-methylenedioxytetrahydro-protopapaverine and -protoberberine; (*b*) tetrahydro-berberine, -coptisine, -palmatine, -*ψ*-berberine, -*ψ*-coptisine, -berberrubine, -worenine, -papaverine, 8-methyltetrahydroberberine, *dl*-laudanosine, 6 : 7-dimethoxy-1-*m* : *p*-dimethoxybenzyl-1 : 2 : 3 : 4-tetrahydro*iso*quinoline; (*c*) cryptopine, protopine, hydrastinone (6 : 7-dimethoxy-1-keto-2-methyl-1 : 2 : 3 : 4-tetrahydro*iso*quinoline); (*d*) hydrastine, narcotine, narceine; (*e*) papaverine and its methochloride; (*f*) hydrastinine, cotarnine, berberine, coptisine, worenine; Class II (structure analogous with II): (*a*) *apo*morphine, bulbocapnine, dicentrine, *iso*dicentrine (domesticine methyl ether); (*b*) thebaine; (*c*) morphine, codeine, sinomenine, dihydrosinomenine, dehydrosinomenine. The groups (*a*, *b*, *c*, etc.) within the two main classes indicate closely similar spectra.

C. Hollins.

Synthetical experiments in the *iso*quinoline group. VII. Synthesis of 3 : 11-dimethoxyprotoberberinium salts. VIII. Synthesis of protoberberinium salts. S. N. CHAKRAVARTI, R. D. HAWORTH, and W. H. PERKIN, jun. (J.C.S., 1927, 2265—2274, 2275—2281).—VII. The influence of methoxyl groups on the ease of synthesis of alkaloids of the berberine type has been investigated by the preparation of 3 : 11-dimethoxytetrahydroprotoberberine (I, X=OMe). m-*Methoxyphenyl*-β-m-



methoxyphenylethylamide, an oil, obtained by condensation of β-*m*-methoxyphenylethylamine and *m*-methoxyphenylacetic acid (or the corresponding chloride) yields, when heated with phosphorus oxychloride, 6-*methoxy*-1-(3′-*methoxybenzyl*)-3 : 4-*dihydro*-iso*quinoline*, an oil (*picrate*, m. p. 155°). The *sulphate* of this base is reduced by zinc and sulphuric acid to 6-*methoxy*-1-(3′-*methoxybenzyl*)-1 : 2 : 3 : 4-*tetrahydro*-iso*quinoline*, an oil (*hydrochloride*, m. p. 192°; *sulphate*; *picrate*, m. p. 148°). Condensation of the tetrahydrobase with formic acid affords the N-*formyl* derivative and when heated with phosphorus oxychloride, this undergoes ring closure in what is presumed to be the *para*-position to give 3 : 11-*dimethoxydihydroprotoberberine*, m. p. 130° (*hydrochloride*, $+4H_2O$; *hydriodide*; *picrate*, m. p. 232°). Reduction of this base with zinc dust and sulphuric acid yields 3 : 11-*dimethoxytetrahydroprotoberberine* (I), m. p. 111° [*hydrochloride*; *hydriodide*, m. p. 205°; *picrate*, m. p. 139—140° (decomp.)]. Addition of iodine to a boiling alcoholic solution of (I) in the presence of sodium acetate gives a *periodide* from which is obtained 3 : 11-*dimethoxyprotoberberinium iodide* (II), m. p. 242° (*chloride*, m. p. 200° and $+3H_2O$; *picrate*, m. p. 238°). Treatment of the chloride with hot potassium hydroxide solution yields a mixture of 3 : 11-*dimethoxyoxyprotoberberine*, m. p. 143°, and 3 : 11-dimethoxydihydroprotoberberine, separated by extraction of the latter compound with dilute hydrochloric acid. When (I) is heated with methyl iodide it gives a mixture of α-3 : 11-*dimethoxytetrahydroprotoberberinium methiodide*, m. p. 224° (α-*methochloride*), with the β-*methiodide*, m. p. 245° (decomp.) [β-*methochloride*, m. p. 245° (decomp.)]. Treatment of the mixed methochlorides with alcoholic potassium hydroxide yields *anhydro*-3 : 11-*dimethoxytetrahydroberberine* (III) (*hydrochloride*, m. p. 236°), an oil which



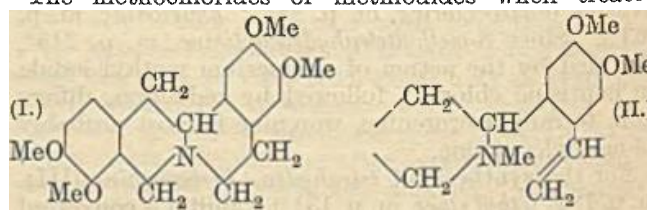
is unchanged by boiling with chloroform or aqueous alcohol but decolorises bromine in chloroform solution or acid permanganate. Base (III), together with some 3 : 11-*dimethoxytetrahydroprotoberberiniummethocarbonate*, m. p. 216°, is the only base obtained by the action of silver hydroxide on the mixed αβ-protoberberinium salts.

VIII. The synthesis of tetrahydroprotoberberine (I) (X=H), the parent substance of the alkaloids in the palmatine–berberine series, has been effected by a group of reactions similar to those described above. The very poor yields obtained in the two stages where ring closure is involved are ascribed to the absence of the methoxyl groupings. 1-Benzyl-1 : 2 : 3 : 4-tetrahydro*iso*quinoline (cf. Forsyth, Kelly, and Pyman, A., 1925, i, 1167) [*sulphate*, $+5H_2O$, $+H_2O$, m. p. 191° (decomp.)] from 1-benzyl-3 : 4-dihydro*iso*quinoline (*sulphate*, m. p. 216°) reacts with anhydrous formic acid to give the N-*formyl* derivative. This compound when treated with phosphorus oxychloride under strictly defined conditions yields dihydroprotoberberine (not isolated), which is reduced with zinc dust and hydrochloric acid to *tetrahydroprotoberberine* (I), m. p. 85° (*hydrochloride*, m. p. 232°; *hydriodide*; *picrate*, m. p. 151°). Compound (I) is oxidised by alcoholic iodine in the presence of sodium acetate to a *periodide*, from which *protoberberinium iodide* (II) (X=H), m. p. 232°, is obtained (*chloride*, $+4H_2O$, $+0{\cdot}5H_2O$; *picrate*, m. p. 192—193°). Treatment of protoberberinium chloride with hot aqueous potassium hydroxide yields *oxyprotoberberine*, m. p. 102°, and dihydroprotoberberine (not isolated). With methyl iodide, tetrahydroprotoberberine gives the α- and β-*methiodides*, m. p. 210° and 230—232°, respectively (*methochloride*). The methiodide with methyl-alcoholic potassium hydroxide gives *anhydromethyltetrahydroprotoberberine* (III) (X=H), an oil (*hydrochloride*, hydrated, m. p. 234—235°), also produced by the action of silver hydroxide on the quaternary salt. This anhydro-compound is unchanged when boiled with methyl alcohol or chloroform or when heated with dilute hydrochloric acid.

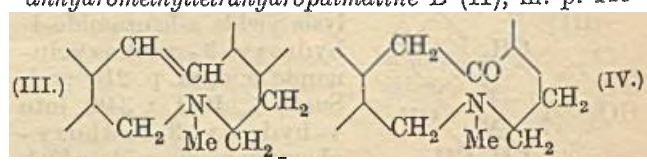
M. CLARK.

Manufacture of derivatives of cinchona alkaloids. C. F. BOEHRINGER and SOEHNE, etc.—See B., 1927, 828.

Conversion of palmatine into its cryptopine analogue (cryptopalmatine). R. D. HAWORTH, J. B. KOEPFLI, and W. H. PERKIN, jun. (J.C.S., 1927, 2261—2265).—Tetrahydropalmatine (I) forms an α-*methiodide*, m. p. 230°, and a less soluble β-*methiodide*, m. p. 266° (decomp.), which are converted into methiodides [α, syrupy; β, m. p. 250° (decomp.)]. The methochlorides or methiodides when treated



with methyl-alcoholic potassium hydroxide give *anhydromethyltetrahydropalmatine B* (II), m. p. 115—

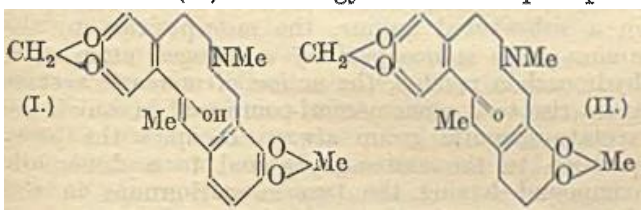


116° [*hydrochloride*, m. p. 210° ($+H_2O$, decomp.)]. The methohydroxide, obtained by the action of

silver hydroxide on the methiodide, when evaporated in a vacuum yields a mixture of this compound with *anhydromethyltetrahydropalmatine A* (III), m. p. 131—132°. The latter, oxidised with perbenzoic acid in chloroform, is converted into the *amine oxide* [*hydrochloride*, m. p. 198—200° (decomp.)], from which *cryptopalmatine* (IV), m. p. 148—150°, is obtained by warming with hydrochloric–acetic acid.

C. HOLLINS.

Alkaloids of *Corydalis cava*. IX. Constitution of corycavine and corycavamine. E. SPATH and H. HOLTER (Ber., 1927, 60, [*B*], 1891—1898; cf. von Bruchhausen and Stippler, this vol., 683).—Corycavine is reduced to dihydrocorycavine and the latter substance is converted into the quaternary *iodide*, $C_{21}H_{22}O_4NI$, m. p. 296—297° (corr.), which, when heated at 260°/0·01 mm., gives a mixture of bases in 50% yield separable by means of their hydrochlorides into two stereoisomeric *substances*, $C_{20}H_{19}O_4N$, m. p. 140° and 203°, respectively. Removal of the methylenedioxy-groups from the base of m. p. 140°, followed by exhaustive methylation of the tetrahydroxy-base thus produced with diazomethane, affords *dl-meso*-corydaline, m. p. 162—163°, whilst similar treatment of the base of m. p. 203° gives *dl*-corydaline, m. p. 135—136°. The results show that corycavine has the structure of corydaline if its protopine-like constitution is taken into account and confirm in its essentials the formula (I) proposed by Gadamer and von Bruchhausen. The authors, however, prefer the ketonic form (II) in analogy with other protopine



alkaloids and also because corycavine does not evolve methane when heated with magnesium methyl iodide. The conversion of corycavamine above its m. p. into corycavine, regarded by Gadamer and von Bruchhausen as a transformation of the ketonic into the enolic form, is considered by the authors as a case of simple racemisation and corycavamine as the optically active form of corycavine. Oxidation of corycavine in dilute aqueous solution at the atmospheric temperature with potassium permanganate gives a mixture of crystalline acids from which hydrastethylimide, m. p. 167°, and 3 : 4-*methylenedioxybenz*-1 : 2-*dicarbonethylimide*, m. p. 125°. Synthesis of the latter compound is effected by the oxidation of 3 : 4-methylenedioxyphthalide dissolved in potassium hydroxide by permanganate and conversion of the dicarboxylic acid into the ethylimide.

H. WREN.

Yohimbine. A. SCHOMER (Arch. Pharm., 1927, 265, 500—524).—Analyses of the free base, m. p. 231—232°, agree with the formula $C_{22}H_{28}O_3N_2$ (cf. Barger and Field, A., 1915, i, 835), but the *hydrochloride*, *hydrobromide*, *hydriodide*, and *nitrate*, m. p. 269—270°, agree with the formula $C_{21}H_{26}O_3N_2$, as do analyses of yohimboaic acid, m. p. 258—259°, and its hydrochloride. Yohimbine is converted by acetic anhydride and sodium acetate into *diacetylyohimbine* m. p. 183° (*hydrochloride*, $3H_2O$, $[\alpha]_D^{20}$ −7·5°), and an amorphous *monoacetylyohimbine*, m. p. about 150° (*chloroaurate*, blood-red, m. p. 170°), indicating the presence of a secondary nitrogen atom. Oxidation with mercuric acetate produces a mercury *derivative* but neither this nor the demercurated oxidation product was obtained crystalline. The latter on reduction gives the original dextrorotatory yohimbine, together with a sparingly soluble isomeride, *l-yohimbine*, m. p. 253—254° (*hydrochloride*, $[\alpha]_D^{20}$ −27·22°). The alkaloid reacts with bromine water to give mono- and di-bromoyohimbines, described by Barger and Field, the analyses agreeing with $C_{21}H_{25}O_3N_2Br,HBr$ and $C_{21}H_{24}O_2N_2Br_2,HBr$, respectively. Ring scission of yohimbine cannot be effected by treating the methiodide, m. p. 249—250°, or the methochloride with sodium hydroxide or amalgam and alcohol. Yohimbine is reduced by sodium and alcohol to *yohimbyl alcohol*, m. p. 202°, or $+2H_2O$, m. p. 148—149° (*hydrochloride*, $[\alpha]_D^{20}$ +37·5°). The ring in yohimbyl alcohol is extremely stable, since the *methiodide*, m. p. 215°, is unaffected by alkalis, the *methochloride* by sodium amalgam and alcohol, and the methiodide on distillation gives methyl and yohimby alcohols. Cyanogen bromide reacts with yohimbine, giving 70% of yohimbine hydrobromide, $[\alpha]_D^{20}$ +52·22°, and an amorphous *substance*, m. p. 70—80°, $[\alpha]_D^{20}$ −26·61°. It is concluded, therefore, that yohimbine contains a tetrahydroquinoline ring (cf. von Braun, A., 1907, i, 899; 1917, i, 169; 1918, i, 185).

S. COFFEY.

Preparation of homatropine. F. CHEMNITIUS (J. pr. Chem., 1927, [ii], 117, 142—146).—Full experimental details are given for isolating tropic acid and tropine from the mother-liquors in the preparation of atropine (Chemnitius, B., 1927, 669) in kilogram quantities, by hydrolysis with barium hydroxide. The isolated tropine is then converted, by treatment with mandelic acid in aqueous hydrochloric acid solution, into homotropine, which is purified by conversion into its hydrobromide, etc. The preparation of homotropine hydrochloride, sulphate, and salicylate is also described.

J. W. BAKER.

Alkaloids of *Aconitum Stoerckianum*, Reichenbach. H. SCHULZE and G. BERGER (Arch. Pharm., 1927, 256, 524—541).—The alkaloids are similar to those of *Aconitum napellus*, L., the chief constituent being identical or isomeric with aconitine and the minor constituent neopelline (A., 1925, i, 282). The crude alkaloid mixture was separated into ether-insoluble, ether-soluble, and chloroform-soluble fractions. The main constituent from the ether-insoluble fraction had m. p. 191·5° (mixed m. p. with aconitine, m. p. 198°, 194·5°) [*hydrochloride*, $+3\frac{1}{2}H_2O$, m. p. 158° (decomp.) after sintering at 155°; *hydrobromide*, m. p. 203° after sintering at 198°; *hydriodide*, m. p. 221°, decomp. 224°; *perchlorate*, blackening at 220° 226°, decomp. 229° (a mixed m. p. with aconitine perchlorate showed no change), $[\alpha]_D^{17}$ −47·73°]. From a comparison with aconitine (see A., 1906, i, 599) it is difficult to say whether the two alkaloids are identical or isomeric.

Neither the ether-soluble alkaloid nor its salts could

be obtained crystalline. Treatment with alcoholic potassium hydroxide furnished neoline (hydrobromide darkening at 198°, sintering at 200°, m. p. 205°) together with benzoic and acetic acids.

S. COFFEY.

Alkaloid trichloroacetates. Use of trichloroacetic acid in toxicology. G. FLORENCE (Bull. Soc. chim., 1927, [iv], **41**, 1097—1100).—*Trichloroacetates* of the following have been prepared: aniline ($+H_2O$), *o*-toluidine ($+H_2O$), *p*-toluidine ($+H_2O$), strychnine ($+3H_2O$), brucine ($+3H_2O$), morphine ($+3H_2O$), codeine ($+2H_2O$), quinine ($+4H_2O$), quinidine ($+4H_2O$). They are well-defined, crystalline salts decomposing in boiling aqueous solution to the alkaloid, chloroform, and carbon dioxide. The solubilities of the salts in water are given, and are such as enable their easy separation from coagulated albumins. Crystalline salts could not be obtained from cocaine, nicotine, atropine, and cinchonine.

H. BURTON.

Alkaloids of the animal kingdom. M. SCHENCK (Z. angew. Chem., 1927, **40**, 1081—1086).—A summary of recent work.

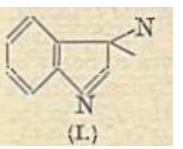
Derivatives of *o*-aminophenylarsinic acid. H. BURTON and C. S. GIBSON (J.C.S., 1927, 2387—2388).—When either o-*ethylaminophenylarsinic acid*, m. p. 128—129° [*nitroso*-derivative, m. p. 160° (decomp.)], or its *acetyl* derivative, m. p. 187—188° (*silver* salt), is reduced by sulphur dioxide in alcohol–hydrochloric acid–iodine solution, arsenic is eliminated from the molecule. 4-*Nitro*-2-*aminodiethylaniline* (*hydrochloride*, m. p. 205—206°; *benzylidene* derivative, m. p. 97—98°), prepared by reduction of 2 : 4-dinitrodiethylaniline with ammonium sulphide, is converted by the Bart reaction into 3-*nitro*-6-*diethylaminophenylarsinic acid*, m. p. 195—196° (decomp.), which is convertible normally into 3-*nitro*-6-*diethylaminophenylarsenious chloride* [3-*nitro*-6-*diethylaminophenyldichloroarsine*], m. p. 143—144°. M. CLARK.

9-Methylcarbazole-3-arsinic acid and its reduction products. H. BURTON and C. S. GIBSON (J.C.S., 1927, 2386—2387).—3-Amino-9-methylcarbazole has been converted by the usual procedure into 9-*methylcarbazole*-3-*arsinic acid*, m. p. above 300°, 9-*methylcarbazole*-3-*arsenious chloride*, m. p. 121—122°, and 9-*methylcarbazole*-3-*arsenious oxide*, m. p. 182—185° (decomp.). 9-*Methylcarbazole*-3-*azo*-β-*naphthol* has m. p. 212° (decomp.). M. CLARK.

Syntheses by means of magnesylpyrroles. Series II, Note X. B. ODDO and Q. MINGOIA (Gazzetta, 1927, **57**, 473—479).—The action of carbonyl chloride on magnesylmethylketole yields: (1) principally 3 : 3-*carbonyldimethylketole*, $CO\left(\cdot C<\begin{matrix}C_6H_4\\CMe\end{matrix}>NH\right)_2$, m. p. 290°, which forms a *diacetyl* derivative, m. p. 230°; (2) 1 : 1-*carbonyldimethylketole*, $CO\left(\cdot N<\begin{matrix}C_6H_4\\CMe\end{matrix}>CH\right)_2$, m. p. 180°; (3) 1 : 3-*carbonyldimethylketole*, $CH<\begin{matrix}C_6H_4\\CMe\end{matrix}>N\cdot CO\cdot C<\begin{matrix}C_6H_4\\CMe\end{matrix}>NH$, p. 135°. The products of the interaction of carbonyl chloride and magnesylindole are: 3 : 3-*carbonyldi-indole*, $C_{17}H_{12}ON_2$, m. p. 280°, which forms a silver derivative, but yields no phenylhydrazone, oxime, or semicarbazone; 2 : 2-*carbonyldi-indole*, m. p. 198°; and 1 : 1-*carbonyldi-indole*, m. p. 245°. In contradiction to the statement of Majima and Kotake (A., 1923, i, 150), the formation of indole-1-carboxylic acid by the action of carbon dioxide on magnesium indolyl iodide in ethereal or anisole solution (A., 1911, i, 486) is confirmed.

T. H. POPE.

Mechanism of the Grignard reaction in the indole series. R. MAJIMA and T. HOSHINO (Proc. Imp. Acad. Tokyo, 1927, **3**, 339—341).—When magnesium indolyl iodide reacts with an alkyl (or acyl) halide, the active halogen of the latter first removes the magnesium iodide group, and, the free indolyl radical immediately changing to the form (I), the alkyl group enters the 3-position. In warm solutions a similar course is followed in the reaction with a carbonyl-containing compound, and, after hydrolysis in this case, an aldehyde group remains in the 3-position. In the cold, however, the tautomeric change to (I) does not take place with sufficient rapidity, and the aldehyde group assumes the 1-position.


(I.)

B. W. ANDERSON.

Position occupied by acetatomercuric groups, Hg·OAc, in anilines having in the nucleus a halogen group or a hydrocarbon residue. I. L. VECCHIOTTI (Gazzetta, 1927, **57**, 485—497).—Previous results (cf. Jackson and Peakes, A., 1908, i, 523; Schoeller and Schrauth, Ber., 1912, **45**, 2812; Vecchiotti, A., 1924, i, 957) show that when, in a substituted aniline, the *meta*-position to the amino-group is occupied by a halogen atom or a hydrocarbon residue, the action of mercuric acetate gives rise to a monomercuri-compound in which the acetato-mercuric group always occupies the *para*-position to the amino-group and to a dimercuri-compound having the two mercuri-groups in the 2 : 5- or, more usually, in the 4 : 6-positions.

Treatment of *m*-chloroaniline in alcoholic solution with aqueous-alcoholic mercuric acid gives: (1) 4-*Acetatomercuri*-3-*chloroaniline*, $NH_2\cdot C_6H_3Cl\cdot Hg\cdot OAc$, m. p. 155°; the corresponding *hydroxymercuri*-compound, decomp. 210°, *chloromercuri*-compound, decomp. 202°, *acetyl* derivative, m. p. 205°, and *mercury di*-o-*chloro*-p-*aminophenyl*, $(NH_2\cdot C_6H_3Cl)_2Hg$, m. p. 162°, were prepared. Treatment of the acetyl derivative in acetic acid solution containing calcium chloride, with a current of chlorine yields 3 : 4-dichloroacetanilide. (2) 4 : 5-*Diacetatomercuri*-m-*chloroaniline*, $NH_2\cdot C_6H_2Cl(Hg\cdot OAc)_2$, m. p. 190°, which forms an *acetyl* derivative, m. p. 245°, convertible into 3 : 4 : 6-trichloroacetanilide.

The action of aqueous alcoholic mercuric acetate solution on *m*-iodoaniline (2 mols.) gives 4(?)-*acetatomercuri*-m-*iodoaniline*, m. p. 176°, which forms the corresponding *hydroxy*-, m. p. 172°, *iodo*-, m. p. 193° (decomp.), and *acetyl* compounds, m. p. 192°, the latter being convertible into 3 : 4(?)-*di-iodoacetanilide*, m. p. 167°. In aqueous solution this reaction gives 2 : 4 : 6(?)-*triacetatomercuri*-m-*iodoaniline*, m. p. 190° (decomp.).

T. H. POPE.

Preparation of lead tetraphenyl. H. GILMAN and J. ROBINSON (J. Amer. Chem. Soc., 1927, 49,

2315—2317).—Detail improvements are described in the preparation of lead tetraphenyl from lead chloride and magnesium phenyl bromide (cf. Pfeiffer and Truskier, A., 1904, i, 544). F. G. Willson.

Effect of alkali, acid, and enzymes on proteins, peptones, polypeptides, 2 : 5-diketopiperazines, and related compounds. E. Abderhalden and H. Mahn (Z. physiol. Chem., 1927, **169**, 196—222).—Experiments similar to those carried out previously on silk peptone (Abderhalden and Schnitzler, this vol., 686) have been made with elastin. A solution has been obtained by heating dried defatted powdered elastin with *N*-hydrochloric acid for 5—6 hrs. at 70—75° and in some cases by the action of pepsin in acid solution. The hydrolysis of the dissolved elastin by *N*-hydrochloric acid and by *N*-sodium hydroxide at various temperatures has been followed by Sorensen "formol" titrations or by Willstatter's methods, and by measurements of the optical rotation of the peptone solution and its copper salts. The hydrolysis of dipeptides and anhydrides by various amounts of acid and alkali at different temperatures has been measured by amino-nitrogen determinations; it is found that certain polypeptides are not hydrolysed by *N*-hydrochloric acid at the ordinary temperature, but are attacked by *N*-sodium hydroxide under similar conditions. The bearing of these results on the theories of protein structure is discussed and the conclusion is reached that linkings other than those of polypeptide and 2 : 5-diketopiperazine nature are present. A. Wormall.

Blood pigments. VII. Behaviour of prosthetic groups in different solvents. F. Haurowitz (Z. physiol. Chem., 1927, **169**, 235—262).—Spectrophotometric measurements of the spectra of hæmin, mesohæmin, dimethylmesohæmin, and ætiohæmin and the corresponding hæmochromogens have been made in the presence and absence of pyridine and cyanides. The spectrum of hæmin in pyridine differs significantly from that of hæmochromogen, The preparation of trimethylhæmatin from methylhæmatin and methyl sulphate results in the change: C:C ⟶ CH·C(OMe) in the unsaturated side-chain, the Fe·OH grouping not being methylated. In all the solvents used, the chlorine atom of hæmin chloride dissociates as the anion, and in acid solution the coloured residue behaves as cation. In alkaline solutions both hydrogen and chlorine are dissociated, even with a preparation esterified at both carboxyl groups. Thus hæmin contains a third acid group (cf. this vol., 1092). Hydrogen cyanide is not bound by hæmin in the same way as chlorine, bromine, or hydroxyl groups. The action of hydrogen cyanide on hæmin chloride is similar to that of pyridine or aniline; the coloured portion of the compound behaves, however, as cation with pyridine or aniline and as anion with hydrogen cyanide. Pyridine resolves hæmoglobin into globin and pyridine-hæmochromogen, oxyhæmoglobin into the same products together with oxygen, and methæmoglobin into globin and pyridine-oxyhæmin. The constitution of the different hæmins is discussed. A. Wormall.

Effect of irradiation on the tyrosine and tryptophan contained in protein. F. Lieben (Biochem. Z., 1927, **187**, 307—314).—Tyrosine and tryptophan, when forming part of a protein molecule, are oxidatively destroyed when irradiated both in diffused daylight (in presence of a sensitiser) and with the mercury lamp, the destruction not being as rapid, however, as when these acids are free. Addition of alkali increases the action and of formaldehyde accelerates the attack on tryptophan.

P. W. Clutterbuck.

Catalytic hydrogenation of hæmateric acid and hæmin. A. Papendieck (Z. physiol. Chem., 1927, **169**, 59—63).—Hæmateric acid in acetic acid solution is catalytically hydrogenated (cf. A., 1926, 631) to a porphyrin not distinguishable from mesoporphyrin. The maximum amount of hydrogen absorbed is equivalent to 6 atoms of hydrogen per mol. of hæmateric acid; no decolorisation occurs. Mesoporphyrin solutions absorb hydrogen irregularly, and are not decolorised. Appreciable hydrogenation of hæmin occurs in acid solution with the formation of mesohæmin and mesoporphyrin. In alkaline solution, approximately 6 atoms of hydrogen are absorbed per mol. of hæmin, but spectroscopical examination reveals no mesohæmin.

A. Wormall.

Determination of active hydrogen in hæmin, in some of its derivatives, and in pyrroles. II. H. Fischer and E. Walter (Ber., 1927, **60**, [*B*], 1987—1995; cf. A., 1926, 630).—Determinations are recorded of the number of atoms of active hydrogen per molecule of the following substances, using the method of Zerewitinov (A., 1907, ii, 509; 1908, i, 593; 1911, i, 101) as modified by Flaschentrager (A., 1925, ii, 999). The results are expressed in parentheses after the name of the compound: bis-(3-carbethoxy-2 : 4-dimethyl-5-pyrryl)methane (2·11); bis-(3-carbethoxy-2 : 4-dimethyl-5-pyrryl)methene (1·13); bis-(4-carbethoxy-2 : 3-dimethyl-5-pyrryl)methane (1·94); bis-(4-carbethoxy-2 : 3-dimethyl-5-pyrryl)-methene (0·81); bis-(2-bromo-4-carbethoxy-3-methyl-5-pyrryl)methane (1·01); bis-(2-bromo-4-carbethoxy-3-methyl-5-pyrryl)methene (1·08); product of the condensation of benzaldehyde with 3-acetyl-2 : 4-dimethylpyrrole (2·21); bis-(5-carbethoxy-3-(β-methylmalonic ester)-4-methyl-2-pyrryl)methane (5·3); ethyl 5-carbethoxy-2 : 4-dimethyl-3-pyrryl-β-methylmalonate (2·31); ethyl 2 : 5-dimethyl-4-ethyl-3-pyrryl-β-methylmalonate (1·7); ethyl malonate (1·1); triphenylmethyl chloride (—); *cyclo*pentadiene (0·86); ethyl β-methoxymethylmalonate (0·95); hæmin (3·02—5·11 according to temperature); dihydrohæmin (4·06—4·49); *meso*hæmin ester, $C_{36}H_{40}O_4N_4FeCl$ (2·1); ætiohæmin (1·64—1·98); *iso*ætiohæmin (2·37); protohæmin (4·82, 4·68); coproporphyrin ester (3·82, 4·46); *iso*coproporphyrin ester (4·22, 4·3); β-*iso*coproporphyrin ester (3·72); ætioporphyrin (2·03, 2·09); protoporphyrin diester (1·93); *iso*ætioporphyrin (4·08, 4·32); 1 : 3 : 5 : 7-tetramethyl-2 : 4 : 6 : 8-tetraethylporphin (2·1); 2 : 3 : 6 : 7-tetramethyl-1 : 4 : 5 : 8-tetraethylporphin (2·05, 2·2); 1 : 4 : 5 : 8-tetramethyl-2 : 3 : 6 : 7-tetraethylporphin (2·1); coproporphyrin ester (synthetic) (4·32); iron complex salt of tetramethylhæmatoporphyrin (5·82); uroporphyrin ester (9·46); *iso*uroporphyrin ester (7·37). From the results, it appears that either the

experimental material is insufficient to allow deductions with regard to the constitution of the blood pigments or that the porphyrins and hæmins are able to unite with hydrogen in such a manner that production of methane ensues with Grignard's reagents, particularly in the presence of pyridine. Possibly the Zerewitinov method is not applicable to complex unsaturated systems. H. WREN.

Pyridine-hæmins. A. HAMSIK (Z. physiol. Chem., 1927, **169**, 64—72).—From a solution of hæmin chloride in pyridine, ether slowly precipitates large crystals and it is suggested that a pyridine–hæmin chloride compound has been formed. These crystals become much smaller when washed with ether or alcohol and hæmin chloride is regenerated. Hæmin acetate forms a partly crystalline similar precipitate which, with ether and alcohol, yields a mixture of oxyhæmin and oxyhæmin anhydride. This accounts for the high iron content of hæmin acetate preparations (cf. Küster and Gerlach, A., 1922, i, 596) and their incomplete solubility in pyridine. Hæmin formate, acetate, oxalate, and sulphate, but not hæmin chloride, decompose when heated in pyridine–chloroform solution, giving oxyhæmin and oxyhæmin anhydride. A. WORMALL.

Blood pigments. VI. Relation between hæmin, hæmochromogen, and porphyrin. F. HAUROWITZ (Z. physiol. Chem., 1927, **169**, 91—101; cf. this vol., 686).—Porphyrins can be converted into the corresponding hæmins by ferrous or ferric salts in presence of acetic acid, but with butyric and valeric acids ferrous iron only is introduced. It is concluded that in the acetic acid solution a reduction occurs which is not effected primarily on the ferric salt, but probably on a loose intermediate compound of iron and porphyrin. Hæmatin is not formed on acidification of a solution of hæmochromogen in absence of oxidising agents. Hæmin chloride in pyridine solution can be reduced to hæmochromogen by sodium in the absence of oxygen or compounds containing oxygen, and the hæmochromogen formed contains 4O per mol. The formulæ of porphyrin and hæmin are discussed in relation to the active hydrogen atoms present and the combination of bi- or tervalent iron. A. WORMALL.

Electrodialysis of proteins. W. PAULI (Biochem. Z., 1927, **187**, 403—409).—A reply to Dhere (this vol., 423). P. W. CLUTTERBUCK.

Phosphorus nucleus of ovovitellin. S. POSTERNAK and T. POSTERNAK (Compt. rend., 1927, **185**, 615—617; cf. this vol., 273, 582).—β_1-Ovotyrin, $C_{72}H_{144}O_{78}N_{24}P_{12}$, is hydrolysed by boiling 25% hydrochloric acid to phosphoric acid (12 mols.), pyruvic acid (1·6 mols.), histidine (0·7 mol.), arginine (0·62 mol.), lysine (0·75 mols.), *l*-serine, $[\alpha]_D^{22}$ −6·67° (7·9 mols.), and ammonia (4·9 mols.). The ammonia and pyruvic acid are probably produced by deamination of part of the serine, and when allowance is made for this, serine and phosphoric acid appear in almost equimolecular amounts. Hydrolysis of β_1-ovotyrin with 15% sulphuric acid affords polypeptides with N : P ratios of 1·1—1·3 together with phosphoric acid, serine, and its deamination products. Serine has not previously been isolated directly from a protein hydrolysate. G. A. C. GOUGH.

Determination of organic material by oxidation with chromic acid. T. VON FELLENBERG (Biochem. Z., 1927, **188**, 365—391).—An attempt to extend the use of Bang's micro-determination of fat by combustion with dichromate and sulphuric acid to a large number of organic substances gives the following results. Formic acid yields quantitatively carbon dioxide, acetic acid is not attacked, whilst with propionic and butyric acids more oxygen is used than is required to convert them into acetic acid. Higher fatty acids give very complex results. Malic, tartaric, and citric acids give carbon dioxide quantitatively. Oxalic acid is not attacked and succinic acid only slightly so. Soluble carbohydrates and polyhydric alcohols are oxidised quantitatively, but ethyl, propyl, and *iso*butyl alcohols form one molecule of acetic acid and dimethylethylenecarbinol forms two molecules. Benzoic acid is oxidised quantitatively and salicylic acid almost so. Glycine and alanine are scarcely attacked, whilst tyrosine is oxidised almost completely. Proteins give different values, the smallest being that of gelatin (glycine-rich). The method is adapted for determination of alcohol in acetic acid and of methyl alcohol mixed with a small amount of ethyl alcohol. P. W. CLUTTERBUCK.

Determination of phenylacetylene. F. HEIN and A. MEYER (Z. anal. Chem., 1927, **72**, 30—31).—Phenylacetylene is precipitated from an alcoholic solution as its copper compound by an ammoniacal solution of cuprous chloride. The precipitate is filtered into a glass Gooch crucible, washed with water, alcohol, and ether, and dried in a vacuum over concentrated sulphuric acid. This determination can be checked by treating the precipitate with a solution of ferric ammonium sulphate in dilute sulphuric acid, and titrating the ferrous sulphate formed with permanganate. The error is less than 1%. F. S. HAWKINS.

Volumetric determination of hydroxyl groups in organic compounds. V. L. PETERSON and E. S. WEST (J. Biol. Chem., 1927, **74**, 379—383).—Hydroxyl groups in sugars and other organic compounds may be determined by heating the compound with a known amount of acetic anhydride and pyridine until acetylation is complete, dilution of the reaction mixture with water, and titration of the excess acetic acid. C. R. HARINGTON.

Determination of *iso*propyl alcohol in presence of acetone, and of methylethyl ketone in presence of *sec.*-butyl alcohol. H. A. CASSAR (Ind. Eng. Chem., 1927, **19**, 1061—1062).—Rapid determinations of *iso*propyl alcohol in presence of acetone are effected by quantitative oxidation of the alcohol to acetone with chromic acid solution and back-titration of the excess of chromic acid. The acetone is determined by Messinger's method (J.S.C.I., 1920, 280A), applying a correction of 1—2% for the *iso*propyl alcohol present. *sec.*-Butyl alcohol may be determined in presence of methyl ethyl ketone by this method, but for the determination of methyl ethyl ketone Messinger's method gives high results and a modification thereof is suggested. R. BRIGHTMAN.

Determination of diacetyl and acetylmethylcarbinol. C. B. VAN NIEL (Biochem. Z., 1927, 187, 472—478).—A slight modification of the usual method for determination of diacetyl and acetyl methylcarbinol as nickel dimethylglyoxime is described. P. W. CLUTTERBUCK.

Determination of the methoxyl content of volatile substances in dilute aqueous solutions containing aldehydes. K. WIESLER (Z. angew. Chem., 1927, 40, 975).—The ordinary Zeisel method for the determination of the methoxyl group fails in the presence of aldehydes but good results are obtained by the following modification: The solution is mixed with freshly-precipitated silver oxide and distilled to two thirds its volume, the distillate being collected in a second distillation flask containing 10 c.c. of hydriodic acid (d 1·96). The latter flask is heated gently on the water-bath and is provided with a reflux air condenser connected at its upper end to a small washing flask containing a suspension of red phosphorus in water, whence the vapours pass into a measured volume of 0·1N-alcoholic silver nitrate. Carbon dioxide is passed through the apparatus throughout the determination. The deposited silver iodide is collected and weighed as usual. A. R. POWELL.

Detection of chlorophyll by means of the analytical quartz lamp. P. W. DANCKWORTT and E. PFAU (Arch. Pharm., 1927, 265, 560—562).—Small quantities of powdered drugs or tinctures are treated with water and ether and the mixture is illuminated by the quartz lamp. If chlorophyll is present, even in small quantities, the ethereal solution shows a vivid, red fluorescence. The red colour is not given by carotin or xanthophyll. It is suggested that this reaction might be utilised in separating the two components of chlorophyll (cf. Willstatter and Hug, A., 1911, i, 393), since on treating a methylalcoholic solution of crude chlorophyll with light petroleum, the latter shows a gradually increasing fluorescence, whilst the fluorescence of the alcoholic solution gradually diminishes. S. COFFEY.

Determination of selenium in organic compounds. E. H. SHAW and E. E. REID (J. Amer. Chem. Soc., 1927, 49, 2330—2334).—The sample (0·2—0·4 g.) is mixed with sucrose (0·4 g.), potassium nitrate (0·2 g.), and sodium peroxide (14 g.), the mixture covered with a thin layer of sodium peroxide, and the whole burnt in the Parr bomb in the usual manner. The mass is dissolved in water and the solution boiled, cooled, acidified with hydrochloric acid, filtered, and diluted to 350 c.c. The selenium is then precipitated (*a*) by adding 200 c.c. of hydrochloric acid, heating the mixture not quite to the b. p., and passing in a rapid stream of sulphur dioxide, or (*b*) by adding 50 c.c. of hydrochloric acid and 3 g. of potassium iodide, and gently boiling the mixture, with replacement of evaporated water, until the excess of iodine is volatilised. The selenium is collected on a Gooch crucible, washed with alcohol and water, and dried at 110—120°. The greatest errors recorded in 25 analyses are +0·17% and −0·33%. F. G. WILLSON.

Biochemistry.

Regulation of respiration. IX. Relation of tissue acidity and blood acidity to volume flow of blood as illustrated by hæmorrhage and re-injection. A. B. HERTZMAN and R. GESELL (Amer. J. Physiol., 1927, 81, 563—578).—The changes in acidity of the circulating arterial and venous blood were determined by the manganese dioxide electrode and checked by the hydrogen electrode. Hæmorrhage elicited increased alkalinity of the arterial blood and increased acidity of the venous, decreased oxygen consumption, and increased pulmonary ventilation. Reinjection reversed all these changes. The importance of volume flow of blood and acidity in the control of the normal acid-base equilibrium is emphasised. R. K. CANNAN.

Effects of respiratory gases on density of blood and other fluids. W. F. HAMILTON and H. G. BARBOUR (J. Biol. Chem., 1927, 74, 553—556).—Dissolution of carbon dioxide in water, alkaline salt solution, blood-serum, and whole blood increases the density of these liquids, the increases being in ascending order of magnitude owing to the effect of chemical reactions in causing the increase of volume per c.c. of carbon dioxide to be progressively less. In the case of oxygen, the dissolution of which in whole blood is accompanied by actual diminution in volume, the effect on the density is very much greater. C. R. HARINGTON.

Effect of asphyxia on blood. J. B. COLLIP (Trans. Roy. Soc. Canada, 1927, [iii], 21, V, 151).—Asphyxia produces a slight but definite increase in the serum-calcium and in the inorganic phosphorus content of the blood, and a decrease in blood-p_H of from 0·15 to 0·35 of a unit. H. D. KAY.

Micro-determination of carbon dioxide in blood and other solutions. Efficiency of paraffin in preventing loss of carbon dioxide. D. RAFFEL (J. Biol. Chem., 1927, 74, 839—849).—An apparatus is described in which the carbon dioxide in a small amount of liquid is liberated and aspirated into standard barium hydroxide solution, the excess of which is then titrated with the aid of a micro-titration syringe. The method is applicable to determination of 0·1—0·5 c.c. of carbon dioxide with a maximum error of ±2%. The loss of carbon dioxide from normal blood-serum kept under liquid paraffin does not exceed 2% in 24 hrs., although in presence of higher concentrations of carbon dioxide the loss may be 10%. C. R. HARINGTON.

Oxidation processes in blood-serum. T. R. PARSONS and W. PARSONS (Biochem. J., 1927, 21, 1194—1205).—In the presence of certain oxidising agents such as potassium ferricyanide and potassium permanganate, human blood-serum absorbs oxygen at the rate of about 0·25 c.c. per c.c. per hour when

shaken with air at the ordinary temperature. The same effect is observed in the presence of ferric salts in alkaline solution, but not with ferric salts in acid solution nor with dichromate at any reaction. Extraction with ether reduces the rate at which the serum will absorb oxygen in this way, but this can be restored in some measure by the re-addition of the extracted material, provided that this is recovered by evaporation of the ether extract in an oxygen-free atmosphere. The oxidisable substances are precipitated completely by full saturation with ammonium sulphates, partly by half saturation, and scarcely at all by one third saturation with ammonium sulphate. The substances primarily responsible for the effect are therefore most probably lipins. S. S. Zilva.

Action of essential oils on the formation of methæmoglobin. E. Dessemontet (J. Pharm. Exp. Ther., 1927, **31**, 377—386).—The formation of methæmoglobin in a mixture of defibrinated blood and various essential oils has been studied. Oils containing eugenol, safrole, *iso*safrole, linalool, anethole, anisole, and carvene induce the formation of methæmoglobin within 24 hrs., whilst menthol, thymol, borneol, oil of cloves (eugenol-free), methyl salicylate, and camphor produce no reaction. It is therefore suggested that this property of the alcoholic constituents of essential oils depends on the presence of unsaturated side-chains and on the position of the ethylenic linkings. No relation between velocity of formation of methæmoglobin and degree of unsaturation has been detected in carvene, carvone, pinene, vanillin, and cineole. There appears to be a definite pressure of oxygen specific for linalool, for carvene, and for pinene, at which the formation of methæmoglobin is an optimum. E. A. Lunt.

Calcium and potassium content of the blood. E. Kylin (Acta med. Scand., Suppl., 1927, [xix], 1—112).—The normal calcium content of the blood is 10·6—12·0 (average 11·13) mg. %; below 21 years the average is 11·6 mg., and above 41 years 10·83 mg. %. The regulation of the calcium content is hormonal. The normal potassium content of the blood is 18—24 (average 20·7) mg. %; in pathological conditions the calcium content is usually diminished and the potassium content increased, but in diabetes high blood-calcium values are observed. The response of the human organism to adrenaline is largely dependent on the potassium : calcium ratio.

Chemical Abstracts.

Calcium content of blood-serum of rat. A. T. Cameron and J. E. Williamson (Trans. Roy. Soc. Canada, 1927, [iii], **21**, V, 139—145).—The calcium content of the serum of the normal white rat (on a mixed diet), determined during summer or winter, shows an average value corresponding with that of other mammals, but with greater individual variations. No difference for sex is observable. Values determined in late spring are definitely lower (average 2 mg. lower) while still showing about the same degree of variation. H. D. Kay.

Determination of calcium in blood and urine. J. S. Sharpe (Edinburgh Med. J., 1926, **33**, 27—30).—The cloudiness produced by ammonium oxalate in a protein-free solution in glycerol is compared nephelometrically with a standard. The method is accurate to 0·5 mg. for 10—15 mg. in 100 c.c.

Chemical Abstracts.

Effects of dialysis and of ether extraction on diffusibility of calcium in human blood-serum. R. F. Loeb and E. G. Nichols (J. Biol. Chem., 1927, **74**, 645—649).—Normal human blood-serum, the same serum dialysed until free from calcium, and the same serum extracted with ether, were dialysed under similar conditions against calcium chloride solution; in all cases the equilibrium concentration of calcium attained in the serum was higher than expected from the Donnan equilibrium, the deviation being greatest in the serum extracted with ether and least in the dialysed serum. The view is therefore supported that un-ionised compounds of calcium with protein account for the unequal distribution of calcium attained on dialysing blood-serum against water.

C. R. Harington.

Free sugar of the blood-plasma. E. J. Bigwood and A. Wuillot (Bull. Soc. chim., 1927, **9**, 867—883).—When blood-plasma or -serum is incubated with yeast for ½—1 hr., the reducing power of the deproteinised fluid, determined by the method of Hagedorn and Jensen (cf. A., 1923, ii, 265, 440) does not completely disappear, but becomes approximately constant at a value corresponding with 0·0—0·03% of dextrose. The residual reducing power of the serum of rabbits, dogs, and man is on the average 13·3%, 13·5%, and 14·3%, respectively, of the original reducing power. The total sugar of the cerebrospinal fluid is on the average 67% of that of the blood, but the fermentable sugar of the cerebrospinal fluid is 75% of that of the blood. Conclusive evidence as to the nature of the non-fermentable reducing material was not obtained, but the possibility that it may be uric acid has been excluded, although uric acid may be responsible for the abnormally high values obtained in cases of nephritis.

W. O. Kermack.

Blood-sugar. III. Non-dextrose of blood-filtrates. B. Sjollema (Biochem. Z., 1927, **188**, 465—474).—Further investigations (cf. this vol., 476, 789) of the non-dextrose reducing substances of blood show that when blood-filtrates are shaken with charcoal and acetic acid the ergothioneine and glutathione present cause no appreciable error in the blood-sugar determination with ferricyanide. Both dextrose and the non-dextrose reducing substance reduce ferricyanide but little when the p_H is smaller than 9·5. Dextrose remains completely in solution when both trichloroacetic and tungstic acids are used as precipitants, but a non-dextrose reducing substance is precipitated by the former, but not by the latter. Ergothioneine (0·1%) is not precipitated by trichloroacetic acid. Sulphur determinations of the fractions show that blood-corpuscles contain other non-dextrose reducing substances than ergothioneine and glutathione. An adaptation of the Folin–Wu method is given for determination of dextrose in blood-filtrates. P. W. Clutterbuck.

Total sugar of blood and urine. M. R. Everett, H. A. Shoemaker, and F. Sheppard (J. Biol. Chem., 1927, **74**, 739—759).—The low results obtained by

Folin and Berglund (A., 1922, ii, 400) for the total sugar of blood and urine were due to the interfering effect of the hydrochloric acid used in the hydrolysis, and of silicates in the sodium hydroxide employed for neutralisation, on the subsequent colorimetric determination. Satisfactory results are obtained by hydrolysis with sulphuric acid and neutralisation with potassium hydroxide free from silica. C. R. HARINGTON.

Plasma-proteins of normal dogs. C. W. MATTHEW (J. Biol. Chem., 1927, **74**, 557—560).—The blood-plasma of normal dogs contains, on the average, 0·45% of fibrin, 4·64% of albumin, and 2·12% of globulin. For any one animal the figures remain practically constant. C. R. HARINGTON.

Effect of hydrogen-ion concentration and protein concentration on the osmotic pressure of serum-proteins. J. MARRACK and L. F. HEWITT (Biochem. J., 1927, **21**, 1129—1140).—The osmotic pressure of serum-proteins rises with increase of p_H to an extent which is less than that calculated for ideal solutions if the compound of protein and base is fully dissociated. The activity coefficients of anions are slightly reduced by the presence of protein in solution. The excess of diffusible ions in the protein solution, due to the Donnan effect, and deviations from the state of ideal solution cause the osmotic pressures of proteins not to bear a linear relation to the protein concentration. It is not necessary to suppose that proteins in solution occupy a greater bulk than they do when dry (cf. Verney, A., 1926, 856). S. S. ZILVA.

Role of tissues in maintaining acid–base equilibrium of blood. I. Effect of isolated muscle-tissue. II. Effect of hind-leg preparation. M. G. BANUS and L. N. KATZ (Amer. J. Physiol., 1927, **81**, 628—643, 644—649).—I. Apparatus is described for the perfusion of isolated organs with oxygenated non-acapnic blood under controlled conditions. The gastrocnemius of the dog was perfused with blood rendered acid by addition of hydrochloric acid and the changes were observed in the p_H, chloride content, and carbon dioxide-combining power at constant carbon dioxide tension. No measurable exchange of chloride or alkaline radicals occurred between blood and tissues, and it is concluded that at constant carbon dioxide tension under the experimental conditions muscle does not increase the buffering power of the blood.

II. When the hind-leg was perfused there was some increase in the p_H and carbon dioxide-combining power of the blood, but no change in the chloride-ion concentration. The nature of this buffering effect of some of the tissues of the hind-leg is unknown.

R. K. CANNAN.

Distribution of nitrogen in the blood and urine of the turtle. F. H. WILEY and H. B. LEWIS (Amer. J. Physiol., 1927, **81**, 692—695).—Determinations of the distribution of the nitrogen of the blood, urine, and tissues of the turtle (*Chrysemys pinta*) are reported. The turtle excreted considerable amounts of both urea and uric acid, so that, as regards nitrogen metabolism, it is intermediate between mammals and the reptiles of arid regions.

R. K. CANNAN.

Action of hirudin on thrombin. J. O. W. BARRATT (J. Physiol., 1927, **64**, 47—53).—From determinations of the amounts of thrombin inactivated when solutions of varying concentrations of thrombin and hirudin are mixed, it is concluded that the reaction is of the same type as that of a weak acid with a weak base. R. K. CANNAN.

Determination of catalase in blood and animal tissues. E. GAGARINA (Biochem. Z., 1927, **188**, 284).—A claim of priority over Golzov and Jankovsky (this vol., 689; cf. J. Exp. Biol. Med., 1926, **7**, 33).

P. W. CLUTTERBUCK.

Immunological behaviour of mucoids. J. H. LEWES and H. G. WELLS (J. Infect. Dis., 1926, **40**, 316).—Various mucoids from eggs and blood are antigenic although less so than most other proteins of equal solubility. The ovomucoids from goose and duck eggs were the most closely related to each other, as were also the hen and guinea-fowl mucoids. Seromucoids from sheep, ox, and dog blood were easily distinguishable from one another and showed but little relationship to the ovomucoids.

CHEMICAL ABSTRACTS.

Isolation of substances with immune properties. A. LOCKE and E. R. MAIN (J. Infect. Dis., 1926, **39**, 848).—Diphtheria antitoxin was purified by isoelectric fractionation of the Ramon toxin-antitoxin precipitate. These preparations contain 0·0005—0·0015 mg. of nitrogen per antitoxin unit, have the anaphylactogenic character of horse-serum protein, and are injured by boiling as well as by ageing.

CHEMICAL ABSTRACTS.

Composition of blood and tissues of fœtal calf. J. B. COLLIP (Trans. Roy. Soc. Canada, 1927, [iii], **21**, V, 147—150).—Very high values for serum-calcium and inorganic phosphorus are found, partly due to asphyxia. Whole blood shows a higher non-protein nitrogen figure than does serum, although the urea values for the two fluids are almost identical. Fœtal serum has a low protein content. Amniotic fluid shows great variation in the calcium content, which is apparently unrelated to the blood-calcium value. The fœtal heart-muscle shows a relatively high glycogen content which diminishes with the age of the fœtus. The glycogen content of the skeletal muscle, on the contrary, increases with the age of the fœtus. H. D. KAY.

Mechanism of the Golgi black reaction [of animal tissues]. A. MOSCHINI (Arch. Farm. sperim. Sci. aff., 1927, **43**, 97—114).—Chemical theories of this reaction, the development of a black colour in sections which have been treated with potassium dichromate solution, kept for a few days, and treated with a silver nitrate solution, and of the modified reaction, in which the second reagent applied is mercuric chloride, followed by ammonia or other reagents, are discussed. It is suggested that, by the reducing action of the tissue, potassium chromite is formed, and that this reacts with reagents subsequently applied. E. W. WIGNALL.

Colloid chemical and morphological study of chromosomes. Y. KUWADA and T. SAKAMURA (Protoplasma, 1926, **1**, 239—254).

CHEMICAL ABSTRACTS.

Iron content of animal tissues. C. A. Elvehjem and W. H. Peterson (J. Biol. Chem., 1927, 74, 433—441).—Iron is determined directly in a sample of tissue and in a duplicate sample to which a known amount of iron has been added; if the recovery of the added iron in the second case be not quantitative, the determination is repeated after preliminary removal of phosphates (cf. A., 1926, 443). Figures are given for the iron content of various tissues of the ox and for that of the spleen, liver, and kidney of different animals; the latter organs are rich in iron as compared with the other tissues.

C. R. Harington.

Chemical composition of brain. II. G. V. Stuckert (Cordoba Medica, 1927, 2, 13—19).—Data are given for the chemical composition of the cerebrum, medulla oblongata, and cerebellum of ox-brain. No marked differences exist in respect of their content of total lipins, proteins, and soluble extractives. The individual lipins occur in different proportions. For example, the cerebellum contains twice as much phosphatide as the medulla oblongata, the difference being attributed chiefly to lecithins and kephalins. The medulla oblongata is rich in fats and fatty acids. G. W. Robinson.

Preparation of kephalin. P. A. Levene and I. P. Rolf (J. Biol. Chem., 1927, 74, 713—714).—Practical details are given for the preparation of kephalin from brain. C. R. Harington.

Iodine content of the thyroid gland of various breeds of ox and its relationship to the condition of these glands. T. von Fellenberg and H. Pacher (Biochem. Z., 1927, 188, 339—364).—Of 80 ox thyroid glands examined, the weight varied from 8·7 to 130·4 g., the lower values relating predominantly to the English shorthorn variety and the heavier to the Swiss and Austrian (brown, Simmental, etc.) varieties. The relative iodine content is not directly related to the weight of the gland, the brown and shorthorn varieties having a higher iodine content than the heavier glands. The absolute iodine content generally increases with increasing weight. The colloid content and size of follicle is correlated rather with the iodine content than with the weight of gland. It was not possible, however, to establish a definite race variation or variation due to origin and condition.

P. W. Clutterbuck.

Enzymes of the omentum. J. M. Goldberg (Biochem. Z., 1927, 188, 475—480).—Enzymes possessing proteolytic, lipolytic, and faint amylolytic actions are detected in the omentum of dogs.

P. W. Clutterbuck.

Ultra-violet absorption spectra of certain physiological fluids. M. C. Reinhard (J. Gen. Physiol., 1927, 11, 1—6).—Ultra-violet absorption curves are given of human bile, saliva, pericardial fluid, urine, and hæmoglobin. W. O. Kermack.

Spectrophotometric determinations of purified bilirubin. C. Sheard, F. C. Mann, and J. L. Bollman (Amer. J. Physiol., 1927, 81, 774—781).—Spectrophotometric comparison and tests of the solubilities of purified bilirubin and the pigment in the bile and blood of normal and jaundiced animals further confirm their identity. R. K. Cannan.

Surface energy of some physiological fluids. I. N. Vedenski (Biochem. Z., 1927, 188, 270—278).—Physiological fluids may be surface-inactive (urine, gastric juice), surface-active (blood, milk, bile, saliva), or may hold a mean position (aqueous humour, cerebrospinal fluid). The total surface energy of surface-active liquids shows a maximum at a definite temperature, but of surface-inactive liquids does not change with temperature. The surface tension of the less surface-active physiological liquids decreases directly with the temperature, but that of the surface-active liquids changes according to a typical curve. The total surface energy of milk shows a sharp increase at 60°.

P. W. Clutterbuck.

Measurement of colloid-osmotic pressure in biological fluids. A. Krogh and F. Nakazawa (Biochem. Z., 1927, 188, 241—258).—Two simple methods, each requiring 0·3—0·5 c.c. of liquid, are described for the determination of colloid-osmotic pressure and are used for human, horse, and frog serum, human urine, etc. The methods are accurate to within 10 mm. pressure of water. The results are not affected by changes in salt concentration from 0·5 to 1·5% and of from 7 to 8, but at a lower p_H the pressure decreases. Carbonic acid does not exert any specific effect on the colloid-osmotic pressure. The latter decreases more quickly on dilution than the colloid concentration. Curves showing the relationship of the pressure per cent. and the percentage protein are almost linear and may be used for the investigation of pathological sera. Addition of caffeine does not affect the colloid-osmotic pressure of serum. P. W. Clutterbuck.

Amylase content of dog saliva and the influence of diet. O. Galehr (Fermentforsch., 1927, 9, 224—227).—In view of the conflicting reports as to whether dog's saliva contains a diastatic enzyme, investigations have been made on the saliva of three dogs which have been fed almost exclusively on carbohydrates for several months and that of three control dogs fed on a carbohydrate-free diet. It is found that dog saliva has no "dextrinase," but contains very small amounts of a "polyamylase." The amount of this diastase secreted bears no relationship to the diet and no increase of the starch-splitting activity occurs during long carbohydrate feeding. A. Wormall.

Influence of diet on the inorganic constituents of human saliva. G. W. Clark, J. S. Shell, J. B. Josephson, and M. E. Stockle (Dental Cosmos, 1927, 69, 500—513, 605—617).—The acid–base balance of the ration had little influence on the ability of adults to retain bases. Diets containing green foods increased the retention of calcium, phosphorus, sulphur, and nitrogen. There is no relationship between the quantity of an elemen ingested or retained and the quantity in the circu - ating blood or resting saliva, or between the concentrations of inorganic constituents in the blood an in the saliva. The concentration of inorganic phosphorus was 4—5 times as great in the saliva as m blood-plasma. Chemical Abstracts.

Gastric digestion. Relation of volume, hydrogen-ion concentration, and buffer capacity of the test meal to the gastric contents. W. A. Standish, G. R. Cowgill, and A. T. Shohl (Amer. J. Physiol., 1927, **81**, 696—706).—The amount of gastric juice varies with the volume and concentration of the meal. The p_H of the gastric contents remains nearly constant at a value of about 4 throughout the meal. The buffer capacity of the stomach contents likewise remains fairly constant after an initial rise. R. K. Cannan.

Constituents of sweat, urine, and blood. III. Urea. G. A. Talbert, J. R. Finkle, and S. S. Katsuki (Amer. J. Physiol., 1927, **82**, 153—156).—Tables are given of the urea-nitrogen found in the blood, urine, and sweat of 17 subjects. R. K. Cannan.

Chlorine and sodium in the milk of mammals. L. Barthe and E. Dufilho (Compt. rend., 1927, **185**, 613—615; cf. B., 1926, 644).—The milk of women contains 1·162 g. of chlorine per litre on the 6th day of lactation. This value rises to a maximum of 1·349 g. on the 12th day and falls to 0·923 after 9 months, at which time the milk contains 0·154 g. of sodium per litre. Whilst the amount of chlorine seems to be large during the colostral period, sodium does not appear in considerable amounts until the 45th day. Other elements than sodium are in combination with the chlorine, since the milk of mares, which contains 0·568—1·207 g. of chlorine per litre, contains only traces of sodium. G. A. C. Gough.

Urinary acidity. Electrometric titration of urine. S. Morgulis and W. R. Hamsa (J. Biol. Chem., 1927, **74**, 851—861).—Urine is titrated electrometrically against a buffer solution of p_H 7·4, using the quinhydrone electrode. Much lower values for the acidity of the urine are thus obtained than by the method of titration with phenolphthalein as indicator, owing to the increasing buffering capacity of urine as the reaction becomes more alkaline than p_H 7·4. C. R. Harington.

Determination of acetone in urine. G. Kleyer (Pharm. Ztg., 1927, **72**, 1262—1263).—Details are given for carrying out adapted Rothera and the more delicate Reichardt and Frommer–Emilewicz (salicylaldehyde) tests. P. W. Clutterbuck.

Nitrogenous constituents of hen urine. R. E. Davis (J. Biol. Chem., 1927, **74**, 509—513).—A technique is described for the collection of hen's urine without contamination with fæces. In such urine there was found, on the average, total nitrogen 100 mg. %, of which 62·9% was uric acid, 10·4% carbamide, 17·3% ammonia, and 8·0% creatinine. C. R. Harington.

Salicylsulphonic acid as a protein reagent. G. Roche (Pharm. Ztg., 1927, **72**, 1263).—A claim of priority as the first to suggest the use of sodium salicylsulphonate as a test for protein in urine. P. W. Clutterbuck.

Determination of quinine [in urine] by Hartmann and Zila's method. I. A. Smorodincev and A. N. Adova (Biochem. Z., 1927, **188**, 279—283). This method (A., 1918, i, 328) does not give accurate results and possesses no advantage over the simple extraction with ether. P. W. Clutterbuck.

Proteases of urine. II. Proteolytic action of urine in protracted starvation and with experimentally increased protein catabolism. O. Peczenik (Fermentforsch., 1927, **9**, 166—191; cf. A., 1926, 1275).—After prolonged starvation the urine of the rat, guinea-pig, and cat has a proteolytic action which varies with the type of food administered before the fast. Rats which are starved after a long meat diet give a urine which has strong peptic and tryptic activities, and the protein usage, as determined by the total nitrogen of the urine, is much higher than with rats which are starved after a milk diet. After injection of protein (caseinogen and milk), during prolonged starvation, and under experimental influences which lead to an increased cell disintegration, protein derivatives pass into the circulation and cause secretion of pepsinogen. A. Wormall.

Distribution of protein in blood in experimental anæmia. M. Bodansky, S. W. Morse, V. C. Kiech, and R. B. Bramkamp (J. Biol. Chem., 1927, **74**, 463—471).—Figures are given for the distribution of the various protein fractions in dogs' blood-serum, classified by the method of Howe (A., 1922, ii, 172). More than half of the protein obtained from the red blood-corpuscles by hæmolysis can be salted out within the limits of precipitation of the globulins. In anæmia induced by administration of acetylphenylhydrazine, the albumin : globulin ratio of the serum decreased, whilst the content of fibrinogen, euglobulin, and the protein fraction precipitable by 0·75*M*-sodium sulphate increased. C. R. Harington.

Pernicious anæmia. III. Contrast of the chloride contents of corpuscles and plasma in pernicious anæmia and other conditions. A. T. Cameron and M. E. Foster (Canad. Med. Assoc. J., 1927, **17**, 670—675).—The plasma-chlorine values in the anæmias are normal; cell-chlorine values in pernicious anæmia are low, but in secondary anæmia are high. Both plasma- and cell-chlorine values are low in diabetes and other conditions where increase of blood constituents requires osmotic compensation, and in acute intestinal obstruction. Chemical Abstracts.

Glycolysis in leucæmic blood. H. L. Schmitz and E. C. Glover (J. Biol. Chem., 1927, **74**, 761—773).—In normal blood the rate of glycolysis is 15—23 mg. % per hr. and is independent of the initial concentration of dextrose. In cases of myelogenous leucæmia rates of glycolysis of 18—84 mg. % per hr. were observed, with an approximate parallelism between the rate of glycolysis and the leucocyte count. In lymphatic leucæmia, the rate was not increased. Addition of potassium cyanide to the blood accelerates glycolysis markedly in myelogenous leucæmia and slightly in lymphatic leucæmia, but is almost without effect in normal blood. C. R. Harington.

Cerebral and cardiac glycogen and muscular lactic acid in adrenalectomised rats. B. A. Houssay and P. Mazzocco (Rev. Soc. Argentina

Biol., 1927, **3**, 491—500).—Extirpation of the adrenals in rats is without marked effect on cardiac and cerebral glycogen or on muscular lactic acid and lactacidogen. The increase in muscular lactic acid after 1 min. tetanisation is greater than in the controls. The excess of lactic acid disappears within 5 min., slightly more rapidly in the rats deprived of their adrenals than in the controls.

G. W. Robinson.

Fate of sugar in the animal body. VII. Carbohydrate metabolism of adrenalectomised rats and mice. C. F. Cori and G. T. Cori (J. Biol. Chem., 1927, **74**, 473—494).—In adrenalectomised rats, a starvation period of 24 hrs. caused almost complete disappearance of glycogen from the liver and a marked fall in the blood-sugar, the glycogen of the muscles remaining unchanged. Administration of dextrose to such animals resulted in normal synthesis of glycogen, although the rate of absorption of the dextrose was slower than in the normal animal. The relationship between dextrose oxidised and converted into glycogen after administration of dextrose to adrenalectomised rats with and without insulin was similar to that previously observed for normal rats (A., 1926, 1271); further, the effect of insulin in decreasing the liver-glycogen of normal fasting mice was observed also in adrenalectomised mice. These effects of insulin are therefore to be regarded as specific to this hormone and are independent of the effect of adrenaline. C. R. Harington.

Calcium metabolism in diabetes. E. Kylin (Acta Med. Scand., 1927, **66**, 197—206).—In diabetes of pancreatic origin the blood-calcium is high, falling after injection of insulin with elimination in the urine. Chemical Abstracts.

Acid production in diabetes. M. Odin (Acta Med. Scand., Suppl., 1927, XVIII, 1—573).—In mild diabetes the carbon dioxide capacity of the blood (C), the total acid excretion, and the p_H of the urine are normal, but there is increased acetonuria; in severe diabetes C is generally low. The total acidity of the urine is less when C is less than 30 vol.-% than when it is 30—39 vol.-%. In coma, C is always below 30 vol.-%; when it is below 25 vol.-% there is always coma. During coma there is a rise in the blood-sugar value. The urinary acid and acetone excretion often decreases during coma. Coma due to lack of insulin is ascribed to a lag in the production of ammonia. A fat–vegetable diet causes C to rise, until the urine actually becomes alkaline. Œdema is considered to be due to an excessive value of C. Changes in the value of C, the total acidity and p_H of the urine following a meal have been followed for normal and diabetic subjects. The effects on acid production of varying the diet have also been investigated.

Chemical Abstracts.

Cholesterol content of the blood-plasma as an index of progress in insulin-treated diabetics. I. M. Rabinowitch (Canad. Med. Assoc. J., 1927, **17**, 171—175).—The blood-lipin is a better index of the course of diabetes than is the blood-sugar. An increased blood-cholesterol value is not compatible with an improvement in pancreatic function.

Chemical Abstracts.

Diagnostic value of the diastatic enzyme of the urine. L. Kreyberg (Norsk Mag. Lægevidenskap., 1926, **24**, 992—1003).—Acute diseases of the pancreas and salivary glands are usually accompanied by a considerable rise in the diastatic index of the urine. The normal index (number of c.c. of 1 in 10^3 starch solution transformed by 1 c.c. of urine) ranges between 4 and 64. Chemical Abstracts.

Experimental lead hæmatoporphyria. H. Liebig (Arch. exp. Path. Pharm., 1927, **125**, 16—28).—The administration of lead by mouth or intraperitoneally to rabbits causes them to excrete hæmatoporphyrin in the urine and fæces. The origin of the pigment appears to be in the bone-marrow and it is not secreted in the bile as is the case in sulphonal poisoning. A method is given for the determination of hæmatoporphyrin in the urine and fæces. W. O. Kermack.

Chemical nature of the serum-globulin of the hæmatoporphyrin rabbit. M. Komatsu (J. Biochem. [Japan], 1927, **7**, 19—26).—The nitrogen : sulphur ratios of normal serum-albumin and -globulin of rabbits are 9·94 and 20·5, respectively. The sulphur content indicates that the globulin, which shows an increase of 50% in hæmatoporphyrin rabbits, retains its normal chemical constitution.

Chemical Abstracts.

Blood-chemistry in leprosy. II. Alkali reserve. E. M. Paras (Philippine J. Sci., 1927, **33**, 155—167).—The Van Slyke method for the determination of carbon dioxide capacity has been performed on 110 specimens of blood-plasma from cases of leprosy classified as follows: (*a*) leprosy without complication; (*b*) lepra reaction without alkali treatment; (*c*) lepra reaction with alkali treatment; (*e*) leprosy with tuberculosis; (*e*) leprosy with nephritis; (*f*) leprosy with miscellaneous complications such as malaria, anæmia, osteoarthritis, etc. The mean value obtained for the normal healthy adult was 70 vol.-% of carbon dioxide. The following results have been obtained respectively: (*a*) no significant variation from the normal mean, mean value for 41 cases 67·9; (*b*) no significant variation, mean value for 19 cases 66·5; (*c*) characteristic indications of alkalosis in some cases, mean value for 16 cases 75·7; (*d*) no significant variation, mean value for 7 cases 72; (*e*) significant reduction, mean value for 8 cases 61; (*f*) significant reduction, mean value for 19 cases 59·6. There appears to be no correlation between the alkali reserve, and the duration, type, or stage of the disease. E. A. Lunt.

Identity of urinary albumin. L. F. Hewitt (Biochem. J., 1927, **21**, 1109—1111).—Purified albumins excreted in the urine of patients with chronic nephritis or albuminuria of pregnancy have been isolated, purified, and examined for their rotatory power and dispersion. They do not differ in these respects from serum-albumin. S. S. Zilva.

Kidney phosphatase. II. The enzyme in disease. R. T. Brain and H. D. Kay (Biochem. J., 1927, **21**, 1104—1108).—Both in chronic nephritis in man and in acute experimental nephritis in rabbits the phosphatase activity of the renal tissue is markedly reduced. S. S. Zilva.

Prevention of tetany by oral administration of ammonium chloride. W. F. WENNER (Amer. J. Physiol., 1927, **81**, 612—619).—Oral administration of ammonium chloride prevents and cures tetany in parathyroidectomised dogs. Its action is due, probably, to an increased acidity of the blood and consequent rise in serum-calcium.

R. K. CANNAN.

Decreased nitrogen secretion during pregnancy. S. STEFANCSIK (Magyar Orvosi Arch., 1927, **28**, 156—160).—Accumulation of urea in the liver does not occur. Use of amino-acids by the fœtus accounts for the low concentration of these substances in the blood. CHEMICAL ABSTRACTS.

Theory of muscle contraction with *X*-ray diffraction patterns from relaxed and contracted muscles. J. H. CLARK (Amer. J. Physiol., 1927, **82**, 181—194).—It is suggested that lactic acid production leads to contraction by reason of an abrupt conversion of the substance in the anisotropic bands from the liquid crystal into the solid crystal state. It is shown that under the influence of slight increases in acidity the myelin forms of ammonium oleate contract with the formation of acicular crystals. *X*-Ray diffraction patterns of relaxed and contracted muscles show two distinct differences. In the contracted state the zones, representing first, second, and third order reflexion from equidistant molecular planes, show a fairly well-defined ring at the edge and an increase in diameter. These differences suggest an approach to a microcrystalline state. The distance between the molecular planes is 9·5 Å. in the relaxed and 8·5 Å. in the contracted muscle. The distances probably refer to the widths of the molecules forming the equidistant planes. R. K. CANNAN.

Dextrose and salt solutions recovered from Thiry-Vella loops. H. L. WHITE and J. RABINOWITCH (J. Biol. Chem., 1927, **74**, 449—454).—Solutions of dextrose in water or dilute sodium chloride were introduced into loops of the intestine of dogs with a Thiry-Vella fistula; after removal of the solution no mutarotation was observed. Slight differences which were sometimes observed between the reducing power and rotatory power of such solutions were accounted for by entrance into the solution from the gut of non-reducing lævorotatory or non-dextrose reducing substances. The results of Hewitt and Pryde (A., 1920, i, 508, 648) were therefore not confirmed.

C. R. HARINGTON.

Effect of p_H on the respiratory exchange of the muscle of the frog. M. COMEL (Atti R. Accad. Lincei, 1927, [vi], **5**, 808—812).—The respiratory exchange in the muscle of the frog has been determined between the values p_H 9·1 and 3·0, using Jarisch's and McIlvaine's solutions for the buffering medium. Slight differences in the values obtained are reported, but in both cases the maximum respiratory exchange takes place at p_H 7·1. The use of McIlvaine's solution brings about a more rapid decrease in the respiratory exchange below p_H 5·3 than the use of Jarisch's solution. Variations in the respiratory quotient are also observed. E. A. LUNT.

Furan compounds derived from sugars. J. KARASHIMA (Z. physiol. Chem., 1927, **169**, 278—296).—The administration of chitose to the dog, hen, frog, and rabbit leads to the excretion in the urine of small amounts of hydroxymethylpyromucic acid, the maximum yield being 6·3% of the chitose administered. That hydroxymethylpyromucic acid is one of the main products of metabolism of chitose appears improbable, however, since feeding with hydroxymethylfurfuraldehyde results in the excretion of 66·7% of the acid as hydroxymethylpyromucic acid. Chitonic acid and chitaric acid yield no hydroxymethylpyromucic acid in these feeding experiments. The preparation of *hydroxymethylpyromucyl chloride* (*5-hydroxymethylfuran-1-carboxyl chloride*), b. p. 120°/9 mm., *hydroxymethylpyromucic acid*, m. p. 167° (uncorr.), and *hydroxymethylpyromucylglycine*, $OH{\cdot}CH_2{\cdot}C_4H_2O{\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}CO_2H$, is described.

A. WORMALL.

Behaviour of *iso*quinoline in the animal organism. M. TAKAHASHI (Z. physiol. Chem., 1927, **169**, 297—299).—After subcutaneous injection of *iso*quinoline, the methylated compound has been isolated in small quantities from the urine of the dog and the hen, but not of the rabbit. A. WORMALL.

Detoxication of benzoic acid in man. J. L. BRAKEFIELD (J. Biol. Chem., 1927, **74**, 783—785).—After administration of 5—6 g. of benzoic acid to human subjects, more than 90% was recovered from the urine as hippuric acid; a trace of free benzoic, but no benzoylglycuronic acid was detected.

C. R. HARINGTON.

Utilisation of calcium of spinach. L. McLAUGHLIN (J. Biol. Chem., 1927, **74**, 455—462).—Storage of calcium in adult women was not impaired when 70% of the total intake of this element was supplied in the form of spinach.

C. R. HARINGTON.

Growth and reproduction on synthetic diets. II. G. A. HARTWELL (Biochem. J., 1927, **21**, 1076—1086).—Three generations of rats have been reared on a synthetic diet of butter, caseinogen, potato starch, salt mixture, marmite, and distilled water. The substitution of cod-liver oil for butter in this diet produces less good growth and causes sterility. Synthetic diets are described which produce good growth in young rats, but cause inability of the young to be born and consequent death of the doe. The dietary requirements of the rat vary at different phases of its existence. S. S. ZILVA.

Physiology of reproduction in birds. XXII. Blood-fat and -phosphorus in the sexes. O. RIDDLE and F. H. BURNS (Amer. J. Physiol., 1927, **81**, 711—724).—During the ovulation cycle in female ring-doves there is a notable increase in the fat and lipoid phosphorus of the blood. The relation of the ovary to this increase is discussed and the question of sex inequalities in fat metabolism reviewed.

R. K. CANNAN.

Nitrogen equilibrium and nitrogen balance. Experiments with rye bread. A. PUTTER (Z. Biol., 1927, **86**, 317—344).—A discussion, based on experimental evidence, of the preliminary conditions necessary for the attainment of suitable basal conditions for feeding experiments. Experiments on nitrogen equilibrium in which these conditions are not

fulfilled give too high values for the nitrogen administration with which equilibrium is reached.

W. ROBSON.

Role of the lungs in intermediary nitrogenous metabolism. I. Total and residual nitrogen content of arterial blood and of blood from the right heart in the normal animal and after intravenous injections of serum. II. [With S. KRASSOVITZKAJA.] **Residual nitrogen content of the defibrinated blood flowing to and from the isolated lung.** A. M. TSCHARNY (Biochem. Z., 1927, 188, 372—377; 378—380).—I. In dogs, the arterial blood flowing from the lungs contains much less residual nitrogen than the blood flowing to the lungs from the right heart. This decrease is still greater after injection of serum. Some of the residual nitrogen is therefore retained by the lung.

II. Experiments with the isolated organ confirm the view that nitrogen accumulation takes place in the lung.

P. W. CLUTTERBUCK.

Amino-nitrogen in the egg of *Bombix mori*. M. TIRELLI (Arch. Farm. sperim. Sci. aff., 1927, 43, 115—128).—The determination by Monzini (Ann. R. Staz. Bac. Padova, 1921, [v], 43, [2]) showed that the amino-nitrogen in the eggs of the silkworm moth increases during incubation, but in a slight and transient amount. It is now found that the amino-nitrogen is greater in the fresh or hibernated eggs than in those which have been incubated, in which the values oscillate, decreasing during the first phase and subsequently increasing. Variations in the nitrogen in eggs of the "yellow native" and "white Chinese" moths, and of crosses, are discussed.

E. W. WIGNALL.

Influence of fat and carbohydrate diets on uric acid of blood. V. J. HARDING, K. D. ALLIN, and B. A. EAGLES (J. Biol. Chem., 1927, 74, 631—643).—The increase in the uric acid of the blood, previously observed (A., 1925, i, 604) to result from a diet rich in fat, is accompanied by decreased excretion of uric acid. During the normal puerperium the uric acid of the blood is not increased by a diet low in protein and rich in carbohydrate, although in the puerperium following toxæmia such diets do cause an increase in the uric acid.

C. R. HARINGTON.

Metabolism of uric acid in the living animal. V. S. J. PRZYLECKI (Arch. int. Physiol., 1926, 27, 159—202).—The invertebrates are classified (*a*) according as they excrete (or contain) uric acid, or not (uricopositive, uriconegative), and (*b*) according as they decompose uric acid, or not (uricolytic, uricostatic). Unlike the higher vertebrates, certain invertebrates lack purine oxydases, whilst others readily oxidise endogenous or exogenous purines to uric acid. The decomposition, with vertebrates and invertebrates, of uric acid by uricase proceeds only in the presence of oxygen, and terminates with allantoin. The invertebrates do not contain allantoinase. Some can synthesise uric acid from acyclic compounds; the invertebrates cannot decompose allantoin, alloxan, dialuric acid, or barbituric acid to urea or ammonia. Whilst the first stage in the catabolism of uric acid involves the elimination of carbon dioxide, the last stage is the addition of a molecule of carbamide to the pyrimidine nucleus. The two reactions are biologically irreversible. In the invertebrates no species can form uric acid from purines which cannot convert it into allantoin except those which do not contain it and those which form it from acyclic compounds.

CHEMICAL ABSTRACTS.

Purine metabolism. III. Basal metabolism and purine content. IV. The nuclear-plasmic ratio in dogs in carbohydrate and protein feeding and in starvation. R. TRUSZKOWSKI (Biochem. J., 1927, 21, 1040—1046, 1047—1053).—III. The chemical nuclear-plasmic ratios of whole rats and guinea-pigs differ little from one another. The values obtained for purine- and total nitrogen and for the nuclear-plasmic ratios of liver and of skeletal muscle of rats, rabbits, dogs, horses, and cattle vary within wide limits, but are in no way connected with the basal metabolism of the animals in question. The purine content of animals cannot therefore be identified with the intensity of the metabolism.

IV. The total nitrogen and purine contents of the liver of the dog are respectively 43 and 47% higher when the animal is fed on meat than when carbohydrates are consumed. The nuclear-plasmic ratio of the liver tissue in meat-fed dogs is almost the same as on a carbohydrate diet. The total solids of the skeletal muscle of dogs fed on meat are 14% higher than on carbohydrate diet. The total nitrogen and purine contents of skeletal muscle are respectively 35 and 49% higher in dogs fed with meat than in those fed on carbohydrates. The nuclear-plasmic ratio of skeletal muscle in meat-fed dogs is slightly higher than that found in carbohydrate feeding. In starvation, the nuclear-plasmic ratio of the liver is 10% above normal, whilst that of skeletal muscle is unchanged. These experiments do not support the view of protein storage.

S. S. ZILVA.

Metabolism of sulphur. XIII. Effect of elementary sulphur on growth of white rat. G. T. LEWIS and H. B. LEWIS (J. Biol. Chem., 1927, 74, 515—523).—Addition of flowers of sulphur to a diet deficient in cystine was not only unable to replace the latter, but also caused actual retardation of growth, when given in small amounts. Addition of larger amounts of sulphur, even in presence of an adequate supply of cystine, caused toxic effects, presumably due to formation of hydrogen sulphide in the intestine.

C. R. HARINGTON.

Role of lipins in biology and immunology. L. SURANYI (Magyar Orvosi Arch., 1927, 28, 125—137).—It is suggested that lipins, and especially cholesterol, play an important part in the neutralisation of the normal products of assimilation, whether poisonous or not, and probably in their transport and elimination.

CHEMICAL ABSTRACTS.

Effect of fasting on the urine of steers. T. M. CARPENTER (Amer. J. Physiol., 1927, 81, 519—551).—Comparative analyses are reported of the urine of steers before, during, and after fasting periods of from 5 to 14 days.

R. K. CANNAN.

Kinetics of the swelling of cells and tissues. J. H. NORTHROP (J. Gen. Physiol., 1927, 11, 43—).

—The rates of swelling of *Arbacia* eggs and of slices of carrot and potato conform to the formulæ previously developed (cf. this vol., 825) for the increase in volume of a gelatin solution within a collodion membrane and for the swelling of blocks of gelatin.

W. O. KERMACK.

Influence of external osmotic pressure and disturbance of the cell surface on the permeability of *Spirogyra* for acid dyes. G. W. SCARTH (Protoplasma, 1926, **1**, 204—213).—The cells of *Spirogyra* are normally highly impermeable to acid dyes, the permeability increasing with the osmotic pressure of the medium in which the dye is applied. It is suggested that the permeability is regulated by an organised film on the surface of the cytoplasm.

CHEMICAL ABSTRACTS.

Permeability of living cells. VII. Effects of light of different wave-lengths on the penetration of 2 : 6-dibromophenolindophenol into *Valonia*. M. M. BROOKS (Protoplasma, 1926, **1**, 305—312).—Between 300 and 700 μ the amount of 2 : 6-dibromophenolindophenol penetrating the sap of *Valonia* from a 0·00035*M*-solution in sea-water increased as the wave-length decreased. CHEMICAL ABSTRACTS.

Bioelectrical phenomena. W. J. V. OSTERHOUT (J. Gen. Physiol., 1927, **11**, 83—99).—A discussion of bioelectrical phenomena preliminary to the publication of experimental results. The advantage of using single large cells as of *Valonia* and *Nitella* is emphasised. W. O. KERMACK.

Properties of radiation-substances with weak irradiation. H. ZWAARDEMAKER (Proc. K. Akad. Wetensch. Amsterdam, 1927, **30**, 420—422).—Perfusion of a heart with Ringer's solution deficient in potassium causes its action to cease, but on irradiation the beat recommences after a latent period of ½—1 hr. The perfusion liquid is then capable of regenerating the beat of another heart which has been similarly treated but not irradiated. The active substance has not been isolated, but is soluble in alcohol, stable when the solution is heated, and adsorbed by charcoal and magnesium silicate; it may be dialysed and is ultrafilterable, but does not appear to lower the surface tension of water. H. F. GILLBE.

Relationship between structure and action of cardiac glucosides. W. A. JACOBS and A. HOFFMANN (J. Biol. Chem., 1927, **74**, 787—794).—Saturation of the double linking associated with the lactone group in the cardiac glucosides reduces, but does not abolish, the physiological activity, which is therefore a property of the molecule as a whole. Cymarin, on hydrogenation, gave *dihydrocymarin*, $C_{30}H_{46}O_9,H_2O$, m. p. 128° and 190°, $[\alpha]_D^{22}$ +17·8° in pyridine, of which the toxicity was 1/16 of that of cymarin. Ouabain gave *dihydro-ouabain*, $C_{30}H_{48}O_{12}$, m. p. 105°, $[\alpha]_D^{20}$ −4·4° in water; toxicity 1/23 of that of ouabain. Digitoxin yielded *dihydrodigitoxin*, m. p. 202—204°, $[\alpha]_D^{20}$ +2·4° in pyridine. C. R. HARINGTON.

Pharmacology of galegine. H. MÜLLER and (Arch. exp. Path. Pharm., 1927, **125**,).—Galegine raises the blood-sugar when administered to rabbits or when given in large doses o dogs, but small doses given to dogs lower the blood-sugar. Also when given to depancreatised dogs it causes a decrease in the concentration of sugar in the blood and in the urine. The hyperglycæmic action of galegine is antagonised by ergotamine. When galegine and ergotamine are administered together, hypoglycæmic convulsions may be produced in the rabbit and the dog. W. O. KERMACK.

Physico-chemical causes of the behaviour of the phenol–camphor medicament. P. GUNTHER and M. PEISER (Z. physikal. Chem., 1927, **128**, 189—202).—The fact that an equimolecular mixture of phenol and camphor does not exert any corrosive action on the mucous membrane of the mouth cannot be attributed to compound formation, since f.-p. curves for phenol–camphor mixtures indicate only the existence of an extremely loose compound, and the densities and refractive indices of the mixture are very nearly additively constituted of those of the components. A distribution of the phenol between the camphor and water in favour of the camphor phase is not a possible explanation, for addition of a little water to a mixture containing 15 mols. % of camphor causes the separation of a solid which is nearly pure camphor. With the mixture used medicinally, however, addition of a little more water results in the appearance of a third phase, consisting of an approximately 1·3% aqueous solution of phenol. The efficacy of the mixture is therefore due to the addition of water causing the deposition of finely-divided and nearly pure camphor with subsequent formation of an aqueous solution of phenol which has a bactericidal but not a corrosive action.

R. CUTHILL.

Phenylalanine series. IX. Pharmacological action of hexahydrophenylalanine and hexahydrotyrosine, and of the related amine and its derivatives. E. WASER (Arch. exp. Path. Pharm., 1927, **125**, 129—139).—The pharmacological activity of the following compounds has been investigated; hexahydrophenylalanine, hexahydrotyrosine, and the hydrochlorides of their ethyl esters; hexahydrophenylethylamine hydrochloride; hexahydrotyramine hydrochloride, *N*-methylhexahydrotyramine hydrochloride and *ON*-diacetylhexahydrotyramine. Their toxicity and their action on the pupil, heart, respiration, intestine, and temperature are small, but hexahydrophenylethylamine, hexahydrotyramine, and *N*-methylhexahydrotyramine markedly raise the blood-pressure.

W. O. KERMACK.

Preparation of dibismuthyl monosodium citrate. W. F. VON OETTINGEN, Y. ISHIKAWA, and T. SOLLMANN (J. Pharm. Exp. Ther., 1927, **31**, 353—360).—Dibismuthyl monosodium citrate has been prepared by dissolving monobismuthyl citrate in sodium hydroxide. The formation of a pure product depends on the final p_H of the solution, which should not exceed 7·6, and on the amount of alcohol used to precipitate the dibismuthyl salt. The therapeutic advantages claimed for this substance over the bismuth citrates now in use are that, prepared in this way, the bismuth content is constant, the substance is stable in aqueous solution, and can be readily sterilised.

E. A. LUNT.

Colloidal lead phosphate for use in cancer therapy. F. BISCHOFF and N. R. BLATHERWICK (J. Pharm. Exp. Ther., 1927, **31**, 361—375).—Colloidal lead phosphate is prepared by adding sodium phosphate solution to a hot solution of lead chloride in water containing 4% of gelatin. When administered thus it is relatively non-toxic to rats and rabbits, and it does not affect the fragility of red blood-corpuscles (human) *in vitro*. The rate of excretion by the rabbit of lead given as phosphate is the same as that for lead administered in other forms. Ionic lead, buffered with serum containing enough phosphate to react completely with the lead, is also non-toxic.

E. A. LUNT.

Synthetic medicinals. II. Theory of laxatives. H. P. KAUFMANN.—See this vol., 1075.

Physiological action of two disulphones. A. RÉCSEI (Biochem. Z., 1927, **188**, 405—408).—Butyrone diethylsulphone, with tadpoles, is, with respect to concentration 20 times and with respect to time 30 times as active as sulphonal and the animals recover twice as quickly. *cyclo*Hexanone diethylsulphone is 10 and 20 times as active, respectively, as sulphonal and the animals recover more quickly. A larger concentration acting for a shorter time is less injurious than a more dilute solution for a longer time. With guinea-pigs the lethal dose is about 1 g. per kg. body-weight and the narcotic dose is very near this. This substance is also powerfully antipyretic.

P. W. CLUTTERBUCK.

Localisation of veronal and phenylethyl- and diallyl-barbituric acids in the brain (the problem of sleep). E. KEESER and J. KEESER (Arch. exp. Path. Pharm., 1927, **125**, 251—256).—Phenylethylbarbituric acid, veronal, or diallylbarbituric acid when injected intravenously into rabbits could be recovered from the thalamus and corpus striatum, but not from the great hemispheres, the mesencephalon, the cerebellum, the pons, or the medulla oblongata.

W. O. KERMACK.

Utilisation of carbohydrate in the non-diabetic organism. II. Respiratory exchange after administration of carbohydrate under the influence of adrenaline and substances with adrenaline-like action (pituitary extract, ephedrine, and "ephetonine" [synthetic *dl*-ephedrine]). A. LUBLIN (Arch. exp. Path. Pharm., 1927, **125**, 229—241).—Adrenaline, pituitary extract, and particularly ephedrine and "ephetonine" retard the conversion of carbohydrate into fat, a process which the authors consider is favoured by the action of insulin.

W. O. KERMACK.

Carbon monoxide as a tissue poison. J. B. S. HALDANE (Biochem. J., 1927, **21**, 1068—1075).—The movements of a moth and the germination of cress seed are inhibited by carbon monoxide. The greater the partial pressure of oxygen the more carbon monoxide is required. Rats living on oxygen dissolved in their blood under pressure in presence of sufficient carbon monoxide to combine with almost all their hæmoglobin are killed by the addition of more carbon monoxide. It is concluded that cells contain a catalyst of oxidation which is poisoned by carbon monoxide (cf. Warburg, A., 1926, 1277). Its affinity for carbon monoxide was determined in the case of the moth. Its affinities differ in different species and perhaps in different tissues. The toxic effect is not due to any impurities in the gas.

S. S. ZILVA.

Nitrogenous metabolism in experimental subacute arsenic and antimony poisoning. E. PRIBYL (J. Biol. Chem., 1927, **74**, 775—781).—Subacute poisoning of rabbits with sodium arsenite and with antimony potassium tartrate causes an increase in the non-protein nitrogen of the blood, which is more marked in the case of the arsenite and is chiefly due to an increase in carbamide nitrogen. In the urine, there is an increase in the total nitrogen excreted.

C. R. HARINGTON.

Inhibitory effect of metallic salts on bacterial growth. I. Silver salts. P. H. ANDRESEN (Dansk Tids. Farm., 1927, **16**, 471—489).—In a medium containing peptone, the amount of ionic silver required to inhibit bacterial growth cannot be determined exactly, since the ionic concentration of added silver does not remain constant. If, however, to a synthetic medium containing aspartic acid and a mixture of inorganic salts sodium thiosulphate is added, a culture fluid is obtained which on the addition of silver nitrate displays a definite and constant silver-ion concentration for at least 48 hrs. at 37° (silver-ion concentration measured electrometrically). In such a medium, at p_H 7·2 growth of *B. coli* is prevented at an $Ag^{\cdot}$ as low as $0{\cdot}16\times10^{-11}$. Similar minimum inhibiting values were found for certain other bacteria, which, in absence of silver, grow readily in this medium. The silver-ion concentration is the governing factor in growth inhibition and, no matter how much total silver be present in the medium, the ionic concentration must be maintained at or over the above minimum to ensure complete inhibition.

H. D. KAY.

Antagonism of glucosone and cyanides *in vivo*. A. HYND (Biochem. J., 1927, **21**, 1094—1101).—In the case of mice and rats, a subcutaneous injection of dextrose or of dextrose plus insulin affords no protection against toxic action following either the subsequent subcutaneous injection of either alkali or methyl cyanide or of the inhalation of gaseous hydrogen cyanide. Glucosone, on the other hand, exerts a definite antagonistic action towards cyanides in these circumstances, but is less efficient than cystine. The previous, or simultaneous, intravenous administration of glucosone or of dextrose plus insulin appears to be protective against the intravenous injection of alkali cyanide into rabbits, but the results obtained are somewhat variable.

S. S. ZILVA.

Effect of ethyl cyanide and ethyl carbylamine on biological oxidations. O. H. EMERSON and J. W. BUCHANAN (J. Pharm. Exp. Ther., 1927, **31**, 387—392).—In solutions of the same molar concentration ethyl carbylamine is a more powerful depressant of the oxygen consumption of *Planaria dorotocephala* and *P. maculata* than ethyl cyanide; its action is similar to that of potassium cyanide.

E. A. LUNT.

Purification of malt amylase. E. GLIMM and W. SOMMER (Biochem. Z., 1927, **188**, 290—320).—

A method is described depending on a charcoal treatment of dilute solutions of diastase (Merck) after 3 days' aseptic autolysis (in presence of toluene) at 40°. The original diastase solution contained 9% of carbohydrate (erythrodextrin) and 8% of total nitrogen, readily reduced Fehling's solution, gave strong ninhydrin and peroxidase (with benzidine–hydrogen peroxide) reactions, and had an amylase value of 0·2—0·5. The amylase filtrate obtained after 3 days' aseptic autolysis of this solution at 40° followed by treatment twice with animal charcoal was water-clear, had amylase content 5·8, nitrogen content only 3·8%, was free from reducing carbohydrates, and gave a very faint ninhydrin reaction.

Amylase may be adsorbed by aluminium hydroxide and eluted without loss by means of secondary phosphate solution, 50% of inactive material being separated. Adsorption by stannic acid separated 70% of inactive material, but elution from kaolin, and still more so from stannic acid, caused considerable inactivation of the enzyme, these acid colloids separating the enzyme from its protective agent. Adsorption on gelatinous zinc phosphate succeeded only in presence of 20% alcohol, and since the conversion into crystalline phosphate took some time, most of the amylase became inactivated. After saccharification of starch, amylase is completely adsorbable from the maltose complex and elutable. Amylase may be heated for a considerable time at 50° without injury and remains adsorbable, but is no longer elutable from the adsorbate.

P. W. Clutterbuck.

Taka-diastase. K. Nishikawa (Biochem. Z., 1927, **188**, 386—404).—The optima for the following enzymes of taka-diastase are: for amylase, 6·8—7·2, for tryptase (hydrolysis of gelatin) 7·7—8·3, (hydrolysis of fibrin) 8·2—8·6, and for the milk-clotting enzyme 5·2—6·7. Trypsin, diastase, lipase, and milk-clotting enzyme are adsorbed by fibrin from a taka-diastase solution and may be eluted under suitable conditions by dilute acids and alkalis or by allowing the fibrin–enzyme complex to react with starch solution, when both diastase and trypsin pass into solution. If taka-diastase is heated for 10 min. at 65°, the amylase is considerably inactivated, to a greater extent in presence of sodium or potassium chlorides than in distilled water. Inorganic and organic calcium salts have a protective action on amylase, but barium and magnesium salts are much more injurious. The same applies to tryptase, but the heat action is much more injurious. Zinc is injurious to amylase and zinc and copper to trypsin, but iron, nickel, cobalt, and copper are without effect on amylase. Amylase is inactivated by mercuric chloride and reactivated by adding the corresponding amount of sodium cyanide. Trypsin is similarly inactivated, but requires more cyanide for reactivation. In taka-diastase there is also present a phenoloxidase which oxidises only dihydroxybenzene derivatives (dihydroxyphenylalanine and pyrocatechol) and is without action on tyrosine. Under suitable conditions, taka-diastase converts fibrinogen into fibrin.

P. W. Clutterbuck.

Isolation of diastase from human urine. P. Rostock (Fermentforsch., 1927, 9, 192—194).—The urine of subjects with acute pancreatic necrosis is specially suitable for the preparation of diastase, since the diastatic value is very high in this condition and trypsin and lipase are absent. By dialysis of the urine under sterile conditions and subsequent drying at 37°, a preparation has been obtained which is thirty times as active as the most active commercial preparation (Merck). A. Wormall.

Liver diastase. E. F. Lesser (Biochem. J., 1927, 21, 1128).—Polemical against Eadie (this vol., 482). About two thirds of the liver diastase is adsorbed on the surfaces of the cell and is therefore unable to act on the liver glycogen. This applies also to the parotid gland of the mouse. S. S. Zilva.

Coagulation of egg-yolk by pancreatic diastase. E. Lagrange (Arch. int. Physiol., 1926, 26, 347—361).—Pancreatic juice contains a vitellinase which is more sensitive than lipase to the reaction of the precipitate; its action is prevented by sodium fluoride. Chemical Abstracts.

Influence of thorium-*X* on the activity of emulsin. A. Maubert (Compt. rend., 1927, **185**, 669—671).—The total radiation of thorium-*X* in concentrations down to 0·05 γ per c.c. of liquid, accelerates the action of emulsin on amygdalin, whilst at higher concentrations the reaction is more and more, and with 12 γ per c.c. completely, inhibited. At the latter concentration β- and γ-rays have only a slight effect, and the effect above must therefore be due to the α-radiation (cf. A., 1925, i, 737; 1926, 759; this vol., 483). P. W. Clutterbuck.

Amygdalase, gentiobiase, gentianase. K. Josephson (Z. physiol. Chem., 1927, **169**, 301—304).—The relationship between these enzymes is discussed and it is considered that no definite conclusion can yet be reached as to the identity of gentianase with amygdalase or with gentiobiase.

A. Wormall.

Specific action of plant enzymes. III. Conditions of action of leaf salicinases. A. V. Blagoveschenski and N. I. Sossiedov (Biochem. J., 1927, 21, 1206—1210).—A definite optimal hydrogen-ion concentration exists for the action of salicinases from various species of *Populus* and *Salix*. Different plants contain various amounts of the enzyme. Salicinase is present in *Gossypium hirsutum*; the enzyme is therefore not confined to the Salicaceæ.

S. S. Zilva.

Action of carbon monoxide on certain oxidising enzymes. M. Dixon (Biochem. J., 1927, 21, 1211—1215).—Carbon monoxide has no inhibitory effect on the aerobic oxidation of aldehyde or hypoxanthine by the milk oxidase, or of succinic acid by the succinoxidase of muscle. Its action thus differs from that of cyanide, which strongly inhibits the latter reaction.

S. S. Zilva.

Peroxidase. V. Mathematics of the enzyme action. H. W. Bansi and H. Ucko (Biochem., 1927, **169**, 177—195; cf. this vol., 377).—The oxidation of pyrogallol by peroxidase proceeds according to the equation $u=kt$ where u is

change in time t, k is a constant, and $1/a$ the exponential factor. The calculated values with varying amounts of enzyme, hydrogen peroxide, and pyrogallol, and with variations in the p_H and temperature, agree very well with the experimental results. The factor a is constant for one enzyme preparation with variations in the amount of enzyme and pyrogallol, and, within certain limits, the concentration of hydrogen peroxide; it is influenced chiefly by alterations in p_H and temperature, being increased by a rise in temperature and a rise in C_H. The values for a usually lie between 1 and 2, but with an excess of hydrogen peroxide and a p_H below 4·5 the value rises above 2. The decrease in velocity observed during the course of the oxidation is due to adsorption of the enzyme on the purpurogallin formed, and removal of this product from a reaction mixture, in which the reaction has ceased, leads to a resumption of the oxidation. Hydrogen peroxide inhibits the action of peroxidase only if present in high concentrations. A modification of Willstatter's scheme is suggested for the reactions between hydrogen peroxide and peroxidase, resulting in the formation of an active additive product which gives up oxygen and an inactive product which is dissociated into free peroxidase and hydrogen peroxide under the influence of the substrate. A. WORMALL.

Action of tyrosinase on tyrosine. H. S. RAPER (Fermentforsch., 1927, 9, 206—213).—The mechanism of the oxidation of tyrosine by tyrosinase is discussed (cf. A., 1926, 977; this vol., 278). The first product is 3 : 4-dihydroxyphenylalanine, which is then oxidised to the corresponding quinone; an intramolecular change results in the production of 5 : 6-dihydroxydihydroindole-2-carboxylic acid, which is then oxidised to the corresponding quinone (red compound). This quinone yields 5 : 6-dihydroxyindole and 5 : 6-dihydroxyindole-2-carboxylic acid, the precursors of melanin. From the nitrogen content of melanin (A., 1925, i, 473) it is possible that each molecule of dihydroxyindole oxidised to melanin takes up one atom of oxygen and loses two atoms of hydrogen, and that condensation occurs with the formation of colloidal amorphous melanin. The results do not support the view that melanin production is due to the oxidation of a pyrrole derivative formed from tyrosine. A. WORMALL.

Purification of lactic acid-forming enzyme of muscle. O. MEYERHOF and K. MEYER (J. Physiol., 1927, 64, xvi).—The muscle extract is brought to p_H 5 with acetate buffers, thereby precipitating the protein and enzyme. Subsequent elution with phosphate solution effects dissolution of the enzyme with some protein. After a repetition of this process the activity had increased more than tenfold, and may be further increased by adsorption on aluminium hydroxide prepared by Willstatter's method. The co-enzyme and phosphoric esters are removed during the purification so that boiled muscle extract must be added to obtain glycolysis. Besides enzyme and co-enzyme a hydrolysable ester is necessary. This appears to be a hexosediphosphate. On purification the enzyme becomes more stable and may be preserved for several days. R. K. CANNAN.

Influence of some poisons on the serum-lipase of warm-blooded animals. A. KUDRJAVZEVA (Fermentforsch., 1927, 9, 139—145).—In general, the serum-lipase of the carnivorous animal (cat and dog) is more readily inhibited by atoxyl than is that of the herbivora, the rabbit, however, being an exception. Of these animals, the cat, dog, and rabbit are most sensitive to arsenic. Quinine inhibits most strongly the serum-lipases of the dog, sheep, and cow, and the lipase of the horse, hen, and pigeon to a less extent, whilst it has very little action in the case of the guinea-pig, cat, and rabbit. No relationship can be traced between the sensitivity of the lipases to quinine and the type of food eaten. Morphine exerts little inhibitory action on serum-lipase except with the dog, whilst strychnine has even less influence. The sensitivity of the serum-lipases to morphine and strychnine cannot be correlated in any way with the type of food or with the general sensitivity of the animal to the poison. A. WORMALL.

Specificity of proteolytic enzymes. E. WALDSCHMIDT-LEITZ, W. GRASSMANN, and H. SCHLATTER (Ber., 1927, 60, [*B*], 1906—1909; cf. A., 1926, 323).—Enzymic hydrolysis of triglycine, *dl*-alanyldiglycine, tetraglycine, *dl*-leucyltriglycine, pentaglycine, *l*-leucyltriglycyl-*l*-tyrosine, hexaglycine, and *l*-leucylheptaglycine by intestinal erepsin and pancreas-trypsin activated by enterokinase has been investigated. Lengthening of the peptide chain, for example in glycylglycine or leucylglycine by introduction of further glycyl residues up to the octapeptide, is without influence on the specificity of the enzyme, whereas the conversion of leucyltriglycine into leucyltriglycyltyrosine is accompanied by a qualitative change in the specific action, since the peptide is hydrolysed by trypsin but not by erepsin. The nature of the amino-acid component is therefore of primary importance, but the effect of lengthening the chain is shown by comparison of the hydrolysis of leucyltriglycyltyrosine and glycyltyrosine.

The observation that peptides can be hydrolysed by pancreatic trypsin renders unnecessary the formal distinction between the proteases proper, including trypsin, and the peptidases. H. WREN.

Specific adaptation of polypeptidases. E. ABDERHALDEN and E. SCHWAB (Fermentforsch., 1927, 9, 252—263).—Various polypeptide derivatives have been subjected to the action of polypeptidases, and the nature of the substrate grouping responsible for the affinity for the corresponding enzyme is considered. *dl*-Leucyltyramine is hydrolysed by the erepsin of intestinal and pancreatic press juices, but not by yeast maceration juice. The secondary base, iminodi*iso*hexoyltyramine, is hydrolysed by the yeast juice only, whilst the phenylcarbimides of phenylalanine, leucine, and glycine are unattacked by these juices. Pancreatin hydrolyses benzoyl-*a*-leucylglycylglycine and benzoyl-*dl*-alanylglycylglycine (cf. Imai, A., 1924, i, 921). Tyramine is condensed with α-bromo*iso*hexoyl bromide to give *α-bromoisohexoyltyramine*, m. p. 113°, and this, when heated with ammonia in a sealed tube at 60—70°, yields dl-*leucyltyramine*, decomp. about 100°,

and the secondary base *iminodiisohexoyltyramine*, $NH[CH(C_4H_9)\cdot CO\cdot NH\cdot CH_2\cdot CH_2\cdot C_6H_4\cdot OH]_2$.

A. WORMALL.

Behaviour of *dl*-alanyl-δ-aminovaleric acid and *dl*-leucyl-δ-aminovaleric acid towards polypeptidases. E. ABDERHALDEN and J. HARTMANN (Fermentforsch., 1927, 9, 199—205).—*dl*-α-Bromopropionyl bromide is condensed in an alkaline solution with δ-aminovaleric acid to yield dl-α-*bromopropionyl-δ-aminovaleric acid*, m. p. 112°, which is converted by the action of ammonia into dl-*alanyl-δ-aminovaleric acid*, m. p. 162°. Similarly, δ-aminovaleric acid condensed with *dl*-α-bromisohexoyl bromide yields dl-α-*bromisohexoyl-δ-aminovaleric acid*, m. p. 75—76°, which with ammonia gives dl-*leucyl-δ-aminovaleric acid*, m. p. 164—165°. The two dipeptides, *dl*-alanyl- and *dl*-leucyl-δ-aminovaleric acids, unlike *dl*-leucylglycine, are not hydrolysed by yeast maceration juice.

A. WORMALL.

Behaviour of *l*-leucylglycyl-*l*-tyrosine and *d*-leucylglycyl-*l*-tyrosine towards yeast maceration juice, pancreatic juice, and intestinal juice. E. ABDERHALDEN and N. SCHAPIRO (Fermentforsch., 1927, 9, 234—237).—These enzyme solutions acting on *l*-leucylglycyl-*l*-tyrosine in a phosphate buffer solution at p_H 8 for 24 hrs., eliminate *l*-tyrosine, which has been isolated in the pure condition, whilst *l*-leucine, glycine, and *l*-leucylglycine are also formed. No action occurs with *d*-leucylglycyl-*l*-tyrosine. *d*-α-Bromo*iso*hexoylglycyl-*l*-tyrosine is condensed with glycyl-*l*-tyrosine to give d-α-*bromoisohexoylglycyl*-l-*tyrosine*, an oil, which when treated with ammonia yields l-*leucylglycyl*-l-*tyrosine*, $[\alpha]_D$ −30·9°. d-*Leucylglycyl*-l-*tyrosine*, $[\alpha]_D^0$ +32·8°, is prepared in a similar manner with the intermediate formation of l-α-*bromisohexoylglycyl*-l-*tyrosine*, an oil.

A. WORMALL.

Structure and enzyme reaction. I and II. The systems urea–urease–charcoal and polysaccharide–amylase–charcoal. S. J. PRZYLECKI, H. NIEDZWIEDZKA, and T. MAJEWSKI (Biochem. J., 1927, 21, 1025—1039).—In the system urea–charcoal–urease the enzyme is almost quantitatively adsorbed, whilst the substrate remains almost entirely in solution. The velocity of enzymic reaction in this system is almost the same as in the absence of the adsorbent and is unaffected by the addition of narcotics. Propyl or butyl alcohol does not remove the enzyme from the adsorbent to any appreciable extent. In the system amylase–charcoal–glycogen or –dextrin the enzyme and much of the substrate (50—75%, according to the quantity of charcoal present) are adsorbed. In this case the velocity of hydrolysis is considerably lower than in the absence of an adsorbent, and narcotics can remove the substrate, but not the enzyme, from the charcoal to a great extent. This reduction in the velocity of hydrolysis is due to spatial separation of enzyme and substrate. If the effective concentration of the substrate be taken into consideration, the law of mass action is followed in enzyme reactions in a heterogeneous medium.

S. S. ZILVA.

Experiments on bacteria in relation to the mechanism of enzyme action. J. H. QUASTEL and W. R. WOOLDRIDGE (Biochem. J., 1927, 21, 1224—1251; cf. this vol., 280).—The action of various organic and inorganic reagents on the enzymic activity of *B. coli* has been studied. The evidence obtained militates against the hypothesis that the activity of surfaces is due to their adsorption of specifically active molecules. On the other hand, the results support the conception of "active centres" in the mechanism of enzyme action. This view is developed from the theory previously advanced (Quastel, A., 1926, 434) that dehydrogenations of substrate molecules are induced by electric fields which characterise these "active centres."

S. S. ZILVA.

The equation of alcoholic fermentation. A. HARDEN and F. R. HENLEY (Biochem. J., 1927, 21, 1216—1223; cf. Harden and Young, A., 1906, i, 470).—The reaction which occurs when a mixture of a hexose and an inorganic phosphate is fermented by yeast-juice or zymin (yeast treated with acetone) has been re-examined and the amounts of carbon dioxide, hexosemonophosphate, and hexosediphosphate produced have been determined. The ratio carbon dioxide/total phosphorus esterified is on the average 0·9, indicating that if Harden and Young's equation be taken as correct, about 10% of the phosphorus is esterified without evolution of carbon dioxide. The product of this esterification is probably a monophosphate. The ratio carbon dioxide/diphosphate is on the average 2·38, but varies considerably in individual cases. The fact that this ratio is almost invariably somewhat greater than the value 2 required by Harden and Young's equation suggests that the diphosphate is originally produced in accordance with the equation, but that a part of it is subsequently partly hydrolysed with formation of a monophosphate. The ratios carbon dioxide/monophosphate and monophosphate/diphosphate are highly variable and show no definite relations.

S. S. ZILVA.

Alcoholic fermentation by yeast-cells under various conditions. VIII. E. ABDERHALDEN (Fermentforsch., 1927, 9, 195—198; cf. A., 1923, i, 519).—Experiments have been carried out to determine whether ultra-violet light has any influence on alcoholic fermentation. Irradiated ergosterol, the alcoholic extract of irradiated yeast, and irradiated yeast maceration juice have no significant influence.

A. WORMALL.

Influence of natural and synthetic thyroxines on alcoholic fermentation. E. ABDERHALDEN (Fermentforsch., 1927, 9, 243—245).—Thyroxine has a varying influence on the fermentation of dextrose by bottom yeast in a phosphate buffer solution at p_H 4·5—6·5; usually a definite acceleration is obtained, but often there is no effect or even a very slight inhibition. Natural thyroxine and synthetic thyroxine give identical results with the same yeast.

A. WORMALL.

Alcoholic fermentation of solutions of dextrose in water exposed to the radiation of a quartz mercury vapour lamp. R. DE FAZI (Atti R. Accad. Lincei, 1927, [vi], 5, 901—905; cf. this vol., 592).—Aqueous dextrose solution, prepared immediately after the water used has been exposed to the

radiation from a quartz mercury vapour lamp, is fermented by yeast appreciably more rapidly than one prepared with untreated water. Suspension of the yeast for a time in the irradiated water also enhances the speed of fermentation, but treatment of a highly impure or enfeebled yeast with the irradiated water may result in a considerable lessening in the velocity of fermentation. T. H. POPE.

"Acclimatisation" of fresh culture-yeasts to galactose. H. VON EULER and B. JANSSON (Z. physiol. Chem., 1927, **169**, 226—234).—Top yeast *R* and bottom yeast *H*, previously suspended for long periods in a galactose solution containing phenol, do not acquire the power to ferment galactose. In contrast to earlier experiments (Euler and Nilsson, A., 1925, i, 866), a low phenol concentration, sufficient to prevent any detectable increase in cell count, but not sufficient to prevent fermentation of dextrose, is maintained throughout. Similarly experiments on the fermentation of galactose by fresh bottom yeast *H* at 38° fail to prove that "acclimatisation" can occur without new formation of yeast-cells. "Acclimatisation" to galactose is concerned with the zymase and not with the co-zymase, since "acclimatised" dried bottom yeast washed free from co-zymase ferments galactose on the addition of co-zymase from untreated yeast. A. WORMALL.

Pigment produced by *Chromobacterium violaceum*. J. REILLY and G. PYNE (Biochem. J., 1927, **21**, 1059—1064).—The organism was grown in nutrient lactose broth, filtered, and extracted at 50° with alcohol at reduced pressure. The *pigment* was precipitated from the alcoholic solution by the addition of water. The formula $C_{50}H_{59}O_{15}N_5$ is suggested. One fifth of the total nitrogen is removed by the action of nitrous acid. S. S. ZILVA.

Auto-elimination of ammonia in bacterial cultures. A. BERTHELOT and G. AMOUREUX (Bull. Soc. Chim. biol., 1927, 9. 932—934).—Cultures of *B. proteus vulgaris* which normally develop an alkaline reaction as the result of the production of ammonia do not do so in presence of magnesium sulphate and alkali phosphate, since the ammonia is then eliminated from the solution as ammonium magnesium phosphate. W. O. KERMACK.

Production of acetylmethylcarbinol by *Clostridium acetobutylicum*. P. W. WILSON, W. H. PETERSEN, and E. B. FRED (J. Biol. Chem., 1927, **74**, 495—507).—In butyl alcohol fermentation by the above organism, acetylmethylcarbinol is regularly produced in maximum amounts of 0·3—0·4 g. per litre, the production occurring simultaneously with that of acids and acetone. The amount of acetylmethylcarbinol is increased by addition of phosphates and decreased by protein; the effect of such modifications in the medium on the production of acids and of acetone is less marked. C. R. HARINGTON.

Separation of lipin fractions from tubercle bacilli. Phosphatide fraction of tubercle bacilli. R. J. ANDERSON (J. Biol. Chem., 1927, **74**, 525—535, 537—551).—Tubercle bacilli (3868·5 g.) were extracted with a mixture of ether and alcohol and then with chloroform. The latter removed 427 g. of wax, the bacterial residue amounting to 2902 g.; the alcohol–ether extract was separated into ether-soluble and water-soluble fractions, the former yielding 253·1 g. of phosphatides and 240 g. of fat, and the latter 12·5 g. of basic substances and 33·9 g. of a polysaccharide.

The phosphatides, on further purification, yielded 138·3 g. of a fraction having N 0·4%, P 2·3%, m. p. 210°. On hydrolysis with dilute acid, this gave palmitic acid 30·5%, oleic acid 12·8%, a liquid saturated acid, $C_{20}H_{40}O_2$, 20·9%, dextrose 13·9%, a sugar acid 13·8%, and glycerophosphoric acid 5·4%. No choline was found, the nitrogen being apparently present as ammonia. The *acid* $C_{20}H_{40}O_2$ was separated by fractional crystallisation of the *benzyl-ψ-thiocarbamide* salt, m. p. 143—144°, into an optically inactive fraction and one having $[\alpha]_D$ +3·54°. The sugar acid gave with phenylhydrazine, in the cold, a *substance*, m. p. 194—195°. C. R. HARINGTON.

Soluble specific substance of pneumococcus. V. Aldobionic acid from specific polysaccharide of type III pneumococcus. M. HEIDELBERGER and W. F. GOEBEL (J. Biol. Chem., 1927, **74**, 613—618).—The aldobionic acid obtained by hydrolysis of the specific polysaccharide of pneumococcus (cf. this vol., 77), on oxidation with barium hypoiodite, gave a *dicarboxylic acid*, $C_{10}H_{18}O_9(CO_2H)_2$, *calcium* salt, $[\alpha]_D$ −7·5°; this compound gives the naphthoresorcinol test and yields the same amount of furfuraldehyde, on distillation with hydrochloric acid, as the original aldobionic acid. Further, on hydrolysis with hydrobromic acid in presence of bromine the aldobionic acid yields saccharic acid. The aldobionic acid must therefore be a compound of dextrose and glycuronic acid combined in glucosidic linking through the aldehyde group of the latter. C. R. HARINGTON.

Soluble specific substance of Friedländer's bacillus. IV. Hydrolytic products of specific carbohydrate of type A Friedländer's bacillus. W. F. GOEBEL (J. Biol. Chem., 1927, **74**, 619—629).—On hydrolysis of the specific polysaccharide from Friedlander's bacillus type A with sulphuric acid, there was obtained an aldobionic acid, $C_{12}H_{20}O_{12}$, which is a glucosidic compound of dextrose and glycuronic acid of the same type as and isomeric with the acid obtained similarly from the specific polysaccharide of pneumococcus type III (cf. preceding abstract). C. R. HARINGTON.

Action of free chlorine on micro-organisms. F. DIENERT and P. ETRILLARD (Compt. rend., 1927, **185**, 621—623).—The concentrations of free chlorine required to sterilise aqueous suspensions of micro-organisms, containing about 10^6 per c.c., vary considerably, *e.g.*, *B. coli*, 0·1; *B. subtilis*, 1·0 mg. per litre. Occasionally 4—5 times these concentrations are required to sterilise the suspensions completely. Agitation of the mixture increases the efficiency of the disinfectant since extraneous organic matter shields the organisms to some extent. By adjustment of the concentration of free chlorine it is possible in some cases to obtain a pure culture from a mixed culture. G. A. C. GOUGH.

Functions of the adrenal cortex and mechanism of biological oxidations. A. VON SZENT-GYÖRGYI (Magyar Orvosi Arch., 1927, 28, 138—14[illegible]).

Some biological oxidations require a hydrogen activation as well as an oxygen activation. In the plant the oxygen-activating system has the character of a phenoloxidase. An aromatic substance which is oxidised by the phenoloxidase to a quinone is also present; the quinone is reduced again, thus acting catalytically as a hydrogen carrier. In certain plants there is a second reducing aromatic substance acting as a catalyst in the oxidation system. An analogous substance is present in the adrenal cortex.

CHEMICAL ABSTRACTS.

Effect of the parathyroid hormone on gastric secretion. II. Calcium content of gastric juice. W. C. AUSTIN and S. A. MATTHEWS (Amer. J. Physiol., 1927, **81**, 552—559).—The calcium content of pure gastric juice (dog) is 5—6·5 mg. %. It does not vary greatly during parathyroid hypercalcæmia.

R. K. CANNAN.

Application of the axolotl metamorphosis reaction to the assay of thyroid gland hormones. B. M. ZAVADOVSKY and E. V. ZAVADOVSKY (Endocrinol., 1926, **10**, 550—559).—The average velocity of metamorphosis of axolotls varies directly with the concentration of thyroxine solution (0·1—0·001 g. per litre) to which the animals are exposed.

CHEMICAL ABSTRACTS.

Regulation of the production of insulin. I. Dextrose as the hormone liberating insulin. E. GRAFE and F. MEYTHALER (Arch. exp. Path. Pharm., 1927, **125**, 181—192).—From a study of the blood-sugar curves obtained after administration of dextrose by injecting it into the femoral and pancreatico-duodenal arteries, evidence is adduced indicating that the secretion of insulin by the pancreas is the result of direct stimulation by dextrose.

W. O. KERMACK.

Behaviour of sugars foreign to the body under the action of insulin. I. Effect of insulin on the degree of assimilation of various sugars. F. BASCH and L. POLLAK. **II. Resorption of sugars injected intraperitoneally under the influence of insulin.** L. POLLAK (Arch. exp. Path. Pharm., 1927, **125**, 89—101, 102—128).—I. Insulin does not appear to influence the permeability of the kidneys of the rabbit to dextrose. On the other hand, it markedly increases the tolerance of the animal towards dextrose, less towards lævulose, very slightly towards galactose, and not at all towards mannose, sucrose, and lactose, when these sugars are administered intravenously.

II. When Ringer solution is injected into the peritoneal cavity of a rabbit, the blood-sugar concentration of the peritoneal fluid gradually becomes equal to that of the blood. The rate at which the process occurs does not appear to be influenced by insulin, except in as far as insulin influences the blood-sugar concentration, and it is probably dependent on simple diffusion. The rates of absorption of dextrose, lævulose, and galactose, but not those of mannose and lactose, when these sugars are introduced into the peritoneal cavity are increased by the action of insulin.

W. O. KERMACK.

Effect of certain sugar derivatives on insulinised mice. A. HYND (Biochem. J., 1927, **21**, 1091—1093). Glucosimine, glucose ureide, glucosamine hydrochloride, or chitose cannot relieve the symptoms caused by insulin.

S. S. ZILVA.

Mechanism of the insulin effect on carbohydrate metabolism. H. PHILLIPS (U.S. Naval Med. Bull., 1927, **25**, 309—314).—Cohnheim's, Collip's, and the γ-glucose theories are discussed.

CHEMICAL ABSTRACTS.

Effect of cobalt on insulin hypoglycæmia in rabbits. N. R. BLATHERWICK and M. SAHYUN (Amer. J. Physiol., 1927, **81**, 560—562).—Contrary to Bertrand and Machebœuf (A., 1926, 869), it is found that cobalt is without appreciable influence on insulin hypoglycæmia in rabbits.

R. K. CANNAN.

Food requirements for growth of the rat. I. Growth on diet of purified nutrients. L. S. PALMER and C. KENNEDY (J. Biol. Chem., 1927, **74**, 591—611).—Normal growth was not obtained in rats (kept from access to their fæces) on a diet of purified caseinogen, dextrin, agar, and salts, with butter fat and wheat embryo extract as sources of vitamins-*A* and -*B*; some hitherto unrecognised factor must therefore be necessary for the growth of these animals.

C. R. HARINGTON.

Phosphorus and calcium metabolism on deficient diets. I. Action of ultra-violet light. II. Action of cod-liver oil. III. Changes of phosphorus or calcium content of the diet. P. SCHULTZER (Biochem. Z., 1927, **188**, 409—426, 427—434, 435—447).—I. The action of ultra-violet light on the phosphorus and calcium metabolism of young rats on various diets is investigated. On a non-rachitic diet deficient in phosphorus and vitamin-*B*, the rats lost in weight, and irradiation considerably increased phosphorus retention. On a rachitic diet deficient in phosphorus, irradiation caused increased phosphorus and calcium retention due to greater absorption, and the rachitic changes declined. Acid-soluble phosphorus returned to normal and serum-calcium rose above normal. On a diet deficient in calcium, irradiation caused considerable phosphorus and calcium retention and serum-calcium returned to normal.

II. Investigation of the effect of 12 days' treatment with cod-liver oil on the phosphorus and calcium metabolism of young rats on the above diets showed that cod-liver oil had the same effect as ultra-violet light both in respect to phosphorus and calcium retention and to acid-soluble phosphorus and serum-calcium.

III. The phosphorus and calcium metabolism of young rats is investigated on diets the phosphorus and calcium contents of which are changed during the experiment. Addition of phosphate to a diet rich in calcium and relatively poor in phosphorus causes increased phosphorus retention due to greater absorption and an increased calcium retention due to lessened excretion of calcium in the urine. Excretion of calcium in the fæces increased somewhat, acid-soluble phosphorus increased, and serum-calcium remained unchanged. Decreasing the calcium carbonate content of the same diet caused an increase of both phosphorus and calcium retention, due to increased reabsorption. Serum-calcium remained unchanged.

P. W. CLUTTERBUCK.

Physiological equilibrium in plants. III. Connexion between the course of absorption of soil nutrients and their movement in plants. A. RIPPEL (Biochem. Z., 1927, **187**, 272—282).—With *Helianthus* it is shown that the course of absorption of soil nutrients corresponds with their mobility in the plant. Absorption of readily mobile elements such as nitrogen, potassium, and phosphorus accelerates the formation of dry substance, whilst absorption of less mobile elements such as calcium, sulphur, magnesium, and silicon has a much smaller or no effect. It seems possible that in the young plant, the former, and with increasing age, the latter type of absorption is favoured. P. W. CLUTTERBUCK.

Nature and metabolism of sugars in *Iris*. H. COLIN and A. AUGEM (Compt. rend., 1927, **185**, 475—478).—The sugars occurring in three varieties of *Iris* at various seasons have been investigated. C. W. GIBBY.

Enzymic hydrolysis of turanose. M. BRIDEL and T. AAGAARD (Compt. rend., 1927, **184**, 1667—1669).—From the action of various enzymes on turanose it is inferred that this substance is a glucoside of lævulose, and moreover that the constitution of turanose may require revision. W. ROBSON.

Extraction of asperuloside from *Gallium verum*, L. Probable presence of the glucoside in *Rubiaceæ*. H. HÉRISSEY (Compt. rend., 1927, **184**, 1674—1675).—A method of extraction of this glucoside is described, together with a table showing the results of trial extractions on other members of this family. W. ROBSON.

Allantoic acid in the leaves of *Acer pseudoplatanus*. R. FOSSE and A. HIEULLE (Compt. rend., 1927, **184**, 1596—1598).—The dixanthylallantoic acid obtained by the addition of xanthhydrol to extracts of the leaves of *Acer pseudoplatanus* (cf. A., 1926, 548), followed by crystallisation of the crude product from pyridine, is not derived entirely from the allantoic acid in the extract. It appears that the extract contains some uroxanic acid, the xanthyl derivative of which suffers decarboxylation on crystallisation and is converted into dixanthylallantoic acid. The uroxanic acid, together with carbamide, has been directly isolated from the extract. G. A. C. GOUGH.

ψ-Ephedrine from Chinese *Ephedra*. B. E. READ and C. T. FENG (Chinese J. Physiol., 1927, **1**, 297—304).—Both Chinese and Swiss *Ephedra* contain both ψ-ephedrine and ephedrine. The solubility of ψ-ephedrine hydrochloride in chloroform is 53 times as great as that of ephedrine hydrochloride, and this difference is utilised in the separation of these alkaloids. It is suggested that this difference in solubilities and the inability of a small excess of ammonia to liberate the bases from these salts may account for the many erroneous statements concerning the occurrence of these alkaloids and also for the low assay results reported. W. ROBSON.

Kentucky coffee nut tree seed-oil. C. BARKENBUS and A. J. ZIMMERMAN (J. Amer. Chem. Soc., 1927, **49**, 2061—2064).—The seeds and pods of *Gymnocladus dioica* have, respectively: moisture, 5·98%, 11·41%; ash, 3·85%, 3·18%; protein (N×6·25), 32·30%, 6·50%; crude fibre, 2·01%, 21·12%; free invert-sugar, 0, 3·56%; sugar by inversion, 12·06%, 18·95%; pentosans, 5·67%, 17·29%; and starch (diastase), 13·32%, 18·91%. Light petroleum extracts 19·27% from the seeds, 0·41% from the pods. For ether the corresponding figures are 19·29% and 1·24%, and for 95% alcohol, 49·00% and 42·05%. The oil obtained by ether extraction of the ground seeds deposits a small amount of solid when kept. It is practically odourless, with a bland taste, and has d^{20} 0·9219; n^{20} 1·4769; iodine value (Hanus) 137·5; saponif. value 191·03; Reichert–Meissl value 0·44; acid value 0·39; acetyl value, 11·35; unsaponifiable matter, 1·28%; soluble acids (as butyric acid %), 0·83; insoluble acids, 93·93% (iodine value 132·0); unsaturated acids (corr.), 89·74% (iodine value 145·0); and saturated acids, 4·86% (iodine value 3·4, before correction). The oil contains the glycerides of oleic acid (37·41%), linoleic acid (56·37%), saturated acids (probably stearic and palmitic acid, with a small amount of arachidic acid) (5·08%), whilst a *phytosterol*, m. p. 165—166°, was obtained from the unsaponifiable material. F. G. WILLSON.

Relative proportions of potassium and sodium in plants. G. BERTRAND and D. I. PERIETZEANU (Compt. rend., 1927, **184**, 1616—1618).—In terrestrial plants the ratio K/Na is distinctly higher than unity. The ratio, however, is extraordinarily variable, fluctuating from 3 in the case of the mallow to more than 1000 in the elder. In marine plants, preliminary figures yield ratios also greater than unity. W. ROBSON.

Accuracy obtainable by repetition of simple measurements. A. KROGH (J. Biol. Chem., 1927, **74**, 393—407).—The maximum accuracy obtainable in making simple measurements is given by the average of ten readings, further repetition serving no good purpose. This conclusion is reached both from statistical considerations and from the practical execution of such operations as the measuring of the thickness of needles and cover slips and the use of the polarimeter; in the latter connexion, the degree of accuracy claimed by Lundsgaard and Holbøll (A., 1925, i, 1494; 1926, 861) could not be substantiated. C. R. HARINGTON.

Methods. VIII. L. PINCUSSEN. Determination of total sulphur in urine and in organs. A. KONARSKY (Biochem. Z., 1927, **187**, 398—402).—A method is described for the determination of sulphur in organic substances, tissue, and urine. P. W. CLUTTERBUCK.

Ceruleomolybdate determination of phosphates. B. E. GILBERT and J. B. SMITH (J. Biol. Chem., 1927, **74**, 223—229).—In the method of Deniges (A., 1920, ii, 770) the presence of high concentrations of acid inhibits the development of colour; in such cases, therefore, it is necessary to employ a standard of the same acidity as the unknown solution. The coloured compound formed in the reaction appears to be colloidal. C. R. HARINGTON.

BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

DECEMBER, 1927.

General, Physical, and Inorganic Chemistry.

pp'-Groups in atomic spectra. R. A. SAWYER (Physical Rev., 1926, [ii], 27, 106).—It is suggested that the pp' frequency is associated with the difference in frequency between the two lowest singlet levels in the spectrum concerned and with the difference in level between the two lowest doublet levels in the next spectrum (once more ionised atom).

A. A. ELDRIDGE.

Discharge tubes for producing intense continuous hydrogen spectrum. Z. BAY and W. STEINER (Z. Physik, 1927, 45, 337—342).—Two forms of discharge tube are described, designed for continuous operation at 0·5 amp., 3000 volts *A.C.*, adapted to give an intense source of the continuous spectrum of hydrogen between 3300 and 1950 Å. In one form the light is emitted axially through a suitable window from a column of hydrogen contained in a tube of length 60 cm. and of diameter 5 mm., silvered internally, and immersed in a stream of cooling water. The second form dispenses with the cooling medium by using a glass tube of length 60 cm. and of diameter 5 cm. in which is mounted co-axially a porcelain tube of diameter 8 mm. silvered on its inner surface; the space between the porcelain tube and the containing wall is packed with glass wool. Current–emission data are cited. R. W. LUNT.

Variation of intensity ratios of optically excited spectrum lines with the intensity of the exciting light. R. W. WOOD (Nature, 1927, 120, 725).—It is shown that lines resulting from a two-stage absorption process are reduced to 0·25 and from a three-stage process to 0·125 of their initial intensity values; this explains why it is unsatisfactory to form an image of the lamp on the resonance tube by means of quartz lenses. A. A. ELDRIDGE.

Infra-red radiation of hydrogen. A. H. POETKER (Physical Rev., 1927, [ii], 30, 418—428).—Six higher members of the Paschen series (γ to 0 inclusive) were observed at wave-lengths: —, 10049·8, 9546·2, 9229·7, 9015·3, 8863·4 Å., in agreement with values calculated from Bohr's theory. The secondary spectrum of hydrogen was observed from 10654·5 to 7504·51 Å., about 425 lines, mostly new, being tabulated. A. A. ELDRIDGE.

Spectrum of beryllium. R. F. PATON and W. H. SANDERS (Physical Rev., 1926, [ii], 27, 106).—The spectrum of beryllium from 5200 to 2000 Å. has been examined. A. A. ELDRIDGE.

Instantaneous spectrograms of carbon, silicon, tin, lead, and cerium; antimony, bismuth, and manganese; chromium, molybdenum, and tellurium; iron, cobalt, and nickel; palladium, iridium, and platinum. H. NAGAOKA, D. NUKIYAMA, and T. FUTAGAMI (Proc. Imp. Acad. Tokyo, 1927, 3, 392—397, 398—402, 403—408, 409—414, 415—418).—The method previously described (cf. this vol., 809, 911) has been applied to the above elements and the results obtained are tabulated.

W. E. DOWNEY.

Abnormal multiplets and inter-combinations in the spectrum of O II. F. CROZE and C. MIHUL (Compt. rend., 1927, 185, 702—704).—A study of the Zeeman effect has enabled a classification to be obtained of the groups of combinations observed by Fowler (A., 1926, 650) and Bowen (this vol., 285) in the O II spectrum. A complete list of the combinations of quadruplets and of doublets of terms of the O II spectrum, corresponding with the 3α-orbit of the emission electron, has thence been compiled.

J. GRANT.

Origin of the nebulium spectrum. A. FOWLER (Nature, 1927, 120, 617).—Whilst Bowen's estimate for the $^4S_2$ term of O II was 283,366, the new data indicate a value of 283,028; this is in remarkable agreement with the value 283,020 for the nebular spectrum. It appears that the conditions in nebulæ which facilitate the occurrence of irregular combinations of deep spectroscopic terms are such as to prohibit the regular combinations which produce the ordinary laboratory spectra of the same elements.

A. A. ELDRIDGE.

Natural width and broadening of the absorbed D-line in sodium vapour as a function of the partial pressure of the vapour and of other gases. W. SCHUTZ (Z. Physik, 1927, 45, 30—66).—The theory of Voigt has been used to develop an analysis of the Righi effect in gases as a function of the partial pressure of the absorbing gas, that of any other gas present, and the strength of the magnetic field; this has been employed to interpret data obtained on the width of the D-line absorbed by sodium vapour alone, and in the presence of hydrogen, helium, nitrogen, neon, and argon. At pressures of sodium vapour below 4×10^{-3} mm. the natural width approaches a limiting value in agreement with the classical half-width $\omega_0' = 0{\cdot}64\times10^{-8}$ sec.$^{-1}$ The widths observed at higher pressures, and due to the addition of other gases, are in quantitative agreement with the theory.

R. W. LUNT.

Spark spectra of high order of sulphur and selenium. L. BLOCH and E. BLOCH (Compt. rend., 1927, 185, 761—763).—By means of an oscillating electrodeless discharge in a highly evacuated silica

tube the spark and arc spectra of sulphur and selenium have been separated. Lists of intense rays of the spark spectra corresponding with S II, S III, Se II, and Se III are given. Above the wave-length 4900 Å. only the rays of S II and Se II exist.

J. GRANT.

Intensity of the forbidden potassium line 4642 A. F. RASETTI (Atti R. Accad. Lincei, 1927, [vi], **6**, 54—55).—From measurements of the magnetic rotation, in a field of 1000 gauss, of the $^2S_4$—$^2D_3$-doublet of potassium in absorption, and from known data relating to the doublet 7665, 7699 Å., the number of electrons per cm.^{3} responsible for the observed dispersion is found to be $2{\cdot}7\times10^{11}$ (probable error 50%). This number is approximately 10^{-6} that corresponding with the doublet 7665, 7699 Å.

R. W. LUNT.

Multiplets of the nickel and cobalt arc spectra in the chromospheric spectrum. C. R. DAVIDSON and F. J. M. STRATTON (Month. Not. Roy. Astr. Soc., 1927, **87**, 739—747).—A number of unclassified lines of nickel appearing in the chromospheric spectrum between 3100 and 4000 Å. have been identified with arc multiplets. One line (3769·47) may belong to the ionised atom. A number of fresh multiplets in cobalt lines have also been identified in the chromospheric spectrum.

R. A. MORTON.

Second spark spectrum of zinc, Zn III. O. LAPORTE and R. J. LANG (Physical Rev., 1927, [ii], **30**, 378—386).—Accurate wave-lengths (1839·40—677·55 Å.) of the spectrum of the high-potential spark between zinc electrodes are tabulated, together with a classification of the lines of Zn III. The ionisation potential of the shell of ten equivalent 3$_0$ electrons is 40 volts.

A. A. ELDRIDGE.

Spectral lines of trebly-ionised germanium. S. SMITH (Nature, 1927, **120**, 728).—The first members of the second principal series, $5S_1$—$5P_{1,2}$ were observed at 3554·14 and 3676·61 Å., and a triplet resulting from combinations between 4 $_3$ and $5P_{1,2}$ at 2788·41, 2736·09, 2717·41. A doublet, the second member of the first principal series, is at 441·95, 440·11 Å.

A. A. ELDRIDGE.

Series of the first spark spectrum of tin (Sn I). A. L. NARAYAN and K. R. RAO (Z. Physik, 1927, **45**, 350—363).—A number of lines in the spark spectrum of tin have been determined in the range 6844·26—2449·79 Å. by a grating with a dispersion of 5·6 Å./mm. These lines together with those observed by other workers have been classified in a doublet system. It is shown that the spectra of C II, Si II, Pb II, and Sn II are very similar and are capable of interpretation on Hund's theory.

R. W. LUNT.

Low-voltage arcs in iodine. H. F. FRUTH and O. S. DUFFENDACK (Physical Rev., 1926, [ii], **27**, 248).—It is concluded that 6·5 volts is the minimum radiating potential of the atom, 8·0 the ionising potential of the atom, and 9·5 the ionising potential of the molecule. The spectrum of the abnormal 4·9-volt arc contained only the lines 2062, 2535, and 3135 Å., the continuous band 3460 Å., and several groups of bands. The strongest spark lines commence at 8 volts. Continuous bands at 4080, 4300, and 4800 Å. are present in molecular, but disappear in atomic, iodine. A band system between 2224 and 2050 Å. was observed, and two groups of four bands each at 2880, 2833, 2776, 2716 Å. and 2480, 2379, 2290, and 2243 Å.

A. A. ELDRIDGE.

Intensity of spectral lines. G. I. POKROWSKI (Z. Physik, 1927, **45**, 140—145).—The relationship between the intensity of the barium spark and arc lines 4930, 5540, and 5850 Å. has been investigated as a function of the concentration of barium for low concentrations, for which a satisfactory theoretical expression has been derived. With increasing concentration the apparent width of lines increases; this is due to self-absorption.

R. W. LUNT.

Long wave-length limit of mercury. W. B. HALES (Physical Rev., 1926, [ii], **27**, 809).—The limit is 2735 ± 10 Å., in agreement with Kazda's value for flowing mercury.

A. A. ELDRIDGE.

Absorption of resonance radiation in mercury vapour. A. L. HUGHES and A. R. THOMAS (Physical Rev., 1927, [ii], **30**, 466—472).—The absorption of radiation 2436 Å. per atom decreases rapidly as the amount of absorbing vapour is increased, indicating that the resonance radiation is not homogeneous. The maximum atomic absorption coefficient was $11{\cdot}2\times10^{-14}$; hence an atom can stop the radiation which falls on an area 110 times as large as its cross-sectional area.

A. A. ELDRIDGE.

Determination of certain outer *X*-ray energy levels for the elements from antimony (51) to samarium (62). K. CHAMBERLAIN and G. A. LINDSAY (Physical Rev., 1927, [ii], **30**, 369—376).—Direct determinations of the distances between the $L\beta_2$, $L\gamma_1$, and $L\gamma_4$ lines and the L_{III}, L_{II}, and L_I absorption edges, respectively, for antimony, tellurium, iodine, cæsium, barium, lanthanum, cerium, praseodymium, neodymium, and samarium yield values for the N_{IV}, N_V, and O_{II-III} energy levels, respectively. A graph shows the variation of these levels with the atomic number. For antimony, tellurium, and iodine, the L_I absorption edges are at 2631·7, 2503·9, 2383·9, the L_{II} edges at 2821·9, 2679·3, 2547·5, and the L_{III} edges at 2990·7, 2845·7, 2713·9X., respectively.

A. A. ELDRIDGE.

Absorption of *X*-rays in various elements. E. JONSSON (Nature, 1927, **120**, 695).—Experimental evidence leads to the enunciation of the following laws: (1) The jump of the absorption coefficient on passing the K-absorption limit is $=E_K/E_{L_1}$, where E_K and E_{L_1} are the energy levels corresponding with the K and L_1 levels, respectively; similarly, $\delta_L=E_{L_1}/E_{M_1}$ and $\delta_M=E_{M_1}/E_{N_1}$. (2) If the absorption is calculated per electron, μ_e, instead of per mass-unit, is a function of the product $N\lambda$ (N is the atomic number) for every branch of the absorption curve. (3) One single continuous curve can be drawn for the absorption at all wave-lengths for all elements, with and $N\lambda$ as co-ordinates.

A. A. ELDRIDGE.

Separation of the modified and unmodified scattering coefficients of *X*-rays. O. K. DEFOE and G. E. M. JAUNCEY (Physical Rev., 1926, [ii], 27, 102).—An improved method is described.

A. A. ELDRIDGE.

Zeeman effect in the Ångstrom CO bands. E. C. KEMBLE, R. S. MULLIKEN, and F. H. CRAWFORD (Physical Rev., 1927, [ii], **30**, 438—457).—The qualitative features of the Zeeman effect in the band lines of rigid diatomic molecules as given by the conventional quantum theory and the new quantum mechanics are the same. The results of measurements of the CO bands at 5610, 5198, and 4835 Å. are in agreement with the theoretical predictions.

A. A. ELDRIDGE.

Zeeman effect in the cerium spectrum between 3000 and 5000 Å. H. MARGENAU (Physical Rev., 1927, [ii], **30**, 458—465).—The lines are tabulated according to the general appearance of the Zeeman patterns.

A. A. ELDRIDGE.

Zeeman effect and the structure of the arc spectrum of rhodium. L. A. SOMMER (Z. Physik, 1927, **45**, 147—193).—The Zeeman effect in fields of 30,000 gauss has been examined by a grating method for some 1600 lines of the arc spectrum of rhodium between 2300 and 8600 Å. Approximately 1000 of these lines have been arranged as combinations of the 136 terms of the arc spectrum; they follow the classification of Russell, Pauli, Heisenberg, and Hund. By extrapolation to the series limit the value of 7·7 volts is obtained for the ionisation potential.

R. W. LUNT.

Resonance and ionisation potentials in mercury vapour. C. W. JARVIS (Physical Rev., 1926, [ii], **27**, 808).—The following values (volts) were observed: 1·23, 2·21, 2·80, 3·44, 3·80, 4·21, 4·53, 4·97, 5·22, 5·37, 5·70, 6·05, 6·46, 6·79, 7·13, 7·41, 7·74, 8·02, 8·33, 8·82, 9·33, 9·58, 9·90.

A. A. ELDRIDGE.

Excitation of spectra by high-frequency oscillations. J. R. CLARKE (Nature, 1927, **120**, 727).—The spectrum of mercury can be excited by means of high-frequency oscillations (cf. Wood and Loomis, this vol., 1008). The resonance line 2536·7 Å. appeared first, then lines of the s and d triplet series, then lines of the S and D singlet series, and some combination lines involving the arrival and departure levels of the series lines present. The lines 3984·1, 3860·4, 3820·6, 3790·4, 3751·8, 3561·5, 3543·7, 3390·5, 3351·5, 2820·0, 2686·7, 2660·1, and 2540·4 Å., which have not yet been allocated to any series or combination, were also observed.

A. A. ELDRIDGE.

Secondary emission from molybdenum due to bombardment by high-speed positive ions of the alkali metals. W. J. JACKSON (Physical Rev., 1927, [ii], **30**, 473—478).—An extension of previous work (A., 1926, 1074) to the bombardment of sodium, rubidium, and cæsium ions. In general, heat treatment reduces the secondary emission. When the surface of a target is in a condition to emit electrons due to positive ion bombardment, the percentage secondary emission is a function of the speed of the impacting ion.

A. A. ELDRIDGE.

Rotation of electric discharge in a decomposable gas. C. E. GUYE and B. LUYET (Arch. Sci. phys. nat., 1927, [v], **9**, 191—217, 247—263).—When a discharge from a static induction machine is passed through carbon dioxide in a cylindrical chamber fitted with concentric ring and disc electrodes, and a magnetic field is placed around the chamber, the discharge is seen to rotate. The carbon dioxide begins to decompose as soon as the discharge is set up, so that the system studied is always carbon dioxide–carbon monoxide–oxygen. The speed of rotation falls very rapidly during the first few minutes of the discharge and afterwards more slowly. The diminution in speed is least noticeable (*a*) with low initial pressure, (*b*) at a given initial pressure, after the discharge has been running for a long time. Although the slowing down is ascribed to the decomposition of carbon dioxide, the speed of rotation in the mixture is not intermediate between the speeds for the constituents, and it would appear that the simple theory of the discharge is adequate.

At a pressure of 20 mm. the speed of rotation becomes constant after a few minutes, although decomposition of carbon dioxide is occurring all the time. After 1 hr. the increase in pressure under a discharge of 400×10^{-6} amp. was 9·6, 11·0, and 14·8% at initial pressures of 20, 35, and 50 mm., respectively. The rate of decomposition measured in this way depends on the initial amount of gas as well as on the intensity of the discharge, whilst for pressures between 9 and 30 mm. the speed of rotation also depends on the intensity of the discharge. During the first few seconds the apparent volume of the discharge rapidly increases and the speed of rotation rapidly decreases.

R. A. MORTON.

Motion of slow electrons in a gas. H. FAXÉN and J. HOLTSMARK (Z. Physik, 1927, **45**, 307—324).—On the assumption that the rare gases can be considered as possessing a symmetrical central electrostatic field, the motion of slow electrons through these gases has been calculated by Schrödinger's wave mechanics. By deriving the structure of xenon from Thomas' model for the cæsium ion (this vol., 290) a first approximation with experiment is obtained.

R. W. LUNT.

Effective cross-section of the noble gases, argon, neon, helium, against slow electrons. E. BRUCHE [with (FRL.) D. LILIENTHAL and (FRL.) K. SCHRÖDTER] (Ann. Physik, 1927, [iv], **84**, 279—291).—The effective cross-sections of argon, neon, and helium have been very carefully determined for various electron velocities. The neon curve falls off steeply with decreasing small velocities. The relation between cross-section and molecule formation is discussed.

R. A. MORTON.

Detection of unimolecular ions in air, and the existence of forces between ions and gas molecules. W. BUSSE (Ann. Physik, 1927, [iv], **84**, 327—328).—Schilling's work (this vol., 708) makes certain modifications necessary in the author's earlier views on the rôle of water vapour in ion formation (this vol., 4).

R. A. MORTON.

Molecular structure and relative mobilities of positive and negative gaseous ions. L. B. LOEB and A. M. CRAVATH (Physical Rev., 1926, [ii], **27**, 811—812).—The mobility of the positive ion in hydrogen sulphide is 0·61, and that of the negative ion 0·55 cm./sec. per volt/cm. In water the mobilities are 0·62 and 0·56, respectively. The mobility values

are relative to air, assuming 1·4 for positive and 1·8 for negative ions in cm./sec. per volt/cm. A. A. ELDRIDGE.

Isotopes of calcium. E. K. PLYLER (Science, 1927, **65**, 578—579).—The selective reflexion of polarised radiation (about 6·5 μ) shows maxima at 6·36, 6·54, and 6·62 μ, of which the relative intensities are in agreement with the assumption of the presence of isotopes of mass 39, 40, and 44 in the ratio 0·2 : 1 : 0·05. A. A. ELDRIDGE.

Limit of accuracy of physico-chemical at. wt. determinations. I. Normal molar volume and at. wt. of nitrogen. E. MOLES (Z. anorg. Chem., 1927, **167**, 40—48).—A method is developed for the calculation of at. wt. from limiting density measurements. The normal molar volume of nitrogen, calculated from the mean of accurate density determinations given in the literature, is $22{\cdot}4148 \pm 0{\cdot}0007$, and the at. wt. is $14{\cdot}0082 \pm 0{\cdot}0002$. H. F. GILLBE.

Density and at. wt. of nitrogen. E. MOLES and J. M. CLAVERA (Z. anorg. Chem., 1927, **167**, 49—66).—The mean density of nitrogen, obtained from four different sources, is $1{\cdot}25049 \pm 0{\cdot}00003$ g./litre. The most probable value of the at. wt. is $14{\cdot}0082 + 0{\cdot}00042$. H. F. GILLBE.

At. wt. of antimony from different sources. K. R. KRISHNASWAMI (J.C.S., 1927, 2534—2539).—The at. wt. of antimony has been determined in samples from five different sources by the method of Willard and McAlpine (A., 1921, ii, 405). The results range from 121·744 to 121·754, the variation being less than the experimental error. C. W. GIBBY.

Isolation of protoactinium (element 91). A. GROSSE (Nature, 1927, **120**, 621).—About 2 mg. of protoactinium oxide has been isolated, having a half-value period of 2×10^4 years. Thus, for each g. of radium in a mineral there is approx. 0·4 g. of protoactinium. A. A. ELDRIDGE.

Radioactive products present in the atmosphere of Bombay. S. J. KHAMBATA (Indian J. Phys., 1927, **2**, 25—27).—The amount and character of the active deposit collected on an insulated copper wire, suspended 75 feet above the ground in a N.E.—S.W. direction, and at a negative potential of 560—590 volts, have been determined under varying atmospheric conditions and for varying lengths of time. An average of 56% of the initial activity was due to the active deposit of thorium, the rest being attributable to radium deposit. The calculated ratio of the number of atoms of radon to thoron is approximately 3400; this is in agreement with several other values from different parts of the world. The greatest amount of activity was found in May with a S.W. wind. Bright, cloudless days gave more excited activity than dull, cloudy days, and windy days than calm. M. S. BURR.

Existence of groups of atoms of radio-elements in acid solutions and on surfaces activated by the emanation. (MLLE.) C. CHAMIÉ (Compt. rend., 1927, **185**, 770—772).—Photographic experiments have shown the existence of groups of atoms of radio-elements in acid solutions, and on surfaces activated by exposure to emanations or by evaporation of acid solutions. Since the impressions are always the same, and similar to those obtained with activated mercury (this vol., 605), it is concluded that during activation the mercury receives aggregates of atoms which are absorbed by it without dissociating into individual atoms. J. GRANT.

Mobility of the actinium-*A* recoil atom measured by the cloud method. P. I. DEE (Proc. Roy. Soc., 1927, **A**, **116**, 664—682).—The cloud method has been used to measure the mobility of individual actinium-*A* recoil atoms immediately after they have reached the end of their recoil tracks and during an interval equal to the life of an atom. The conditions are more definite than those in Erikson's experiments (A., 1925, ii, 79), since the recoil atom, if charged, is rapidly removed from ions of the opposite sign, and if neutral, both positive and negative ions are rapidly removed from its neighbourhood. Photographs of four main types of grouped tracks are reproduced, corresponding with the double disintegration actinon —— actinium-*A* —→ actinium-*B*. The relative positions of the origins of these tracks give the mobility and, in some cases, the life of the actinium-*A* atom. The value obtained for the mobility agrees with that usually accepted, viz. 1·56 cm./sec. per volt/cm., and no cases were found of the additional mobility 4·35 found by Erikson for recoil from an active source (*loc. cit.*). The method gives definite evidence that some of the recoil atoms at the end of their recoil paths are uncharged, and the proportion of positively-charged atoms, 84%, agrees well with Briggs' value of 82%, found for thorium-*A* and radium-*A* in air by activity distribution methods (A., 1925, ii, 922). The mean life of 47 actinium-*A* atoms is found to be $1{\cdot}8 \times 10^{-3}$ sec. L. L. BIRCUMSHAW.

Retardation of α-particles by matter. S. ROSENBLUM (Compt. rend., 1927, **185**, 851—853).—A continuation of the author's experiments (A., 1926, 879) has resulted in a more exact numerical expression for the retardation of α-particles during their passage through metals. Experimental constants are given for a number of metals; alloys obey the law of additivity. Within certain limits the field of force opposing the motion of the α-particles depends on the atomic number of the absorbing substance. J. GRANT.

Absorption and reduction in velocity of β-rays on their passage through matter. E. MADGWICK (Proc. Camb. Phil. Soc., 1927, **23**, 970—981).—Bohr's theory of the absorption of β-rays has been experimentally tested using a magnetic deviation method. There is a close parallelism over a very wide range of energies between the theoretical and experimental results which lends strong support to the general truth of the theory. Disparities are discussed. W. E. DOWNEY.

β-Ray spectrum of radium-*E*. E. MADGWICK (Proc. Camb. Phil. Soc., 1927, **23**, 982—984).—The distribution with velocity of the number of particles in the β-ray spectrum of radium-*E* has been determined by an ionisation method. It is concluded that the particles are ejected from the nucleus with velocities which vary continuously. W. E. DOWNEY.

Amount of energy emitted in the γ-ray form by radium-E. G. H. Aston (Proc. Camb. Phil. Soc., 1927, 23, 935—941).—The energy emitted as γ-rays by radium-E has been determined by an ionisation method. The measurement of the energy was derived from that of radium-B and radium-C by comparing ionisations. It is concluded that only one γ-ray quantum is emitted during about thirty disintegrations of radium-E atoms. The bearing of this on the β-ray emission of radium-E is discussed. W. E. Downey.

Scintillation spectra. W. Kutzner (Z. Physik, 1927, 45, 343—349).—The emission spectra of standard preparations of zinc sulphide containing copper, bismuth, or uranium when subjected to irradiation by white light, to α-particles from polonium free from radium-D+E, and to friction have been determined in the range 6678—3888 Å. The three methods of excitation produce different but characteristic emission. It is thought that the α-particle emission is due to ionisation. R. W. Lunt.

Series number and decay constants. W. A. Sokolov (Z. Physik, 1927, 45, 409—415).—It is shown that the relation between the radioactive decay constant λ, for substances emitting α-particles, and the number of the element concerned in the radioactive series n can be expressed in the form $\log\lambda = kn+a$, where k is constant for all three radioactive series, and a a constant characteristic of each series. A similar relationship exists for the decay constants of substances emitting β-particles. R. W. Lunt.

Interpretation of the masses of the electron and proton in the five-dimensional universe. A. Schidlof (Compt. rend., 1927, **185**, 889—891).—A mathematical paper in which de Broglie's geometrical representation of the electrical charge of a material point in a five-dimensional system (J. Phys. Radium, 1927, [vi], 8, 65) is applied to the proton and electron, and equations are obtained defining their masses. J. Grant.

Spinning electron and the structure of spectra. S. Goudsmit and G. E. Uhlenbeck (Physica, 1926, 6, 273—290).—Theoretical. Chemical Abstracts.

Fundamental equation of quantum chemistry. T. de Donder (Compt. rend., 1927, **185**, 698—700).—It is shown mathematically that from the expression defining an Einsteinian conception of gravity, the equation may be deduced for the quantisation of molecular systems containing any number of points having electric mass, and producing a field of gravity $g_{\alpha\beta}$ ($\alpha,\beta=1, \ldots 4$). The fundamental equation of quantum chemistry is thus obtained. J. Grant.

Mutual influence of two hydrogen atoms. S. C. Wang (Physikal. Z., 1927, 28, 663—666).—It is shown mathematically that the mutual potential energy of two hydrogen atoms in the normal state and separated by a distance R is $-243e^2a^5/28R^6$, a being the radius of the first Bohr orbit in the atom. Assuming two dipoles of moment μ and polarisation constants α, the mutual potential energy is $-2\alpha\mu^2/R^6$; this on a quantum basis can be connected with the polarisation effect of two atoms with an electric moment $\mu = 0{\cdot}982ea$ on the classical basis. R. A. Morton.

Spectrophotometry. R. W. Ditchburn (Proc. Camb. Phil. Soc., 1927, 23, 959—969).—For wavelengths below 3200 Å. a Lyman type of hydrogen discharge tube forms a convenient source for spectrophotometry. Various types of reducing sectors are discussed and it is concluded that the radial-aperture sector has many points of advantage over other types. W. E. Downey.

Absorption measurement in the ultra-violet by photographic photometry. H. Ley and F. Volbert (Z. physikal. Chem., 1927, **130**, 308—322; cf. A., 1925, ii, 78).—The more important methods for measuring absorption by photographic photometry are described and criticised, the methods being grouped into: (1) those with equal times of exposure for the absorption and comparison spectra, (2) those with unequal times of exposure, and (3) those involving the use of the rotating sector. The advantages of the authors' combination of Henri's method and Winther's wire-gauge method are discussed. The results obtained from absorption measurements with potassium nitrate by a number of different investigators using different methods are compared, and a mean curve is constructed which might be used as a reference curve for photographic-photometric purposes. L. L. Bircumshaw.

Molecular constants derived from the Swan bands. J. D. Shea and R. T. Birge (Physical Rev., 1926, [ii], 27, 245—246).—For the initial state, the rotation energy (F) in wave-numbers of the non-vibrating molecule is $1{\cdot}7541m^2-6{\cdot}911\times10^{-8}m^4+1{\cdot}22\times10^{-11}m^6$, where $m=k-\varepsilon=k-(0{\cdot}0989+1{\cdot}746\times10^{-5}k^2)$, k being a half-integer, and representing the resultant molecular momentum; hence the moment of inertia $I_0=15{\cdot}792\times10^{-40}$. For the final state $1{\cdot}6295m^2-6{\cdot}594\times10^{-6}m^4+1{\cdot}73\times10^{-11}m^6$, where $m=k-(0{\cdot}0741+0{\cdot}964\times10^{-6}k^2)$; hence $I_0=17{\cdot}000\times10^{-40}$. It is suggested that the molecule HC·CH may be the emitter of the Swan bands. A. A. Eldridge.

Structure of the ultra-violet spectrum of the hydrogen molecule. G. H. Dieke and J. J. Hopfield (Physical Rev., 1927, [ii], 30, 400—417).—See this vol., 89. A. A. Eldridge.

Rotational distortion of multiplet electronic states in band spectra. E. C. Kemble (Physical Rev., 1927, [ii], 30, 387—399).—Hund's theoretical interpretation of the contracting multiplet type band spectra for diatomic molecules is given quantitative form for the doublet case and for the extreme components of higher multiplicities. The theory is applied to the ultra-violet doublet OH bands, which are interpreted as being of the $^2S \longrightarrow {}^2P$ type with the ^2P doublet inverted. A. A. Eldridge.

Fine structure and electron terms in band spectra. E. Hulthen (Z. Physik, 1927, 45, 331—336).—It is shown that the order of magnitude of the fine structure in band spectra of the types $^2P\longrightarrow{}^2S$ and $^2S\longrightarrow{}^2S$ is in agreement with Hund's theory, and that a simple relationship exists between the ^2S term and the transition $^2P_1$—$^2P_2$. These conclusions are discussed with reference to the combination between the atomic and molecular spectra of elements of the second group. R. W. Lunt.

Combination relation in the 3064 A. OH band. W. W. WATSON (Physical Rev., 1926, [ii], 27, 246).—The P,Q,R combination which holds for any normal band is not satisfied in the MgH and OH bands. New measurements have been made, and satellites of the Q lines have been located which, when combined with the main P and R lines, give the required combination. A. A. ELDRIDGE.

Intensities of the lines in the HCl absorption band at 3·5 μ. D. G. BOURGIN and E. C. KEMBLE (Physical Rev., 1926, [ii], 27, 802).—Experimental results are in harmony with the theoretical formula (*ibid.*, 1925, [ii], 25, 1). There is definite evidence of a rotational isotope effect. A. A. ELDRIDGE.

Shape of the carbon dioxide molecule. C. SCHAEFER (Physikal. Z., 1927, 28, 667).—The work of Stark and Bluh (this vol., 922) on a linear structure for carbon dioxide is criticised on the grounds that evidence in the opposite sense (A., 1926, 658) is not disproved. R. A. MORTON.

Specific heat of carbon dioxide and the form of the carbon dioxide molecule. W. H. MCCREA (Proc. Camb. Phil. Soc., 1927, 23, 890—900).—Theoretical. The specific heats of carbon dioxide based on Dennison's (A., 1926, 222) and Eucken's (*ibid.*, 882) models have been calculated. Neither model is found to be entirely satisfactory; a further hypothesis based on the two models to get better agreement between the calculated and observed specific heats is suggested. The new model explains the fine structure of the infra-red absorption bands better than Dennison's. W. E. DOWNEY.

Sodium and potassium absorption bands. W. R. FREDERICKSON and W. W. WATSON (Physical Rev., 1927, [ii], 30, 429—437).—The band heads of the systems are expressed by the following formulæ: green Na_2, $20301{\cdot}62+(123{\cdot}84n'-0{\cdot}79n'^2)-(157{\cdot}57n''-0{\cdot}57n''^2)$; red Na_2, $\nu=15006{\cdot}68+(115{\cdot}69n'-0{\cdot}427n'^2)-(157{\cdot}81n''-0{\cdot}538n''^2)$; red K_2: $\nu=15368{\cdot}63+(74{\cdot}58n'-0{\cdot}30n'^2)-(92{\cdot}01n''-0{\cdot}34n''^2)$. There is a new potassium absorption band system situated with respect to the first doublet in the principal series of potassium as is the red sodium band system with respect to the sodium D-lines. Fine-structure analysis indicates that the green sodium and near red potassium bands are both $^1S-{}^1P$ transitions. For the initial absorption state, the moment of inertia is $7{\cdot}20\times10^{-39}$ g. cm.^{2} for sodium and $8{\cdot}72\times10^{-39}$ g. cm.^{2} for potassium molecules. A. A. ELDRIDGE.

Quantum analysis of the band spectrum of AlO (5200—4650 Å.). W. C. POMEROY and R. T. BIRGE (Physical Rev., 1926, [ii], 27, 107).—The (0,0), (1,0), and (0,1) bands of the blue and green group have been analysed according to the quantum theory. The origin of the (0,0) band is at $\nu_{vac.}=20635{\cdot}3$, and the limiting values of the moments of inertia for initial (emission) and final states are $(46{\cdot}01\pm0{\cdot}04)\times10^{-40}$ and $(43{\cdot}38\pm0{\cdot}04)\times10^{-40}$, respectively. A. A. ELDRIDGE.

Absorption spectrum of dry chlorine. G. KORNFELD and W. STEINER (Z. Physik, 1927, 45, 325—330).—The convergence wave-length of the band spectrum of chlorine has been examined by a grating with a dispersion of 2 Å./mm. No difference within the limit of experimental error could be detected between damp chlorine and the gas after drying by careful fractionation. It is therefore concluded that excited and normal chlorine atoms always exist in chlorine irradiated with blue light, and that the influence of water vapour on the reaction between hydrogen and chlorine must be sought in other stages of the reaction. The dryness of the chlorine examined was evidenced by the fact that it did not react with pure hydrogen in blue light. For 3130 Å. the quantum efficiency in a mixture of such dry chlorine and hydrogen diffused through palladium is 6—7 molecules per quantum. R. W. LUNT.

Ultra-violet absorption spectra of aqueous solutions of calcium, strontium, and barium chlorides. E. VITERBI (Gazzetta, 1927, 57, 615—620).—The work of Pool (Z. Physik, 1924, 29, 311) and of Getman (A., 1925, ii, 837) is repeated, using the method of Henri, with highly purified salts; tables of the molecular absorption coefficients, and curves, are given for a 3·913M-calcium chloride, a 1·864M-strontium chloride, and a M-barium chloride solution in a thickness of 15—50 to 500 mm. Contrary to the results of Getman (*loc. cit.*), each salt has a selective absorption in the middle ultra-violet, with a maximum which shifts towards the extreme ultra-violet with increasing at. wt., and has the values 2785, 2665, and 2624 Å. for the respective salts. There are also broad but distinct minima at 2579, 2550, and 2359 Å. respectively. The absorption band is somewhat indistinct with strontium, but lies close to that of calcium; that of barium is much stronger, although still small. E. W. WIGNALL.

Quantum analysis of the rotational energy of certain molecules. R. T. BIRGE (Physical Rev., 1926, [ii], 27, 245).—Higher order terms of the rotational energy function are calculated for CuH. A. A. ELDRIDGE.

Absorption spectra of borax glasses coloured with copper salts. P. LASAREV and V. LAZAREV (Compt. rend., 1927, 185, 855—856).—The absorption spectra between the wave-lengths 470 and 590 μμ of glasses prepared by fusion of borax with a small quantity of a copper salt differ from those of solutions of copper sulphate. Annealing the glasses destroys their temper, but does not alter their absorption spectra. J. GRANT.

Series of emission and absorption bands in the mercury spectrum. (LORD) RAYLEIGH (Proc. Roy. Soc., 1927, A, 116, 702—719; cf. this vol., 496).—An improved method is described for the study of absorption bands in the mercury spectrum, using a silica discharge tube, containing hydrogen at 2·5 mm. pressure, as the source, and an electrically-heated silica absorption tube, of length varying from 45 to 178 cm. In the less refrangible region (3000—2600 Å.), the wave-lengths and frequencies of 42 emission bands and 48 absorption bands are given. The initial spacing of the observed emission bands is 250 cm.$^{-1}$; the point of convergence is found by extrapolation to be near the resonance line 2537 Å. Both the emission and absorption bands are diffuse and symmetrical,

without heads. The initial spacing of the absorption bands is 148 cm.$^{-1}$; the convergence point, found by extrapolation, is about 2645 Å. The two band systems appear to be coincident over a part of the range, 2734—2696 Å., for seven or eight periods, but beyond this range the absorption bands are more closely spaced than the emission bands in the long wave-length side, and *vice versa* on the side of short waves. Since no uniform shift on the scale of frequencies could bring the two series into coincidence, it has not been found possible to apply the quantum theory to their classification. In the more refrangible region (2350—2290 Å.), a series of symmetrical emission bands has been observed, which has been resolved for a short distance from 2345 Å. These merge into an apparently continuous spectrum which stops abruptly at the forbidden line 2270 Å. A series of four bands which are nearly the counterpart of the first four emission bands has been observed in absorption, and in part superposed on this structure is a much finer one, of which 48 bands have been observed. The bands are of the normal type with heads, and are definitely degraded to the red. The initial spacing is only 18 cm.$^{-1}$ The convergence point, found by two alternative methods of extrapolation to be 2264 or 2222, probably represents dissociation into a neutral atom and one excited to the 1^3P_2 metastable state.

L. L. Bircumshaw.

Depolarisation of light by dispersed systems. G. I. Pokrowski (Z. Physik, 1927, **45**, 135—139).—From a consideration of the maximum and minimum polarisation characteristic of mercuric sulphide, cadmium sulphide, sulphur, arsenic green, madder, and ultramarine dispersed in water with that of water dispersed in air, it is concluded that: (i) the polarisation in coarsely-dispersed systems is less than that anticipated by theory, (ii) this diminution is specific to the nature of the disperse phase and is also due to the irregular size of the particles, (iii) in high concentrations multiple scattering produces depolarisation.

R. W. Lunt.

Spectroscopic investigation of acetylene, methane, and ethylene. F. C. McDonald (Physical Rev., 1926, [ii], **27**, 246).—Although no bands have been observed which can be definitely ascribed to the complete molecules, a new band spectrum (three bands, degraded towards the red, with heads at 2263, 2367, and 2395 Å.) has been observed when methane, in a Wood tube, at a pressure of 2 mm., is excited by a violent disruptive discharge.

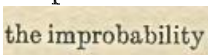
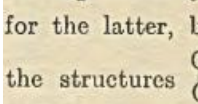
A. A. Eldridge.

Interference method for determining the anomalous absorption of concentrated solutions. E. Adinolfi (Rend. Accad. Sci. fis. mat. Napoli, [iii], **32**, 189—193).—Improvements in the technique for determining the anomalous absorption of concentrated solutions by interference methods are described; data obtained with a solution of fuchsin in ethyl alcohol are discussed to illustrate the method.

R. W. Lunt.

Absorption bands of ergosterol and vitamin-*D*. I. M. Heilbron, E. D. Kamm, and R. A. Morton (Nature, 1927, **120**, 617—618).—Explanatory, and polemical against Rosenheim and Webster (Lancet, 1927, Sept. 17). Further, for the concentration employed by those authors the persistence of the 247 $\mu\mu$ band is constant over a long period; irradiation behind "vitaglass" screens does not effect the expected increase in vitamin concentration.

A. A. Eldridge.

Various spectrochemical observations. K. von Auwers (Ber., 1927, **60**, [*B*], 2122—2142).—Optical comparison of the furazans with the furoxans indicates the improbability of the constitution  for the latter, but leaves open the choice between the structures  and . The carbylamines have higher molecular indices of refraction and dispersion than the corresponding nitriles and are therefore to be regarded as more unsaturated substances. The differences, however, are comparatively slight and it appears unlikely that the carbylamines contain a true bivalent carbon atom in which two valencies are completely unsatisfied. Comparison of the optical behaviour of *s*- and *as*-phthalyl chlorides shows that the refractive and dispersive powers of the asymmetric isomeride which contains only one active conjugation are little lower than those of the normal chloride with its two active conjugations. The exaltation of the refractive index of quinones is such that the presence of a true benzenoid derivative is improbable even if it is admitted that the presence of a peroxide linking of the oxygen atoms somewhat enhances the refraction. Contrary to Levy (Diss., Frankfurt, 1920), the optical behaviour of ethylated hydrindenes is exactly comparable with that of similarly constituted benzenoid hydrocarbons except that the exaltations are generally lower, due to the presence of a *gem*-diethyl group. Chloroformic esters appear to be constituted normally.

The following data, among others, are recorded: dimethylfurazan, $d_4^{14\cdot4}$ 1·0528, $n_{He}^{14\cdot4}$ 1·42829; dimethylfuroxan, $d_4^{14\cdot8}$ 1·1896, $n_{He}^{14\cdot8}$ 1·48599; methylcarbimide, $d_4^{17\cdot9}$ 0·7337, $n_{He}^{17\cdot9}$ 1·34393; ethylcarbimide, $d_4^{17\cdot6}$ 0·7425, $n_{He}^{17\cdot6}$ 1·36321; phenylcarbimide, $d_4^{19\cdot1}$ 0·9823, 1·52828; acetonitrile, $d_4^{21\cdot9}$ 0·7781, $n_{He}^{21\cdot9}$ 1·34186; propionitrile, $d_4^{21\cdot8}$ 0·7758, $n_{He}^{21\cdot8}$ 1·36368; *n*-butyronitrile, $d_4^{16\cdot2}$ 0·7951, $n_{He}^{16\cdot2}$ 1·38588; *n*-valeronitrile, $d_4^{18\cdot9}$ 0·8018, 1·39715; *iso*valeronitrile, $d_4^{19\cdot4}$ 0·7925, $n_{He}^{19\cdot4}$ 1·39179; toluquinone, 1·0830, $n_{He}^{77\cdot9}$ 1·51108; *m*-xyloquinone, $d_4^{78\cdot1}$ 1·0479, $n_{He}^{78\cdot1}$ 1·50740; thymoquinone, $d_4^{99\cdot6}$ 0·9727, $n_{He}^{99\cdot6}$ 1·48250; β-methyl-Δ^β-pentenal, $d_4^{18\cdot1}$ 0·8588, 1·45132; β-methyl-Δ^α-buten-γ-one, $d_4^{22\cdot3}$ 0·8505, 1·42251; Δ^1-menthenone, $d_4^{14\cdot5}$ 0·9376; $n_{He}^{14\cdot5}$ 1·48678; ethyl *iso*phoronecarboxylate, $d_4^{15\cdot5}$ 1·0342, $n_{He}^{15\cdot5}$ 1·48126; ethyl α-*o*-formylphenoxypropionate, $d_4^{18\cdot5}$ 1·1372, 1·51746; *o*-*iso*butyryl-*s*-*m*-xylenyl methyl ether, $d_4^{16\cdot7}$ 1·0116, $n_{He}^{1\cdot7}$ 1·51823; *o*-Δ^γ-pentenoylphenyl methyl ether, $d_4^{9\cdot9}$ 1·0525, $n_j^{19\cdot9}$ 1·53903; β-*p*′-methylchalkone, $d_4^{100\cdot6}$ 1·0258, $n_j^{100\cdot6}$ 1·61715; α-*p*′-methylchalkone, 1·0317, $n_{He}^{99\cdot6}$ 1·61905; ethyl α-methylbenzoylacetate, $d_4^{16\cdot1}$ 1·0895, 1·51355; ethyl *o*-methoxybenzoylacetate, $d_4^{13\cdot1}$ 1·1634, 1·53968; furfurylideneacetone, d_4^{17} 1·0496, n_{He}^{7} 1·58197; ethyl furfurylidenemethyl ketone, $d^{17\cdot1}$ 1·0823, $n_4^{17\cdot1}$ 1·59047; ethyl α-furfurylidene-ethyl ketone, 1·0573, 1·57593; furfurylidenepinacolin, $d_4^{15\cdot6}$ 1·0088, $n_{He}^{15\cdot6}$ 1·55263;

difurfurylidene-γ-methyl*cyclo*hexanone, $d_4^{100\cdot1}$ 1·1181, 1·68812; α-bromo*iso*crotonic acid, $d_4^{99\cdot7}$ 1·5809, n_{He}^{7} 1·48546; αβ-dibromocrotonic acid, $d_4^{100\cdot1}$ 1·9963, n_{He}^{1} 1·53522; ethyl α-*cyclo*hexylidenepropionate, d_4^{18} 0·9989, 1·48483; ethyl 4-hydroxy-*m*-toluate, $d_4^{21\cdot1}$ 1·1035, $n_{He}^{21\cdot1}$ 1·52123; 2 : 2-diethylhydrindene, $d_4^{13\cdot4}$ 0·9295, n_{He}^{13} 1·51820; 2 : 2 : 5-triethylhydrindene, $d_4^{16\cdot2}$ 0·9178, $n_{He}^{16\cdot2}$ 1·51473; 2 : 2 : 5 : 6-tetraethylhydrindene, $d_4^{14\cdot35}$ 0·9246, $n_{He}^{14\cdot35}$ 1·51998; 2 : 2 : 4 : 5 : 6-pentaethylhydrindene, $d_4^{14\cdot1}$ 0·9234, 1·52115; 2 : 2 : 4 : 5 : 6 : 7-hexaethylhydrindene, $d_4^{14\cdot3}$ 0·9263, $n_{He}^{14\cdot3}$ 1·52265; phenheptamethylene, $d_4^{16\cdot}$ 0·9683, $n_{He}^{16\cdot2}$ 1·54856; 3-ethyl-4-*iso*propyltoluene, $d_4^{15\cdot7}$ 0·8756, 1·50227; methyl chloroformate, $d_4^{0\cdot85}$ 1·2240, 1·38882; ethyl chloroformate, $d_4^{15\cdot05}$ 1·1418, $n_{He}^{1\cdot05}$ 1·39861; *iso*butyl chloroformate, $d_4^{17\cdot0}$ 1·0425, n_{He}^{17} 1·40711; *iso*amyl chloroformate, $d^{15\cdot0}$ 1·0321, n_{He}^{0} 1·41916; *O*-benzoate of ethyl benzoylmalonate ("ethyl dibenzoylmalonate"), $d_4^{99\cdot2}$ 1·1129, $n_{He}^{99\cdot2}$ 1·52818.

H. WREN.

Spectrochemical studies of hydroxyazo-compounds. V. T. UEMURA and S. TABEI (Bull. Chem. Soc. Japan, 1927, 2, 249—257; cf. this vol., 1006).—The absorption spectra of neutral and alkaline solutions of the azo-dyes from the three toluidines with phenol and with resorcinol, and from aniline and the mononitroanilines with certain cresols have been investigated and the results correlated with the structure of the compounds. In neutral and alkaline solutions the substances exist in *A*- and *R*-forms, respectively. The previously recorded, hyperchromic influence of the methyl group on a previously non-methylated compound is confirmed. Hydroxyl and nitro-groups exert a maximum effect on the absorption when in the *p*-position with respect to the azo-group. Except when the hydroxyl group occupies an *o*-position with regard to the azo-group, when there are two bands, only one band is shown by the absorption curves.

J. S. CARTER.

Fluorescence and absorption spectra of iodine. F. W. LOOMIS (Physical Rev., 1926, [ii], 27, 802).—Mecke's four series without linear terms in Wood's spectrum of fluorescent iodine are due to four lines of the band (26, 0). Values are obtained as follows: $B_0''=0{\cdot}03835$, $B'=0{\cdot}02480$ cm.$^{-1}$; $J_0=7{\cdot}21\pm0{\cdot}03\times10^{-38}$ The absolute values of *m* are half-integral. Lines of Mecke's series II belong alternately to the *P* and *R* branches of band (27, 0).

A. A. ELDRIDGE.

Application of the spectrography of fluorescence to the examination of powdered alkaloids. A. ANDANT (Compt. rend., 1927, 185, 713—715).—The author has applied his method (this vol., 538) to the spectrographical examination of the fluorescence produced from small quantities of powdered alkaloids excited by the rays of the mercury arc. The spectrograms obtained indicate the degree of purity of the sample, each pure alkaloid having a characteristic fluorescence spectrum for a particular exciting radiation. The differences between the spectra produced by the various alkaloids are most marked when exciting rays of short wave-lengths are used.

J. GRANT.

Luminescence produced by bombarding solidified gases with electric rays at the temperature of liquid helium. L. VEGARD and W. H. KEESOM (Proc. K. Akad. Wetensch. Amsterdam, 1927, 30, 514—520).—An improved form of the apparatus originally used for the investigation of the luminescence of solidified gases, under the action of cathode and canal rays (Vegard, Onnes, and Keesom, A., 1925, ii, 474), is described. In an attempt to obtain a spectrogram of the luminescence of solidified hydrogen, produced by swift cathode rays, no impression was obtained on the photographic plate, in spite of the intensity of the source of light. Hence, if any line spectrum is obtained in this way, it must be extremely faint compared with the continuous spectrum. Under the bombarding action of hydrogen canal rays, with velocities corresponding with a parallel spark gap of 3 mm., the total intensity of luminescence is smaller than for the swift cathode rays, but the spectrogram shows a well-marked line spectrum of which the strong lines belong to the Balmer series. A number of faint lines between these appear to belong to the ordinary second hydrogen spectrum, but some may be lines characteristic of the solid state. The luminescence of solid nitrogen, produced by canal rays at the temperature of liquid helium, has also been examined. The four bands N_1, N_2, N_3, and N_4, and also a diffuse band series, *A*, previously found at the temperature of liquid hydrogen (A., 1926, 660), were reproduced, but with a different intensity distribution. In addition, some new lines, *e.g.*, 6004, 5766, 3870, and 3849 Å., were observed. Some of these appear to belong to the positive band spectrum of nitrogen.

M. S. BURR.

Mechanism of chemiluminescence reactions in gases. V. KONDRATEEV (Z. Physik, 45, 67—82).—The radiation emitted when potassium vapour interacts with that of mercuric chloride has been examined. At temperatures above 350° potassium lines alone are emitted from the apparently homogeneous region in which the gases interact; as the temperature is diminished to 200—250° a bluish-violet glow appears on the walls of the containing vessel in the neighbourhood of the reaction zone. These two phenomena are thought to correspond with two independent reactions, the latter taking place on the surface of the containing vessel. The following scheme is suggested to explain the mechanism of reaction: (1) $HgCl_2+K=Hg+KCl+Cl$, (2) $Cl+K=KCl^*$, and (3) $KCl^*+K=KCl+K'$. From an analysis of the velocity of reaction in terms of the velocity constants of reactions (1) and (2), and of the diffusion coefficients of K, HgCl, and Cl at the measured temperature, an expression is obtained for the length of the luminous reaction zone as a function of temperature which is in agreement with experiment. Since the light emitted by the surface reaction contains a number of bands identical with those of mercuric chloride, it is thought that this is due to monatomic potassium vapour reacting with solid mercuric chloride forming solid potassium chloride and an activated HgCl molecule. This hypothesis leads to a value for the thickness of the luminous layer, derived from the life of an excited HgCl molecule and its mean velocity of thermal agitation, of $2{\cdot}5\times10^{-2}$ mm., in satisfactory agreement with experiment. Similar phenomena have been observed in the interaction of sodium and of potassium

vapours with mercuric bromide and iodide and with cadmium chloride. R. W. LUNT.

Quantitative study of the luminescence of mercury vapour excited by electronic shock. P. BRICOUT (Compt. rend., 1927, 185, 707—709).—A rapid and convenient method is described for the determination of the relationship between the intensity of the radiation emitted by mercury vapour and the speed of the exciting electrons, for wave-lengths less than 4000 Å. A heated carbon filament is the source of electrons, and the excited radiations pass through a quartz window and are registered spectrographically. The densities of the photographs obtained are compared with those from sources of ultra-violet light of known intensities. An accuracy of about 5% is obtainable if corrections are applied for the variations in the initial speeds of the electrons, the effect of the spatial charge (this vol., 85), variations in the density of the vapour, and the diminution in transparency of the quartz window owing to the deposition of carbon (from the filament) and droplets of mercury. J. GRANT.

Quantitative study of the luminescence of mercury vapour excited by electronic shock. P. BRICOUT (Compt. rend., 1927, 185, 846—849).—A formula for the function of excitation is deduced assuming it to be the product of the probability of shock, which depends on the initial speed and position of the electron, and the probability of the transfer of the optical electron from one orbit to another, as a result of collision with an electron of given initial speed. It is $f=C/U^2\sqrt{U/U_1-1}$, where C, U_1, and U are a constant, the resonance potential, and the potential of the exciting electron, respectively. The rule agrees with experiments with the resonance radiation of mercury 2536 (preceding abstract) and with Dauvillier's results for the distribution of energy in the continuous X-ray spectrum. It is therefore suggested as general for all radiations excited by the passage of electrons from a basic orbit at a speed insufficient to produce ionisation. J. GRANT.

Lattice constant of calcium sulphide- and strontium sulphide-samarium mixed phosphors. E. RUMPF (Ann. Physik, 1927, [iv], 84, 313—322).—By means of Debye-Scherrer photographs it is shown that the transition between pure calcium sulphide–samarium phosphor and pure strontium sulphide–samarium phosphor is perfectly continuous as far as lattice constants are concerned. The lattice constant increases gradually until the strontium sulphide content has risen from zero to 30% and much more rapidly in the range 40—100% SrS. Similar changes occur with the phosphorescence emission of mixed phosphors. R. A. MORTON.

Emission from phosphors. I. Behaviour of samarium in sulphides and sulphates. R. TOMASCHEK (Ann. Physik, 1927, [iv], 84, 329—383; cf. A., 1925, ii, 12, 354).—The banded emission spectra of samarium phosphors have been measured and tabulated. Sulphide phosphors containing magnesium, calcium, barium, strontium, or zinc sulphide show three band systems in the region 5500—6800 Å., and in each case the fine structure is more easily obtainable at −150° than at 20°. Observations on calcium sulphide–samarium phosphors at 300° and 20° show that rise of temperature not only alters the relative intensities of the bands, but also affects the relative intensities of fine-structure components within a band. A distinct broadening is noticed for the line emission. The influence of changes in the mode of preparation affecting the dielectric constant of a given phosphor has been investigated in relation to the phosphorescence phenomenon.

Similar measurements have been carried out on sulphate phosphors in which the samarium is present with the sulphate of an alkali or alkaline-earth metal, or of magnesium, zinc, cadmium, aluminium, and lanthanum. R. A. MORTON.

Absorption spectra of phosphors produced by the addition of lead and thallium to halides of the alkali metals. R. HILSCH (Z. Physik, 1927, 44, 860—870).—The absorption coefficients of the alkali halides containing 0·1—0·01% of lead or thallium (as nitrate or chloride) have been determined in the range 3200—1800 Å. In all cases the maxima of absorption are shifted by the addition of lead or thallium towards the red to the extent of from 180 to 300 Å. R. W. LUNT.

Absorption spectra of alkali halide phosphors containing silver and copper. A. SMAKULA (Z. Physik, 1927, 45, 1—12; cf. this vol., 917).—The influence of the addition of 0·2—1·0% of silver or copper as chloride on the absorption of the halides of sodium and potassium has been investigated from observations of the extinction coefficient of the substances produced in the range 2000—4000 Å. The following cases have been examined and the data cited refer to the absorption maxima to which the excitation of phosphorescence can be traced, and the half width in Å. of these respectively: sodium chloride–silver 2100, 100; sodium bromide–silver 2190, 100; sodium chloride–copper 2550, 300; sodium bromide–copper 2590, 300; potassium chloride–copper 2650, 400; and potassium bromide–copper 2650, 300. In the same range the extinction coefficients of pure sodium bromide, potassium iodide, 99% potassium chloride −1% potassium iodide, and 85% sodium chloride −15% silver chloride are sensibly zero at 2200, 2100, 3000, 2500 Å., respectively. At shorter wave-lengths rapidly increasing absorption characterises these substances, and the data show that the absorption due to silver chloride commences at a wave-length less than 2500 Å. In potassium chloride and bromide the presence of silver ions produces practically no deviation from the normal continuous absorption. The width of the absorption bands produced by the addition of copper is considerably greater than those due to lead and thallium; for the chlorides the curves indicated the existence of second maxima between those recorded and the wave-lengths at which they normally commence to exhibit absorption (sodium chloride 1700, potassium chloride 1810 Å.). These two bands are thought to be due to (*a*) the formation of mixed crystals and (*b*) the distortion of the alkali chloride grating by copper ions, which is smaller with sodium chloride. The extinction coefficients of the bands produced by the addition of copper are approximately proportional to the copper concen-

trations, and similarly those produced by the addition of silver either as chloride or nitrate to sodium chloride are approximately proportional to the silver concentrations. R. W. LUNT.

Dielectric constant of helium and oxygen in a magnetic field. B. B. WEATHERBY and A. WOLF (Physical Rev., 1926, [ii], 27, 252).—For helium (20 cm. pressure), air (76 cm.), and oxygen (76 cm.) at the ordinary temperature there is no change in the dielectric constant on exposure to an electric field (5000—10,000 volts/cm.) parallel or normal to a magnetic field (8000—10,000 gauss). A. A. ELDRIDGE.

Dielectric constant for very dilute solutions of electrolytes. A. DEUBNER (Ann. Physik, 1927, [iv], 84, 429—456).—A new technique, based on the application of a new short-wave generator devised by Hollmann to the first Drude method, has been developed so as to ensure values accurate to 0·1% in pure water and 0·2—0·3% in solutions up to a maximum strength of 0·005*N*. The method is discussed critically and results on solutions of sucrose, sodium chloride, and copper sulphate are detailed. The work of Hellmann and Zahn (A., 1926, 778; this vol., 7) is in agreement, but that of Sack (this vol., 409) is not in agreement with that of the author. R. A. MORTON.

Optical constants of single-crystal bismuth. L. H. ROWSE (Physical Rev., 1926, [ii], 27, 247).—The index of refraction rises from 1·05 at 470 to 1·55 at 670 *mu*, whilst the extinction modulus rises from 2·7 to 3·6. A. A. ELDRIDGE.

Relation between refractive index and density. D. BURNETT (Proc. Camb. Phil. Soc., 1927, 23, 907—911).—Theoretical. The formula proposed by Macdonald (Proc. Roy. Soc., 1926, A, 113, 237) for the dependence of the refractive index of a medium on its density has been examined for water, alcohol, aniline, benzene, and ethyl ether. The formula gives as satisfactory an agreement with experiment as that of Lorenz and Lorentz in most cases and occasionally a better. W. E. DOWNEY.

Natural rotatory dispersion of molybdomalic complexes. E. DARMOIS and R. DESCAMPS (Compt. rend., 1927, 185, 705—706).—The rotatory dispersions of solutions of complex molybdomalates of the types $[4MoO_3,2C_4H_5O_5](NH_4)_4+5H_2O$ (dextro-) and $[MoO_3,2C_4H_5O_5]K_2+2H_2O$ (lævo-) have been measured for wave-lengths between 5780 and 3655 Å. The dispersion is least for the lævo-salt, and in each case $[\alpha]$ may be expressed by a formula of the type $[\alpha]=A/(\lambda^2-\lambda^2_1)+B/(\lambda^2-\lambda^2_2)$. Since the values of λ_1 are in the region of the ray 3655 Å., it is probable that the condition of negligible absorption assumed for the purposes of the formula does not hold exactly for this ray, a supposition supported by the results. J. GRANT.

Molecular arrangement of uniaxial optically active crystals. W. G. BURGERS (Proc. Roy. Soc., 1927, A, 116, 553—585).—With the object of determining whether optical activity must be ascribed to pseudo-symmetrical intergrowths of biaxial lamellæ or to special arrangements of the atoms within the unit cells, *X*-ray examinations have been made of the following uniaxial optically active crystals: *d*-potassium rhodium oxalate, $K_3[Rh(C_2O_4)_3],H_2O$; sodium metaperiodate, $NaIO_4,3H_2O$; ethylenediamine sulphate, $C_2H_4(NH_2)_2,H_2SO_4$, and guanidine carbonate, $(CN_3H_5)_2,H_2CO_3$. The dimensions of the unit cells and the corresponding space-groups were determined chiefly by means of 20°-oscillation photographs about various crystallographic directions, Laue photographs being taken to confirm the crystal symmetry. For *d*-potassium rhodium oxalate, the space-group is D_3^4 (or D_3^6), the dimensions of the hexagonal unit cell, $a=11·28$, $c=20·25$ Å., the number of groups of $K_3[Rh(C_2O_4)_3],H_2O$ per unit cell is 6, and this group possesses no plane of symmetry. For sodium metaperiodate, the space-group is C_3^4, the dimensions of the orthohexagonal unit cell, $a=10·38$, $b=6·00$, $c=13·13$ Å., the length of the edge of the rhombohedral unit cell, $a'=5·58$ Å., the rhombohedral angle $\alpha=65°\ 1'$; there are six ($NaIO_4,3H_2O$) groups in the orthohexagonal cell, one in the rhombohedral cell, and the group has an axis of threefold symmetry. For ethylenediamine sulphate, the space-group is D_4^4 (or D_4^8), $a=5·96$, $c=17·99$ Å., there are 4 molecules in the unit cell, and the molecule possesses an axis of twofold symmetry. For guanidine carbonate, the space-group is D_4^4 (or D_4^8), $a=6·95$, $c=19·45$ Å., there are 4 molecules in the unit cell, and the molecule has an axis of twofold symmetry. The view is held that the rotatory power of the crystals is not due to a spiral arrangement of biaxial lamellæ (cf. definite spiral piles of thin mica plates), but to some definite arrangement of atoms within a unit of structure. This unit is a real unit if the crystal is truly uniaxial, but is a pseudo-unit if the crystal is built up of very many twinned lamellæ which are individually too small to give separate *X*-ray reflexions (" pseudo-paramorphic " structures). It is shown that the similarity between the rotatory dispersion curves of crystals and solutions of *d*-potassium rhodium oxalate is not due to the presence of parallel molecules in the crystalline state. The molecules occupy a spiral arrangement in the crystal, which may account for the movement of the inversion point of the dispersion curve on transition from solution to crystal. The marked difference in rotatory power between tetragonal–pyramidal and tetragonal–trapezohedral crystals is considered in connexion with the spiral arrangements of the molecules. The exceptional place occupied by potassium lithium sulphate as an optically active crystal is discussed. L. L. BIRCUMSHAW.

Number of dispersion centres in saturated sodium vapour. W. WEINGEROV (Z. Physik, 1927, 45, 416—429).—The number of dispersion centres in saturated sodium vapour has been determined from measurements of the magnetic rotation of the D_1- and D_2-lines. The necessity for a knowledge of the magnetic resolution is obviated by using a new compensation method. Plane polarised light travels successively through two cylindrical co-axial vessels of different length containing sodium vapour; each vessel is placed symmetrically and coaxially in one of two equal solenoids, the fields of which are equal and opposing, exterior to the furnaces heating the tubes containing sodium. For any given temperature

of the longer tube the magnetic rotation in this tube can be compensated by that of the shorter tube, provided that some higher temperature is maintained. Under these conditions the number of dispersion centres per unit volume in each tube is equal. Observations have been made for three different ratios of the lengths of the two tubes containing sodium in the temperature range, and the results show that the number of dispersion centres per unit volume is proportional to the density of the saturated vapour. Using the vapour-pressure data of Haber and Zisch and those of Ladenburg and Minkowski, the chemical constant calculated from the data now cited is, respectively, 0·43, 0·50: the theoretical value of Stern is 0·46. R. W. LUNT.

Relation of Tyndall effect to osmotic pressure in colloidal solutions. C. V. RAMAN (Indian J. Phys., 1927, 2, 1—6).—Theoretical. The fluctuation theory is applied to the interpretation of the optical behaviour of colloidal solutions. On the assumption that colloidal and strongly scattering molecular solutions are analogous, and that in these solutions the simple Rayleigh theory of scattering cannot be regarded as valid, an expression for the light-scattering power of the former is derived thermodynamically in terms of the variations of osmotic pressure and refractive index with concentration. M. S. BURR.

Scattering of light by liquids at high temperatures. S. R. RAO (Indian J. Phys., 1927, 2, 7—24).—In an apparatus which is described, the variations in the intensity and depolarisation factor of transversely scattered light have been studied for *iso*pentane, *n*-pentane, *n*-hexane, ethyl ether, methyl acetate, and ethyl formate at different temperatures up to the critical point. The depolarisation factor diminishes extremely slowly up to a certain temperature characteristic of the liquid. Beyond this the decrease becomes more rapid until the critical temperature is approached, when it again slows down. Only with *iso*pentane, *n*-pentane, and ethyl ether could values for the intensity ratio between the different temperatures and 30° be compared with calculated values. The results, for all temperatures, agree very closely with Ramanathan's modified formula (*ibid.*, 1927, **1**, 401). The intensity increases with temperature, at first slowly and then rapidly as the critical temperature is approached. The molecular anisotropy at different temperatures, calculated for all six liquids, apparently increases with temperature and tends to attain the value for the vapour state. This change is attributed to the anisotropy of the local polarisation field acting on the molecules at lower temperatures. Since the molecules are less closely packed at higher temperatures, they can approximate more nearly to a perfectly chaotic distribution which is attainable, however, only in the vapour state. Two sources of error, affecting the measurements of the depolarisation factor in the neighbourhood of the critical point, are discussed. One is the strain produced in the glass of the observation window by the great increase of pressure at this temperature; the other is the inefficient background at temperatures near the critical temperature, when the scattered light has considerable intensity and the liquid surrounding the track is illuminated by secondary scattering. M. S. BURR.

Scattering of light by aromatic compounds. A. N. BANERJEE (Indian J. Phys., 1927, 2, 51—60).—The methods of measurement of the depolarisation factor and of the relative intensity with respect to benzene of the light scattered by a large number of aromatic compounds are described. The results are tabulated and compared, where possible, with those calculated from the modified Einstein and Smoluchowski's formula, and also from Ramanathan's more recent formula (*ibid.*, 1927, **1**, 420). Agreement with the new formula is slightly better than with the old. M. S. BURR.

Light-scattering data for ten gases and sixty-three vapours of organic compounds. I. R. RAO (Indian J. Phys., 1927, 2, 61—96).—The various methods for the determination of the depolarisation of light scattered by gases and vapours have been experimentally examined, and the method of Cabannes (J. Phys. Radium, 1923, [vi], 4, 429; 1926, [vi], 7, 340; A., 1926, 559), in which the two images of the scattered light, as seen through a double image prism viewed in a common background, is selected as trustworthy. The effect of finite convergence on the incident pencil of light has been determined experimentally. It appears to be unnecessary to correct for this and a theoretical explanation of the null effect is offered. The depolarisation values of a number of gases and vapours are given. The anisotropies in the gaseous and liquid states have been calculated for the vapours. Except for the fatty acids and methyl formate where the converse holds, the anisotropy in the liquid is smaller than in the corresponding vapour. This may be due either to the association of molecules in the liquid state, resulting in the formation of scattering units more isotropic than the individual molecules themselves (Raman, Nature, 1923, **111**, 428), or to the close packing of the molecules in the liquid state, in consequence of which the influence on a single atom, of the atoms in the neighbouring molecules, may be comparable with the influence of the other atoms in the same molecule, thus conducing to greater optical symmetry (Krishnan, A., 1925, ii, 1030). The anomalous behaviour of the fatty acids may be explained as due to the lack of coincidence between the longest geometrical axis of the molecule and the axis of largest refractivity. In the hydrocarbons the depolarisation does not increase regularly with the size of the molecule and the anisotropy is small, but is increased by halogen substitution. Unsaturated compounds show much larger depolarisation than saturated. Alcohols show very small depolarisation and small anisotropy, trimethylcarbinol being almost isotropic. The fatty acids and esters decrease steadily in anisotropy and depolarisation with increasing mol. wt. The cyclic compounds are invariably more anisotropic than the aliphatic, and all benzene compounds examined, except benzylidene chloride, are more anisotropic than benzene. The depolarisation factor of double ring compounds is greater than that of single ring compounds. For water vapour, a depolarisation value of 1·91 has been

obtained, which does not agree with Havelock's predicted values (this vol., 189). The anisotropy of the carbon atom is discussed. M. S. BURR.

Relation between shared electrons and valency: principal and contra valencies. W. A. NOYES (Z. physikal. Chem., 1927, **130**, 323—333).—The generalisation is proposed that in balancing the positive charge of the kernel of an atom a pair of shared electrons is equivalent to a single unshared electron. This generalisation is strongly supported by the hypothesis that a covalent link consists of a pair of electrons rotating in opposite directions in orbits which include two positive kernels or two nuclei. Further support is obtained from the following considerations: the ionisation of quaternary ammonium compounds, radioactive changes, dissociation of elements at high temperatures, the Hückel-Grimm law, semi-polar linkings, principal and contra valencies, atoms without full octets, and condensations of carbon compounds. By accepting the evidence of Sugden (A., 1925, ii, 936) and of Phillips (A., 1926, 159) for semipolar linkings, the formulæ under this generalisation agree very nearly with those assumed by Lewis for the sulphate and perchlorate ions, with the limitation that the pair of electrons which are the occasion for the polar part of a semipolar linking are not available for a covalency. The pair of electrons of a covalent link rotate about the kernels of the two atoms which are held together, whilst the electrons of a polar link rotate about the kernel of only one of the atoms. L. L. BIRCUMSHAW.

Electronic theory of valency. Stereochemical representation of the elements. G. DUPONT (Bull. Soc. chim., 1927, [iv], **41**, 1101—1137).—A lecture.

Contraction of molecules in the liquid state. S. G. MOKRUSHIN (J. Physical Chem., 1927, **31**, 1581—1583; cf. Richards, A., 1925, ii, 362).—Theoretical. Further evidence is advanced that molecules contract on passing from the gaseous to the liquid state. A change in shape from that of a sphere first to that of a hexahedral prism and finally to that of a honeycomb cell is suggested. L. S. THEOBALD.

Rast's micro-method for mol. wt. determinations. J. H. C. SMITH and W. G. YOUNG (J. Biol. Chem., 1927, **75**, 289—298).—A description of a slightly modified technique. C. R. HARINGTON.

Crystal structure of carbon steels. I. N. SELJAKOV, G. KURDJUMOV, and N. GOODTZOV (Z. Physik, 1927, **45**, 384—408).—*X*-Ray measurements on hardened carbon steels have demonstrated the existence of a tetragonal-centred lattice little different from that of α-iron. The ratios of the lattice parameters are functions of the carbon content, and of the temperature of hardening. The existence of a surface-centred cubical grating has also been established and identified with that of austenite; this grating can be considered as that of a solid solution of carbon in α-iron. The process of hardening is shown to be due to a transition of γ- into α-iron. R. W. LUNT.

Atomic grouping in "permalloy." L. W. MCKEEHAN (J. Franklin Inst., 1927, **204**, 501—524; cf. A., 1926, 892).—The explanation of the peculiar magnetic properties of "permalloy" which was given previously in terms of an hypothetical atomic grouping, comprising one iron atom with four adjacent nickel atoms and of specified dimensions and orientation, is inconsistent with the known cubic symmetry of iron–nickel alloys unless the lattice unit is very large or the arrangement of the groups random. The probable number of such atomic groupings resulting from a random or partly random arrangement of the component atoms has been studied by a method which involved the preparation of charts representing the sections of a crystal with 1688 atoms (20% Fe) to the various parts of which the atoms were assigned by means of a lottery machine. It is concluded tentatively that the formation of a sufficient number of the groupings to explain the magnetic properties of the alloy is improbable except when the stipulations regarding the dimensions and orientation of the unit group are abandoned and arrangements with more than two adjacent iron atoms discarded. G. A. ELLIOTT.

Crystal structure of calcium hydroxide. A. REJNA (Atti R. Accad. Lincei, 1927, [vi], **5**, 1008—1010).—By assuming a value for u in the neighbourhood of 0·25 the grating constants of calcium hydroxide are $a=3·52$, $c=4·93$; the calcium atom is at (0, 0, 0), the oxygen atoms at 0 $\frac{2}{3}$, u) and ($\frac{2}{3}$, $\frac{1}{3}$, u). R. W. LUNT.

Crystal structure of nickelous and cobaltous chlorides. A. FERRARI (Atti R. Accad. Lincei, 1927, [vi], **6**, 56—59).—Nickelous and cobaltous chlorides have cell structures similar to that of magnesium chloride; the grating constants a and c are, respectively, 7·08, 17·35; 7·07, 17·32. R. W. LUNT.

Lattice parameters and densities of copper, silver, and tungsten. W. P. DAVEY and T. A. WILSON (Physical Rev., 1926, [ii], 27, 105).—New measurements are as follows: copper has side of unit cube 3·605 Å., d 8·95, thus changing Patterson's values for chromium and titanium by 0·3%. Silver has d 10·481; tungsten has side of unit cube 3·155 Å., d 19·32. A. A. ELDRIDGE.

Crystallographic investigation of silver subfluoride. H. STEINMETZ and A. HETTICH (Z. anorg. Chem., 1927, **169**, 75—76).—The crystals belong to the trigonal system; $a:c=1:1·880$; $\alpha=71°\ 52'$. H. F. GILLBE.

Grating constant of purple of Cassius. G. R. LEVI and C. FONTANA (Atti R. Accad. Lincei, 1927, [vi], **5**, 996—1000).—With the Debye–Scherrer method values have been obtained for the grating constant of samples of purple of Cassius prepared in different ways and containing varying amounts of stannic oxide. Assuming a cubical cell the mean value of the constant is 36 Å.; the amount of stannic oxide present has no influence on the constant. R. W. LUNT.

Crystal structure of cæsium mercuric chloride. G. NATTA (Atti R. Accad. Lincei, 1927, [vi], **5**, 1003—1008).—Cæsium mercuric chloride crystallised from solutions containing excess of cæsium chloride has a cubic lattice of constant 5·44 Å.; the mercuric ion

is at ($\frac{1}{4}$, $\frac{1}{2}$, $\frac{1}{2}$), the cæsium ion at (0, 0, 0), and the chlorine ions at ($\frac{1}{2}$, $\frac{1}{2}$, 0), (0, $\frac{1}{2}$) and ($\frac{1}{4}$, 0, $\frac{1}{4}$), $d_{calc.}$ is 4·53, $d_{obs.}$ 4·266. R. W. Lunt.

Crystal structures of mercuric and mercurous iodides. M. L. Huggins and P. L. Magill (J. Amer. Chem. Soc., 1927, 49, 2357—2367).—The unit tetragonal cell of mercuric iodide contains $2HgI_2$ and has the dimensions a_0=4·34, c_0=12.34 Å. The mercury atoms are at (0, 0, 0) and ($\frac{1}{2}$, $\frac{1}{2}$) and the iodine atoms at (0, $\frac{1}{2}$, u), (0, u), ($\frac{1}{2}$, 0, u), and (0, $\frac{1}{2}$, $u+\frac{1}{2}$), where u=0·140±0·003 (cf. Bijvoet, Claassen, and Karssen, A., 1926, 889). The valency electrons are probably in pairs at the corners of tetrahedra surrounding both mercury and iodine atoms. Each mercury atom is linked to four iodine atoms, each of the latter being linked to two mercury atoms.

The unit tetragonal cell of mercurous iodide contains $2Hg_2I_2$ and has a_0=4·92, c_0=11·64 Å. The mercury atoms are at (0, 0, u), (0, 0, u), ($\frac{1}{2}$, $\frac{1}{2}$, $u+\frac{1}{2}$), and ($\frac{1}{2}$, $\frac{1}{2}$—u); the iodine atoms are at (0, 0, v), (0, 0, v), $v+\frac{1}{2}$), and ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$—v), where u=0·117 and v=0·353 A. (cf. Havighurst, A., 1926, 995).

S. K. Tweedy.

Crystal structure of thallium. K. Becker (Z. Physik, 1927, 45, 450).—The author maintains his original contentions (this vol., 503) with regard to the crystal structure of thallium and refutes those of Levi (this vol., 1013) in which a hexagonal structure is claimed. R. W. Lunt.

***X*-Ray investigations on the structure of formaldehyde polymerisation products.** J. Hengstenberg (Ann. Physik, 1927, [iv], 84, 245—278).—Johner and Signer have studied the polymerisation of formaldehyde and many of their products have been examined by the powder method. Highly polymerised polyoxymethylenes of the types $OH{\cdot}CH_2{\cdot}[O{\cdot}CH_2]_x{\cdot}O{\cdot}CH_2{\cdot}OH$, x being about 60; $HSO_3{\cdot}O{\cdot}CH_2{\cdot}[O{\cdot}CH_2]_x{\cdot}O{\cdot}CH_2{\cdot}O{\cdot}SO_3H$, and $OMe{\cdot}CH_2{\cdot}O{\cdot}[CH_2{\cdot}O]_x{\cdot}CH_2{\cdot}OMe$, etc., all show the same *X*-ray diagram. By heating polyoxymethylenes with acetic anhydride, oxymethylene diacetates of the type $COMe{\cdot}[O{\cdot}CH_2]_x{\cdot}OAc$ are obtained and a number of solid diacetates in which x varies from 8 to 22 have been separated by fractional crystallisation. Using a specially pure diacetate in which x=9, the *X*-ray study leads to the cell dimensions (A.) of 25·2×8·30×4·47 (=935 Å.^{3}), and since the volume of a single molecule is calculated to be 451 Å.^{3}, the number of molecules per unit cell is 2 within the limits of error. Similarly, when x=15 the cell dimensions are 36·8×7·89×4·56 with again 2 molecules per unit cell. For every fresh CH_2O-group the length of the unit cell increases by about 1·9 Å. For soluble diacetates it is therefore evident that the molecule is the unit with which the lattice is built up. Similar conclusions follow from the study of the dimethyl ethers, which are built on a pseudo-trigonal form. When mixtures of products of a low degree of polymerisation are examined it is found that molecules of the same length always crystallise together so that mixed crystals are not formed. On the other hand, in the diacetates in which x is high, and in the other highly-polymerised products, molecules of different lengths may be attached end to end and the lattice is not built up with molecules as units.

The work lends support to Staudinger's idea of a relatively simple formaldehyde polymerisation product as the unit in the cellulose structure. In certain lattices it must be assumed that with the $[CH_2O]_x$ alinement, the lattice forces must be chemical in nature in one direction, thus accounting for the fibre structure. With a more complicated unit group, the lattice forces may represent chemical affinity in several directions so that the entire crystallite may be regarded as one large molecule.

R. A. Morton.

Comparison of *X*-ray spectra of organic compounds in the solid and liquid states. R. O. Herzog and W. Jancke (Z. Physik, 1927, 45, 194—199).—The comparison was undertaken by the Debye–Scherrer method. A strong undifferentiated band in the spectrum of a liquid occurred, generally in the neighbourhood of an especially intense interference line in the spectrum of the corresponding solid (but not always *vice versa*). If several intense lines lie close together in the spectrum of the solid, these are converted by liquefaction into a single wide amorphous band. Bands close to the point of intersection of the incident ray with the photographic plate are at a greater distance from that point than the corresponding intense lines of the solids, whilst bands which occur near the periphery are displaced towards the centre. G. A. Elliott.

***X*-Ray liquid diffraction.** C. M. Sogani (Indian J. Phys., 1927, 2, 97—133; cf. this vol., 924).—*X*-Ray diffraction data for fourteen further liquids, including formic, acetic, butyric, lauric, palmitic, erucic, and brassidic acids, pyridine, piperidine, quinoline, methyl and ethyl benzoate, phenetole, and mercury, have been obtained. All the acids, except formic and butyric acids, have also been studied in the solid state in order to compare the corresponding prominent spacings in the two states of aggregation. On the basis of these and the previous data (*loc. cit.*), the molecular constitution of liquids is discussed. It is shown that there must be fairly regular spacings between the molecules of a liquid, and that the shape of molecules influences considerably their orientation. *X*-Ray haloes of liquids composed of spherical molecules will have a single maximum in the diffraction halo corresponding with the mean distance between neighbouring molecules, the sharpness depending on the compressibility of the liquid. Liquids having elongated or flat molecules are characterised, in general, by two maxima in the diffraction pattern, corresponding with the two principal dimensions of the molecules, in the first case the cross-sectional, and in the second the linear dimensions of the flat surface. In discussing the haloes of molecules in which the distribution of the scattering electrons is very unsymmetrical, it is probably sufficient to regard the optical centre of the molecule as the centre of mass of the electrons. From the point of view of these typical cases the diffraction haloes of all the liquids investigated are discussed and their important features explained.

M. S. Burr.

Diffraction of *X*-rays in liquids. G. W. STEWART, R. M. MORROW, and E. W. SKINNER (Physical Rev., 1926, [ii], **27**, 104).—Camphor at 21° or 205° shows the same location of intensity peaks when allowance is made for expansion. Liquid naphthalene, α-naphthol, and β-naphthol give broad peaks which are approximately the mean of the peaks given by the solids. For methyl, propyl, hexyl, octyl, and decyl alcohols, a single broad peak is accompanied by smaller ones, indicating a larger "grating" spacing. The phenomena are probably interatomic in origin. A. A. ELDRIDGE.

Magnetic susceptibility of iron-carbon alloys at high temperatures, and the equilibrium diagram of the system. K. HONDA and H. ENDO (Sci. Rep. Tohoku Imp. Univ., 1927, **16**, 627—637).—The magnetic susceptibility of steels containing up to 5% of carbon has been measured both in the solid and in the molten state, and between about 800° and 1300°. In general, the susceptibility–temperature curves are rectilinear, but points of inflexion may be observed corresponding with the liquidus and solidus points, and with the solubility of cementite, so that from the measurements the equilibrium diagram of the system may be constructed. The susceptibility of cementite, determined by extrapolation of the susceptibility–composition curves, which are also rectilinear, is found to decrease in a linear manner with rise in temperature. The susceptibility of the molten steels does not vary with the temperature. R. CUTHILL.

Piezo-electric effect in sodium bromate. J. VALASEK (Physical Rev., 1926, [ii], **27**, 254).—The change of the lattice constant for sodium bromate with temperature is 0·0000286, whilst the temperature coefficient of the piezo-electric constant is approx. 100 times as great. This is not in accord with simple expansion of all atomic distances. A. A. ELDRIDGE.

Recrystallisation of silver and copper. H. WIDMANN (Z. Physik, 1927, **45**, 200—224).—A study has been made of the changes in the *X*-ray spectra, tensile strength, and extension of silver and copper foil, when rolled to varying extents and subsequently heated. The crystals of a thoroughly rolled foil are oriented in a definite manner, whilst on heating a process of recrystallisation takes place whereby the plane of orientation changes at a more or less sharply defined temperature. Further heating may cause the crystal arrangement to become quite irregular. Cold-rolled copper which has been previously worked at a higher temperature, however, does not change from the recrystallised state on further heating, whilst foil which has been incompletely rolled changes directly to the irregular condition. In the recrystallised state, the (113) plane of silver and the (100) plane of copper are parallel to the plane of rolling. The process of recrystallisation is accompanied by a softening of the metal and an increase of its extension. The influence of small amounts of impurities on the temperature at which recrystallisation begins has also been studied. G. A. ELLIOTT.

Alteration of the crystal orientation of iron on rolling. G. TAMMANN and A. HEINZEL (Z. anorg. Chem., 1927, **167**, 173—182).—The influence of rolling on the crystal structure of iron has been determined under various conditions. H. F. GILLBE.

Internal stress [in tungsten wires] as revealed by *X*-ray photographs. (FREIHERR) VON GOLER and G. SACHS (Z. Metallk., 1927, **19**, 410—411).—The blurring of the $K\alpha$ doublets in the Debye–Scherrer *X*-ray photographs of drawn tungsten wire gradually disappears with rise in annealing temperature and has totally vanished at about 1000°. The tensile strength of the wires increases slightly to a maximum at about 800°, then decreases fairly rapidly with further rise in the annealing temperature. These results indicate that the blurring of the interference lines by cold work has nothing to do with the hardening action of cold deformation, but is probably caused by internal stresses in the wire which are completely relieved by annealing it at 900° without appreciably reducing its hardness or strength. A. R. POWELL.

Photo-elastic properties of transparent cubic crystals. H. B. MARIS (J. Opt. Soc. Amer., 1927, **15**, 194—200).—The photo-elastic coefficients of rock salt, sylvite, and fluorite have been measured for the mercury lines 436, 546, and 578 μμ. Compared with glass the coefficient is positive for rock salt, negative for sylvite; for fluorite stressed normal to a cube face it is positive and when stressed normal to an octahedral face negative. For all cases except the last the relative retardation, Δ, plotted against stress per cm.^{2} gave a straight line for loads between 10,000 and 20,000 g./cm.^{2}; this line extended cut the axis of Δ above zero. The relation between photo-elastic effect and applied force for cubic crystals is therefore not the simple direct relation assumed for non-crystalline materials. C. J. SMITHELLS.

Electrical birefringence of benzil. R. DE MALLEMANN (Compt. rend., 1927, **185**, 709—711).—Benzil is the optical analogue of quartz, but is more convenient for electro-optical studies on account of its low m. p. and its solubility. Measurements conducted with solutions of benzil in benzene have shown that the specific birefringence increases with the concentration and that Kerr's constant is negative and higher in absolute value than that of any other known negative substance. The conclusions suggested by the results are the same as those arrived at in the interpretation of the electrical and optical properties of quartz (Rev. gen. Sci., 1927, **38**, 474). J. GRANT.

Maxwell effect in liquids. C. V. RAMAN and K. S. KRISHNAN (Nature, 1927, **120**, 726—727).—A molecular theory of the Maxwell effect is presented. A. A. ELDRIDGE.

Influence of *X*-rays on time lags of the Faraday effect and on optical rotation in liquids. F. ALLISON (Nature, 1927, **120**, 729).

Influence of *X*-rays on the crystallisation of antimony. (SNA.) M. CAMPA (Rend. Accad. Sci. fis. mat. Napoli, 1926, [iii], **32**, 170—173; cf. Adinolfi, A., 1925, ii, 485).—*X*-Rays (maximum frequency ν—$1{\cdot}46\times10^{19}$) produce a decrease in the Hall coefficient of antimony during solidification similar to that given by mesothorium radiation

(13—17%), causing a thermo-electric current in a circuit containing the unexposed metal, the thermo-electromotive force having a mean value of $2{\cdot}0\times10^{-6}$ volts at 0—18·5°. E. W. WIGNALL.

Photomagnetic effect in silver chloride and in selenium. C. W. HEAPS (J. Opt. Soc. Amer., 1927, **15**, 190—193).—Contrary to the results of Garrison (A., 1925, ii, 371), no change in the magnetic susceptibility of silver chloride and selenium was found when these materials were exposed to the light from a tungsten lamp. This result is considered to support Bohr's theory that free electrons do not contribute to diamagnetic susceptibility. C. J. SMITHELLS.

Determination of the coefficient of magnetisation of certain liquids. G. P. ARCAY and M. FALLOT (Compt. rend., 1927, **185**, 849—851).—Solutions of gelatin (0·1 and 0·4%), gum arabic (0·2%), albumin (0·1%), gelose (0·02%), casein (0·01%), and of silica gel behave abnormally during the determination of the coefficient of magnetisation by compensating the change in level produced in the arms of a U-tube, one of which is placed in a magnetic field, by the addition of a measured quantity of liquid from a burette. A secondary change of level, often of the same order as that produced initially, was observed, the effect being greatest and least for gum arabic and gelose, respectively. Collodion (28%), glycerol (at 30°), sulphuric acid (*d* 1·825), benzene, "vaseline," and olive oil behaved normally. The phenomenon is associated with the same substances as the Schwedoff effect, and may be related to the rigidity of the liquid. J. GRANT.

Magnetic susceptibilities of vapours of organic liquids. V. I. VAIDYANATHAN (Physical Rev., 1927, [ii], **30**, 512—515).—The following values of the molecular (volume) susceptibility ($\times10^6$) of vapours are tabulated: methyl acetate 51, ethyl formate 50, carbon tetrachloride 79, chloroform 73, ether 70, *n*-pentane 82, *n*-hexane 89, *n*-heptane 97, methyl formate 38, acetone 34, carbon disulphide 75, benzene 83. A. A. ELDRIDGE.

Specific heats of solid substances at the temperatures attainable with the help of liquid helium. I. Measurements of the atomic heat of lead. W. H. KEESOM and D. H. ANDREWS (Proc. K. Akad. Wetensch. Amsterdam, 1927, **30**, 434—443).—The specific heat of lead has been determined by the method of Nernst and Eucken (cf. Keesom and Onnes, A., 1915, ii, 83; 1916, ii, 12) between 2° and 20° Abs. The results are much less accurate at the lower temperatures than at the higher, the average deviation from the mean being 20% at 2—4°, 7% at 4—8°, and 2% at 8—16° Abs. There is satisfactory agreement with the results of Keesom and Onnes (*loc. cit.*) in the liquid hydrogen range. The atomic heat of lead at the lower temperatures is several times as great as that calculated from the formula of Debye, if the value $\theta=88$ which reproduces approximately the observed values at higher temperatures be adopted. It is not possible to decide from the measurements whether, on approaching 0° Abs., the atomic heat capacity approaches zero or a positive value. It may approach zero at a smaller rate than Debye's T_3 rule suggests. M. S. BURR.

Specific heat of water vapour and the theory of the dissociation of water vapour at high temperatures. W. H. MCCREA (Proc. Camb. Phil. Soc., 1927, **23**, 942—950).—Theoretical. The theory of the vibrational specific heat together with the theory of the dissociation of the H_2O molecule at high temperatures accounts for the observed facts. At temperatures near 100° an effect due to polymerisation is found. W. E. DOWNEY.

Thermal properties of butane, *iso*butane, propane, and ethane. L. I. DANA (Physical Rev., 1926, [ii], 26, 819).

F. p. [and b. p.] of organic compounds. X. J. TIMMERMANS (Bull. Soc. chim. Belg., 1927, **36**, 502—508).—The f. p. and, wherever possible, the b. p. of a large number of organic compounds are listed. J. S. CARTER.

Has pure aluminium an allotropic transformation point? M. HAAS (Z. Metallk., 1927, **19**, 404—406).—Dilatometric experiments with rods of pure aluminium containing only 0·044% Si, 0·040% Fe, and 0·07% Cu failed to indicate any allotropic transformation at temperatures up to 610°. A. R. POWELL.

Vapour pressure of liquid mercury. A. W. C. MENZIES (Z. physikal. Chem., 1927, **130**, 90—94).—The temperature scale employed by Smith and Menzies in reporting the vapour pressure of mercury (A., 1910, ii, 1037) has been revised from the sulphur b. p. value of 445° to the new figure 444·6°. Taking into account the new data of Menzies (A., 1920, ii, 11), new values for the constants of the Kirchoff–Rankine–Dupre–Hertz equation, $\log p=A-B/T-C\log T$, have been evaluated, giving $B=3283{\cdot}92$ and $C=0{\cdot}665240$. The average divergence of the pressure measurements of Smith and Menzies from this equation is 0·10%, whilst the measurements of other workers show in general considerably larger differences. Despite this, the equation holds from 0° to 1200°, *i.e.*, over a pressure variation of 1—2,000,000,000, within the limits of experimental error. S. J. GREGG.

Atomic volumes of zirconium and hafnium. A. E. VAN ARKEL (Z. physikal. Chem., 1927, **130**, 100—104).—Hafnium and zirconium apparently violate the usual rule that in a given group of the periodic table atomic volume increases with increasing atomic weight. Hence accurate determinations of their atomic volumes are of importance. The metals were obtained in pure condition by thermal dissociation of their iodides, and were then drawn into wires suitable for *X*-ray examination by the Debye–Scherrer method. The following results were obtained: the density of zirconium is $6{\cdot}53\pm0{\cdot}01$, of hafnium $13{\cdot}08\pm0{\cdot}05$; the atomic volume of zirconium is $13{\cdot}97\pm0{\cdot}02$, of hafnium $13{\cdot}66\pm0{\cdot}06$. S. J. GREGG.

Thermal expansion of silver between +101° and −253°. W. H. KEESOM and (MISS) A. F. J. JANSEN (Proc. K. Akad. Wetensch. Amsterdam, 1927, **30**, 576—580).—The coefficients of linear expansion of silver over the temperature ranges −252·8° to −182·8°, −182·8° to −102·5°, −102·5° to 0°, and 0° to 101·1°, determined by the method

previously described (A., 1926, 1197), are 9·81, 15·89, 17·61, and $19·15 \times 10^{-6}$, respectively. As with copper, an equation involving powers of t up to the fourth is necessary to represent the expansion over the whole temperature range. J. S. CARTER.

Relation between temperature and energy of a gas. II. E. WERTHEIMER (Z. Physik, 1927, 45, 231—260; cf., A., 1926, 1088).—The previous calculation of the energy of a rarefied gas—considered as the sum of the internal molecular energy, the kinetic energy of the molecules, and the energy associated with the black-body radiation from the walls of the enclosure and with the individual temperature spectrum of the gas—as a function of temperature, has been extended to gases of finite concentration. The latter energy term is considered to arise from radiations associated with the elastic collisions of the molecules with the walls of the enclosure or with one another, and it has the form $u' = \phi(v)T$, where v is the specific volume of the gas or vapour. $\phi(v)$ may be expressed as: const. T_S^z (z—6, 9, 12, 15), where T_S is the b. p. corresponding with the given value of v and z depends on the nature of the gas. For a saturated vapour, in which case there is a state of equilibrium between the kinetic and internal molecular energies, the discussion has been simplified by means of considerations based on the law of corresponding states and on Trouton's rule. The resulting vapour-pressure equation has the form $p + Ap_2 = CT^n$ (n=13 for normal vapours, and 16 for anomalous vapours), where A and C are constants. This equation is in good agreement with experiment (usually within 5%) for *iso*pentane and water vapours, and the deviations of the calculated from the experimental values are explained qualitatively in terms of the variation of the curvature of the molecular paths with the specific volume, and of the average angle of collision against the enclosure with the mean free path of the molecules. G. A. ELLIOTT.

Dependence of surface tension on the electric charge. E. BOGOSLOVSKI (Ann. Physik, 1927, [iv], 84, 323—326; cf. Ruff, Niese, and Thomas, this vol., 402).

Surface tension of sodium. F. E. POINDEXTER (Physical Rev., 1926, [ii], 27, 820).—The surface tension of sodium is 222 dynes/cm. at 100°, and 211 dynes/cm. at 250°, the temperature gradient being 0·072 dyne per 1°. The results indicate that the molecules of liquid sodium are polyatomic. A. A. ELDRIDGE.

Diffusion of non-electrolytes. E. N. GAPON and G. E. MUCHIN (Ukraine Chem. J., 1926, 2, 459—473).—A new empirical formula for the rate of diffusion in solution has been derived from a study of the various factors which affect diffusion. For various organic substances the formula yields results in fair agreement with experimental figures. Assuming that the rate of diffusion is a linear function of temperature, an equation for the temperature coefficient for normal and associated liquids is obtained. A. RATCLIFFE.

Diffusion. E. N. GAPON (Ukraine Chem. J., 1926, 2, 474—496; cf. preceding abstract).—The formula deduced for the rate of diffusion has been applied to solutions of indifferent substances. It is shown that the empirical equation can be applied to the determinations of mol. wt. The results obtained are in good agreement with values obtained by cryoscopic methods. A. RATCLIFFE.

Dielectric constants of binary mixtures. III. Electric moments of certain organic molecules in carbon tetrachloride solution. I. J. KRCHMA and J. W. WILLIAMS (J. Amer. Chem. Soc., 1927, 49, 2408—2416).—The dielectric constants and densities at 25° of solutions of eight organic compounds in carbon tetrachloride are recorded (cf. this vol., 819). In the case of benzene and toluene, the molecular polarisation of the solute is independent of the concentration. The electric moments of the solute molecules are calculated and compared with the results of previous workers. S. K. TWEEDY.

Dielectric constants of binary mixtures. IV. Benzene as solvent for certain solid substances. J. W. WILLIAMS and R. J. ALLGEIER (J. Amer. Chem. Soc., 1927, 49, 2416—2422).—The dielectric constants and densities at 25° of benzene solutions of benzoic acid, phenol, iodine, antimony iodide, stannic iodide, and silver perchlorate are recorded. The molecular polarisation of the solutes is proportional to the mol. fraction; this could not be confirmed for antimony iodide because of its low solubility. Stannic iodide has a zero electric moment in benzene solution. The values calculated for the other solutes are discussed in the light of recent solubility work. S. K. TWEEDY.

Properties of mixtures of hexane and nitrobenzene. V. TIMOFEEV and K. STACHORSKI (Ukraine Chem. J., 1926, 2, 395—407).—In large concentrations, the mol. wt. of hexane, as calculated from the observed depression of the f. p. of its solution in nitrobenzene, is twice its normal mol. wt. In general, this method of determining mol. wt. is not applicable when the determination is made with almost saturated solutions. When the mixture is almost saturated the fluidity curves show a change of curvature as the temperature approaches the saturation temperature. The addition of benzoic, butyric, or valeric acid increases the solubility of hexane in nitrobenzene, whereas *o*-nitrophenol and resorcinol decrease it. The addition of the last two substances does not greatly decrease the solubility unless a large proportion of hexane is present, when the saturation temperature rises rapidly. E. ROTHSTEIN.

Eutectic f.-p. depression in binary mixtures. II. E. KORDES (Z. anorg. Chem., 1927, 167, 97—112; cf. A., 1926, 798).—From the author's previous equations relationships have been deduced between the eutectic temperature and concentration of a binary system and the m. p. of the pure components. The relative eutectic depressions of the f. p. of the components are related to one another inversely as the ratio of the concentration of the components in the eutectic mixture. Eutectic melting is ascribed to the reciprocal breaking down of the crystal lattices as a result of diffusion in the solid state. H. F. GILLBE.

Relation between the turbulent internal friction and the constitution of binary liquid mixtures.

R. KREMANN, R. SPRINGER, and H. ROTH (Z. physikal. Chem., 1927, **130**, 415—421).—An apparatus is described by means of which the rate of hydraulic or turbulent streaming of liquids can be measured, and it has been used to obtain the internal friction curves of the following binary liquid mixtures: acetone–chloroform, aniline–phenol, aniline–nitrobenzene, and benzaldehyde–ethyl alcohol. A comparison with the true internal friction curves shows that in the case of turbulent friction the positive deviations are greater, the negative deviations smaller, and no minimum is found with the alcohol–benzaldehyde mixture (cf. Dunstan, A., 1904, ii, 805). The existence of compounds is readily shown by this method. L. L. BIRCUMSHAW.

Distillation and rectification of complex mixtures. L. GAY (Chim. et Ind., 1927, **18**, 381—393; cf. this vol., 928).—The study of the five possible methods for working a set of three fractionating columns for the separation of a mixture of four alcohols is continued and the minimum heat consumption necessary to effect the separation of a mixture of given composition by each method is calculated from the tetrahedral diagrams previously given. These minimum heat values presuppose a column of infinite height, but the results bear a definite relationship to those attainable in practice. The " domains " of the five methods in the composition tetrahedron are then mapped by calculating the points at which the frontier planes cut the edges (*i.e.*, binary mixtures). Certain of the lines made by the planes cutting the faces are exactly calculable, others are approximations. The positions of these boundary planes within the tetrahedron are further partly worked out. C. IRWIN.

New binary azeotropes. VII. M. LECAT (Ann. Soc. scient. Bruxelles, 1927, **47**, *B*, [i], 108—114; cf. this vol., 819).—A further list of binary azeotropic mixtures and non-azeotropic systems is given. R. CUTHILL.

Azeotropism in the binary systems alcohols–organic halides. M. LECAT (Ann. Soc. scient. Bruxelles, 1927, **47**, *B*, [ii], 39—62; cf. this vol., 405).—The published data for azeotropic mixtures in the above systems, supplemented with some new determinations, have been used to derive empirical formulæ connecting the difference in b. p. of the constituents, Δ, with the azeotropic lowering, δ, on the one hand, and with the alcohol concentration on the other. In every instance the azeotrope is more volatile than either of its constituents. For a given value of Δ, δ decreases with increase in the number of carbon atoms in the alcohol, but the curves connecting Δ and δ are the same for isomeric substances. R. CUTHILL.

Fluidity of metals and alloys in the liquid state. II and III. L. LOSANA (Notiz. chim.-ind., 1927, 2, 63—66, 121—125).—II. Values are recorded of the coefficient of fluidity of tin (250—950°), lead (350—900°), cadmium (360 750°), zinc (450—900°), lead–tin alloys (250—900°), tin–antimony (0—20%) alloys (250—600°), tin–copper (0—10%) alloys (300—600°), tin (86—96%)–copper (2—8%)–antimony (2—12%) alloys (300—600°), and tin (10—85%)–copper (4—5%)–antimony (5—20%)–lead (4—80%) alloys 300—500°).

III. An examination of zinc–tin, zinc–aluminium, aluminium–silicon, aluminium–iron, aluminium–copper, aluminium–magnesium, aluminium–copper–silicon, aluminium–silicon–magnesium, aluminium–copper–magnesium, aluminium–copper–zinc, copper–tin, copper–tin–lead, copper–tin–zinc, and copper–zinc alloys, special brasses, and aluminium. The copper–cupric oxide eutectic has m. p. 25° below that of pure copper. CHEMICAL ABSTRACTS.

Hardness, micro-structure, and electrical conductivity of platinum–silver alloys. N. S. KURNAKOV and Y. A. NEMILOV (Ann. inst. platine, 1926, No. 4, 306—316).—Brinell hardness (kg./mm.^{2}), tensile strength (kg./mm.^{2}), and conductivity values are given for platinum, silver, and 15 alloys. The tensile strength of platinum is 28·56, and of silver 18·04; the conductivity of platinum is $7{\cdot}291\times10^4$ at 25°, $6{\cdot}012\times10^4$ at 100°, and that of silver is $62{\cdot}973\times10^4$ at 25°, $48{\cdot}828\times10^4$ at 100°. Photomicrographs show the absence of compound formation. CHEMICAL ABSTRACTS.

Solubility of non-irradiated cholesterol in liquid ammonia. R. G. GUSTAVSON and J. B. GOODMAN (J. Amer. Chem. Soc., 1927, **49**, 2526—2528).—The solubility of cholesterol in liquid ammonia from −38° (0·00) to +49° (0·545 g. per 100 c.c.) has been determined (cf. Frank and Gustavson, J. Amer. Med. Assoc., 1925, **84**, 1715). F. G. WILLSON.

Fractional crystallisation of radioactive substances. II. Equilibrium in the system barium bromide–radium bromide–hydrogen bromide–water at 0° and 25°. V. CHLOPIN and B. NIKITIN (Z. anorg. Chem., 1927, **166**, 311—338; cf. A., 1925, ii, 438).—The distribution of radium bromide between solid barium bromide and a saturated solution of barium bromide containing varying amounts of hydrogen bromide at 0° and 25° has been investigated. Although with increasing concentration of acid the distribution coefficient ultimately increases in favour of the solid phase, yet in view of the variation in the composition of the aqueous phase, the distribution as a whole must be regarded as obeying the Nernst distribution law, and neither Schlundt's empirical formula (U.S. Bur. Mines, Tech. Paper, 1922, No. 265) nor the formula of Doerner and Hoskins (A., 1925, ii, 381) is applicable. The distribution constant does not vary greatly with the temperature. Measurements on the system barium bromide–hydrogen bromide–water at 0° and 25° show that the addition of hydrogen bromide to a saturated solution of barium bromide precipitates an approximately equivalent amount of the salt. R. CUTHILL.

Electrolyte adsorption on pure ash-free charcoal. I. M. KOLTHOFF (Rec. trav. chim., 1927, **46**, 549—573).—The ash-containing charcoals which have usually been employed by past workers on adsorption from solution are undesirable, as the ash exerts a disturbing effect. The charcoal used in this investigation was therefore prepared from pure commercial sugar, by precipitating an aqueous solution with alcohol, its ash content then being less than 0·001%. It was then carbonised by heating in a platinum basin, roughly powdered, heated for 20 hrs. (Meker burner) in a quartz crucible with tightly-fitting lid,

and sieved (sample *A*). Sample *B*, obtained by activating *A* in a porcelain tube with free access of air at 920—1000°, exhibited hydrolytic adsorption (the acid only being adsorbed from solutions of salts), whereas *A* did not, the difference between them being due to the volatile impurities which are only expelled at the higher temperature. The usual procedure of washing the charcoal first with hydrochloric acid and then with water until neutral was proved unsatisfactory, for on further heating and washing more acid was liberated. Activation of the charcoal is due to enlargement of the surface by oxidation, mere heating in a closed tube at 900—1000° being insufficient. Heating in a hydrogen stream for 24 hrs. has no effect, showing that activity is not due to the presence or removal of products formed by the reaction of the charcoal with the activating gas.

The adsorption of inorganic acids is purely molecular, equal quantities of both ions being adsorbed. The order of adsorption is $HCNS > HI > HNO_3 > HIO_3 > HCl = HBr = HClO_4 \gg H_2SO_4$; $H_3PO_4 = 0$, and between 0·1 and 0·005*N* the adsorption isotherm follows the Freundlich equation, the exponent $1/n$ usually being larger, the greater the adsorbability of the acid. The adsorption is greatly increased by the presence of the corresponding neutral salts, the Freundlich exponents being then all changed to about 0·20. This increase is due to the fact that in strong electrolytes there is equilibrium between the pseudo-form of the molecule (responsible for capillary activity) and the ionogen form, which equilibrium is displaced towards the former by the presence of the neutral salt. Capillary-active non-electrolytes, being in general more active than inorganic acids, tend to displace the latter from adsorption.

Of basic substances, alkali hydroxides are not adsorbed, whilst ammonia, primary aromatic and aliphatic amines, diphenylamine, piperidine, and pyridine are well adsorbed; the alkaloids, however, although strongly capillary active at the water–air interface, are not adsorbed by the charcoal. Inorganic neutral salts are only hydrolytically adsorbed, the acid alone being taken up; their order of adsorption is the same as that of the free acids, the nature of the cation being immaterial. The general rules of hydrolytic adsorption are (1) salts of capillary-active acids and capillary-inactive bases are only hydrolytically adsorbed (*e.g.*, inorganic salts of the alkalis); (2) salts of capillary-active acids and capillary-inactive bases are adsorbed both hydrolytically and molecularly if the acid exhibits well-marked polar and apolar portions (*e.g.*, salts of most organic acids); (3) salts of capillary-active acids and capillary-active bases are adsorbed molecularly and also hydrolytically, if the base possesses a strong polar group; (4) salts of capillary-active acids and capillary-active bases, both containing strong polar groups, are adsorbed mainly molecularly.

Hydrolytic adsorption (of potassium thiocyanate) at the air–water interface has also been demonstrated by drawing a current of air through an aqueous solution of the substance and collecting the bubbles; these showed greater, and the remaining liquid less, acidity than the original solution. S. J. Gregg.

Heat of adsorption of oxygen on charcoal. II. W. E. Garner and D. McKie (J.C.S., 1927, 2451—2457).—The heat of adsorption of oxygen on charcoal has been measured between 18° and 200° in a vacuum calorimeter. The heat varies with the amount of oxygen adsorbed and reaches a maximum value of 70 kg.-cal. for $1·5 \times 10^{-5}$ g.-mol. of oxygen per g. of charcoal. The maximum value has a large positive temperature coefficient. The bearing of the results on the constitution of the C_xO_z complex is discussed.

C. W. Gibby.

Sorption of ammonia by glass. (Time, pressure, and temperature relationships.) M. Francis and F. P. Burt (Proc. Roy. Soc., 1927, **A**, **116**, 586—602; cf. Bangham and Burt, A., 1925, ii, 284).—A continuation of previous work (*loc. cit.*). By heating glass wool at 200° for long periods of time in an atmosphere of ammonia, until further treatment produces no more change, the glass may be maintained indefinitely in such a condition that its behaviour towards ammonia can be closely reproduced. The shape of the sorption curve depends on the water content of the sorbent. For a state of maximum dryness it is S-shaped, but at higher temperatures the upper part only of the S curve is observable. The sorption process can be divided into two parts, represented by straight lines by plotting log (sorption rate) against log time. The slope of each line is independent of pressure and varies only slightly with temperature. Their points of intersection lie on a straight line and correspond with 50% sorption. The first half of the sorption process is probably of a different nature from the second, where the rate of change of log ds/dt with log t is more than doubled. The complete sorption process can be represented as a single-valued continuous function of temperature, pressure, and time, by a suitable choice of co-ordinates. As regards temperature variation, this is only approximately true. At 50% sorption, the rate of sorption is very nearly directly proportional to the pressure at constant temperature, and $d \log (ds/dt)/d \log p = 0·9$. At constant pressure, the rate of sorption is approximately doubled for every 20° rise in temperature. At constant temperature, log sorption, in the limit, is a linear function of log pressure between 0·5 and 1 atm. Below about 300 mm. there appear to be alternative values for the sorption. At constant pressure, sorption, in the limit, is a linear function of the reciprocal of the absolute temperature. An outstanding feature of the phenomenon investigated is the extraordinary slowness of the later stages of the process, making the experimental attainment of equilibrium quite impracticable. L. L. Bircumshaw.

Reduction of weights of powders in air to weights in a vacuum. II. R. Ruer and J. Kuschmann (Z. anorg. Chem., 1927, **166**, 257—274; cf. A., 1926, 1089).—The study of the removal of adsorbed air from various powders by heating in a vacuum has been continued. Cupric oxide prepared from the basic nitrate has a very small adsorptive power, which is a maximum when the temperature of ignition has been about 500°, but the adsorbed air is not completely removed by evacuation at the ordinary temperature. The oxide obtained by precipitating the

nitrate with potassium hydroxide adsorbs much larger amounts of air, and if the preparation is heated at 440° in a vacuum its adsorptive power at the ordinary temperature is further increased, apparently owing to the removal of adsorbed water. This latter phenomenon is also manifested by ceric oxide, the adsorptive power of which is considerable, but varies with the mode of preparation. Silicic acid ignited at 600° has the greatest adsorptive power of any of the oxides examined, but this is almost completely destroyed by ignition at 1220°. In confirmation of Scott's results (Proc. C.S., 1909, 25, 286), it is found that thoroughly dried potassium chloride adsorbs a very small amount of air, which is removed satisfactorily by evacuation at the ordinary temperature. Lead sulphate behaves like potassium chloride, but cerous sulphate has an appreciable adsorptive power when quite dry. Reduced copper and iron do not adsorb nitrogen and argon to any appreciable extent, and their apparently large adsorptive power in respect of air involves oxidation effects. R. CUTHILL.

State of moisture adsorbed on acid earth. H. ISOBE (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1927, **6**, 155—190).—Measurements of the vapour pressure of specimens of Japanese acid earth containing varying amounts of adsorbed moisture showed that from 2 to 20% the vapour pressure increased linearly with the amount of adsorbed moisture, and by applying the Clausius–Clapeyron equation the heat of vaporisation of the adsorbed moisture was found to be greater than that of pure water, but to approach it with rise of temperature. Microscopical observations showed that the earth contained cracks or cavities amounting to 55·7% of the total volume, and with 20% adsorption the water layer is several molecules thick. Density determinations over a range of temperature showed that part of the adsorbed water is denser than unadsorbed moisture, and by heating the earth to high temperatures it was found that 42% by weight of the moisture is combined with the earth, and is not evolved at temperatures below 200°.

F. S. HAWKINS.

Influence of water on the solidity of powdered substances after heating. B. GARRE (Z. anorg. Chem., 1927, **167**, 77—80).—Pellets of inert material containing various percentages of water and of benzene have been prepared and their mechanical strength after heating for 30 min. at 900° has been studied. Those prepared with benzene are easily crushed, the solidity being altered but little with change of the benzene content of the powder. Pellets prepared with water are much more stable, their solidity increasing with increase of water content up to about 30%.

H. F. GILLBE.

Adsorption and chemical nature of some organic compounds. N. SCHILOV and B. NEKRASSOV (Z. physikal. Chem., 1927, **130**, 65—72).—The adsorbent was Merck's "Carbo medicinalis," 0·05 g. being shaken for 20 min. with 15 c.c. of an aqueous solution of the substance in question, usually of 0·01—0·005*M* concentration. After filtering, the concentration of the dissolved substance was determined acidimetrically or iodometrically. It was found that (1) in homologous series, the increase in adsorption due to the introduction of a CH_2 group reaches a maximum at about the fifth or sixth member; (2) the substitution of most radicals for hydrogen increases the adsorption, whilst the hydroxyl and sulphonic groups lower it; (3) the optically active isomerides and the racemic form have about equal adsorption, whilst the inactive form has lower adsorption; (4) differences are shown in the adsorptions of the stereoisomeric benzene derivatives and of the α- and β-substituted aliphatic compounds; (5) the *trans*-form of compounds which contain a double linking is more strongly adsorbed than either the *cis*-form or the corresponding saturated compounds; (6) for an equal number of carbon atoms, an aliphatic compound is more strongly adsorbed than the corresponding aromatic compound.

S. J. GREGG.

Surface area and sorption. M. TARLÉ (Bull. Chem. Soc. Japan, 1927, **2**, 243—245).—Sameshima's conclusion (this vol., 304) that the sorption of carbon dioxide by charcoal is independent of the surface area and is hence to be regarded as a dissolution phenomenon is not supported by the actual experimental numbers recorded. Since charcoal is a very porous substance, powdering has a negligible effect on the surface area. Sameshima's figure for the density of his charcoal (2·1) is held to be too high. J. S. CARTER.

Surface area and sorption. J. SAMESHIMA (Bull. Chem. Soc. Japan, 1927, **2**, 246—249; cf. preceding abstract).—Pointing out that uncertainty regarding his density figure, which incidentally is in agreement with values recorded by Howard and Hulett (A., 1924, ii, 823), has but a negligible effect on the nature of the results, and producing evidence to show that powdering of charcoal produces an appreciable increase in surface area, the author defends the plausibility of his original conclusion.

J. S. CARTER.

Adsorption on dissolved molecules. N. S. MARINESCO (J. Chim. physique, 1927, **24**, 572—585).—A review of measurements of the dielectric constants, viscosities, and coefficients of diffusion for various coloured substances in solution. Theoretical considerations show that these data may be used to estimate the degree of adsorption of the solvent on the molecules of the solute. G. A. ELLIOTT.

Electrical condition of hot surfaces during the adsorption of gases. I. Gold and silver surfaces at temperatures up to 850°. G. I. FINCH and J. C. STIMSON (Proc. Roy. Soc., 1927, **A**, **116**, 379—400).—A gold or silver surface becomes charged when heated either in contact with a gas or in a high vacuum. The magnitude of the charge is independent of the gas pressure. Gold in the presence of oxygen or air and silver in the presence of oxygen, air, or hydrogen lose their charges slowly on evacuation but rapidly in the case of other gases. The lingering charges on gold or silver may be rapidly removed by burning off with the appropriate gas. It is suggested that the charge on a hot gold or silver surface in contact with a gas is due to activation of the gas, whereby its molecules become electrically charged; also, that the activation of a compound molecule such as water vapour or carbon dioxide involves its dissociation.

W. E. DOWNEY.

Gibbs on adsorption. W. D. BANCROFT (J. Physical Chem., 1927, **31**, 1501—1506).—From the work of Gibbs (Scientific Papers, 1906, **1**, 235), it follows that the criterion for the applicability of the Freundlich equation to the case of the adsorption of a gas by a liquid in which it is practically insoluble is that the change in surface tension is proportional to the change in adsorption. The exponent in this equation is a measure of the change in surface tension with adsorption. L. S. THEOBALD.

General theory of absorption and distribution phenomena. W. SEMENTSCHENKO (Z. physikal. Chem., 1927, **129**, 176—185).—Boltzmann's e theorem has been applied to the statistical consideration of the distribution of a substance between two phases and the boundary relations. An expression equivalent to Henry's law is derived and this shows that the solubility of a gas runs parallel with the generalised electric moment of its molecules, some measure of which may be afforded by the excess of its dielectric constant over unity. For solutions, an expression is obtained which leads to a relation similar to Gibbs' equation, from which it appears that if the moment of the solute molecules is less than that of the solvent molecules the concentration of the solute will be greater in the surface layer than in the main body of the solution, and *vice versa*. This explains the connexion between the dielectric constants of solvent and solute and the surface activity of the former, previously observed by Rehbinder (A., 1926, 674). For two solutions with the same solute but different solvents in contact with each other, the solute will be concentrated at the surface of separation, with resulting lowering of the surface tension, if the moment of the solute molecules is intermediate between those of the molecules of the solvents. Nernst's distribution law also follows, but the theory requires that the distribution ratio shall be a function of the concentration, and of the difference between the dielectric constants of the solvents. Where a substance is distributed among any number of other substances, the maximum concentration of the solute will occur in that solvent for which the value of the dipole moment is nearest to its own.

R. CUTHILL.

Diffusion in a gravitational field. R. FÜRTH (Z. Physik, 1927, **45**, 83—85; cf. A., 1926, 21).—A reply to a criticism by Weaver (Z. Physik, 1927, **43**, 296), in which it is conceded that the previous calculation of the sedimentation time for the metal hydrosol used by Burton (Proc. Roy. Soc., 1922, **A**, **100**, 414) gave a value which is much too large. Further calculation shows, however, that Burton's sol either comprised particles of varying sizes, or else these particles were not metallic. The author's previous statement that the time of sedimentation of finely-dispersed colloids is so great that no sedimentation can be observed in large vessels, is maintained.

G. A. ELLIOTT.

Boundary surface activity and dielectric constants. I. Dependence of boundary surface activity and adsorption at various surfaces of separation on the polarity and dielectric constants of the two phases forming the boundary surface, and of the adsorbed substance. P. REHBINDER (Z. physikal. Chem., 1927, **129**, 161—175).—It is suggested that the properties of a surface of separation of two phases are functions of the difference in polarity of the two species of molecules, which may be represented by the difference in the dielectric constants or by the free surface energy, although for single liquids there does not seem to be any simple relation between the dielectric constant and the surface tension. In accordance with this theory, it is found that the adsorption of a substance with surface activity at the surface of separation of two phases increases with increase in difference in polarity of the phases (cf. this vol., 930). The rule is formulated that if the added substance is adsorbed by both sides of the surface of separation it will tend to reduce the difference in the polarity and dielectric capacity of the phases. It is found experimentally that, in general, the greater the difference between the dielectric constant of the more polar phase and of the active substance dissolved in it, the greater is the surface activity of the latter.

R. CUTHILL.

Ring method for surface tension measurement. J. M. JOHLIN (Science, 1926, **64**, 93—94).—A criticism of the ring method; the accuracy attained is not so great as is assumed. In particular, no method can yield "absolute" values for the surface tension of colloidal solutions. A. A. ELDRIDGE.

Compressibilities of aqueous solutions of some fatty acids. S. VENKATESWARAN (J. Physical Chem., 1927, **31**, 1521—1525).—Data for the adiabatic compressibilities of aqueous solutions of formic, acetic, propionic, and butyric acids, and for water, at a pressure of 1—2 atm. are given. The isothermal compressibilities for water and for the first two acids have been calculated. The values of the adiabatic compressibility for water ($45{\cdot}66\times10^{-6}$ at 22°) and for acetic acid are in good agreement with those of Tyrer (J.C.S., 1914, **105**, 2534). The compressibility of formic acid is lower than that of the other acids, and in all cases investigated the adiabatic compressibilities increase at first slowly with the concentration, and more rapidly at higher concentrations. L. S. THEOBALD.

Molecular structure in solution. II. Refractive indices and surface tensions of aqueous solutions of cobalt chloride and hydrochloric acid. O. R. HOWELL (J.C.S., 1927, 2039—2051).—The surface tension and refractive index of solutions containing a fixed quantity of cobalt chloride and varying amounts of hydrochloric acid have been compared with the corresponding data for a series of hydrochloric acid solutions. The curves obtained by plotting the differences of the constants of corresponding solutions against the concentration of the hydrochloric acid show inflexions near the concentration where the colour change of red to blue occurs. The colour change is explained by a change in the groups co-ordinated with the cobalt atom, the red complex being $Co(H_2O)_6^{\cdot\cdot}$, and the blue $CoCl_4^{\prime\prime}$, the inflexions on the curves occurring when the two complexes are present in equal numbers. The surface-tension measurements show that there should be a greater concentration of blue complexes in the surface layer,

and, in support of this, it is found that the inflexion on the surface-tension curve occurs at a slightly smaller concentration of acid than the inflexion on the refractive index curve. The colour change is somewhat indefinite, and, as the blue form has the more intense colour, the maximum colour change occurs at a smaller acid concentration than the inflexions. F. S. HAWKINS.

Synthesis and properties of uranium colloids. S. J. DIACHKOVSKI (Ukraine Chem. J., 1926, 2, 340—352).—Stable colloidal suspensions have been prepared by hydration of insoluble uranium salts. Analyses of the progressive hydration products point to the formation of complex intermediate compounds during the process. Complete hydration is obtained after continuous dialysis in running water. Dehydration leads to coagulation of the sol resulting in the precipitation of a hydrate of uranic acid. When hydration is incomplete the precipitate formed on coagulation corresponds with $Na_2U_2O_7$. In either case on treatment with water a colloidal solution is again formed. The whole synthesis can be represented: $nNa_2U_2O_7$ — $[Na_2U_2O_7,H_2UO_4]_{n-1}$ — $[H_2O(UO_3)_2UO_2(OH)_2]_n$ — $[UO_2(OH)_2]_{n+1}$, the equilibrium being disturbed if sodium diuranate or uranic acid is removed from the sphere of reaction. The particles are negatively charged and their velocity in an electric field corresponds with a charge of $1{\cdot}984\times10^{-8}$ e.s.u. The density of the sol is 7·45 and the size of the particles varies from $1{\cdot}144\times10^{-15}$ to one amicron, showing that the system is polydisperse. The effects of hydrochloric acid, barium chloride, and aluminium chloride on the coagulation were studied. The sign of the charge changes after treatment with aluminium chloride. A. RATCLIFFE.

Formation of colloid systems by trituration. H. NEUGEBAUER (Kolloid-Z., 1927, 43, 65—67).—The production of colloid systems by grinding substances in a machine mortar, both alone and in the presence of 0·1%, 1·0%, and 10% of lactose, was studied. The amount of colloid formed increased with the concentration of the lactose. The substances used can be arranged in the following order, representing a decreasing tendency to dispersion by this means: indigo, selenium, sepia, graphite, antimony sulphide, silver, gold, copper. The curves which connect the quantity of colloid formed with the duration of grinding show that dispersion takes place rapidly during the first 2 or 3 hrs., after which further production of colloid is slow. E. S. HEDGES.

Preparation of colloidal solutions. S. ROGINSKI and A. SCHALNIKOV (Kolloid-Z., 1927, 43, 67—70).—For the preparation of colloidal solutions a method is developed which is based on the following principle. If a metal is distilled in a vacuum and the vapour is allowed to condense on a surface cooled by liquid air, the condensate is almost entirely amorphous, consisting of a highly disperse system of aggregated particles. By distilling simultaneously in this way a metal and a substance which is liquid at the ordinary temperature, a condensate is obtained which, when melted, produces a highly dispersed sol of the metal in the liquid employed. An apparatus is described for this work, in which the relative amounts of the substances in the condensate can be varied by suitable control of their distillation temperatures. The method has been employed successfully for the preparation of hydrosols of mercury, cadmium, selenium, sulphur, and phosphorus, and for organosols of mercury, cadmium, sodium, potassium, rubidium, and cæsium (using benzene, hexane, xylene, toluene, and in some cases ether and alcohol as dispersion media). The method is particularly suitable for the production of sols of the alkali metals, since no carbonisation of the organic medium occurs. The solid sols (condensates) have characteristic colours (sodium, reddish-violet; potassium and rubidium, bluish-green; cæsium, brownish-green), which disappear shortly after the sol is melted. The colour is considered to be due to atoms of the alkali metal, which later undergo aggregation. Examination showed the systems to be polydisperse. E. S. HEDGES.

General colloid chemistry. XXII. Aluminium oxide sols. W. PAULI and E. SCHMIDT (Z. physikal. Chem., 1927, 129, 199—222; cf. A., 1926, 901).—Alumina sols obtained by boiling solutions of aluminium chloride with amalgamated aluminium have been titrated conductometrically with solutions of various silver salts. It is found in this way that the chloride ion in the sol may be completely replaced by the anion of the added salt, the conductivity being depressed by an amount which, for univalent anions, varies from anion to anion, and affords some measure of the extent to which the substituent ion is deactivated. Activity measurements show that when hydrochloric or sulphuric acid is added to alumina sols such as the above it is taken up rapidly at first but the amount soon tends to a limit, which is much less than would be equivalent to the total amount of aluminium present. The conductivity changes in this process suggest that the colloid particles undergo partial disintegration, the surface layers probably being removed, leaving the nucleus unattacked. With increasing dilution, the hydrogen-ion activity falls considerably, but the dissociation of the colloid particles does not change very much.

R. CUTHILL.

Constitution of colloidal platinum. S. W. PENNYCUICK (J.C.S., 1927, 2600—2613).—The conductivities of platinum sols prepared by sparking under conductivity water have been measured. A variation in conductivity with time was observed, and specific conductivities as high as 66·1 gemmhos were obtained by boiling sols. It is suggested that some of the platinum is oxidised, and forms an ionic micelle $[Pt_x(PtO_4)_y]^n$, in equilibrium with an equivalent amount of hydrogen ion (cf. Pauli, Trans. Faraday Soc., 1921, 16, 14). Pure platinum sols contain free hydrogen ions, which form a layer on the surface of the sol particles. Equilibrium is disturbed by temperature changes, and the redistribution proceeds with measurable velocity. Consideration of titration curves with various bases shows that platinum sols behave as weak acids, but that the equilibria are not reached instantaneously. The bearing of the equilibrium between free and adsorbed ions on the coagulation of colloids is discussed.

C. W. GIBBY.

Amorphous carbon or graphite? O. RUFF, P. MAUTNER, and F. EBERT (Z. anorg. Chem., 1927, **167**, 185—189).—Although the adsorptive activity of graphite increases with increase of surface area there is no simple relationship between the state of division and activity. Further, specimens differing in activity give the same Debye–Scherrer diagrams. The existence of active corner atoms is postulated; the number of such atoms which are exposed, and therefore active, depends on the method of preparation of the specimen and on the degree of subdivision. H. F. GILLBE.

Optical properties of disperse mercuric sulphide. G. P. VORONKOV and G. I. POKROVSKI (Kolloid-Z., 1927, **43**, 78—81).—Substances which are coloured red or yellow in the massive form are observed to change in colour when finely divided, whilst blue substances remain unchanged by subdivision. A formula was derived theoretically for the intensity of light of definite wave-length scattered by the particles, and was tested experimentally with suspensions of red cinnabar. The experiments showed that the optical properties of mercuric sulphide change gradually from those of the massive substance to those of the colloidally dispersed material. The change becomes noticeable in particles of size about 1 μ. E. S. HEDGES.

Consistence of mixtures of true fluid and of a fluid with solid particles. A. MALLOCK (Nature, 1927, **120**, 619—620).

***X*-Rays and colloids.** G. L. CLARK (Fourth Colloid Symposium Monograph, 1926, 145—173).—*X*-Radiation, hydrogen peroxide, or ozone coagulates cerous hydroxide and albumin sols; the radiation may therefore cause formation of peroxide. Heterogeneous rays may inexplicably fail to produce the effects of homogeneous radiation. Colloidal platinum, when exposed to radiation, exhibits a variable increase in catalytic power in the oxidation of sulphur dioxide. Biological colloidal systems, polymerisation, crystalline and sub-crystalline states are discussed. Katz' view that raw rubbers exhibit crystals which disappear on mastication or heating was not confirmed; when *Hevea* rubber is stretched a crystal-like fibre diagram appears, but vulcanised rubber requires much greater extension before the effect appears. The results of *X*-ray examination of balata, gutta-percha, gelatin, collagen, and glue are described. The various kinds of cellulose show a crystal structure; there are profound changes after treatment with 1% sodium hydroxide solution. The maximum spacing is 5·7 Å. CHEMICAL ABSTRACTS.

Hydrodynamics of systems of variable viscosity. M. REINER and R. RIVLIN (Kolloid-Z., 1927, **43**, 72—78).—The indefiniteness of the term involving the virtual volume of the disperse phase in the Einstein–Hatschek viscosity formula is removed by the derivation of the following formula, connecting the virtual volume with the velocity of shear: $f-f_\infty=(f_0-$ where f_0 and f_∞ are respectively the relative virtual volumes of the disperse phase at rest and at extreme rate of shear, G is the velocity of shear, and c_1 is a constant for the sol. A formula is also derived for the resistance value w of the Couette apparatus: $w=(\eta_0-\eta_\infty)e^{c_1\Omega(R_E^2+R_A^2)/(R_E^2-R_A^2)}+$, where η_0 and η_∞ are respectively the viscosity coefficients of the sol in a state of rest and under extreme shearing, R_A and R_E the radius of the inner and outer cylinder respectively, and Ω the velocity of rotation of the outer cylinder. E. S. HEDGES.

Structural changes in amorphous materials. Silica gel. W. A. PATRICK, J. C. FRAZER, and R. I. RUSH (J. Physical Chem., 1927, **31**, 1511—1520).—The structural changes produced in silica gel by heating to various temperatures in the range 100—1150° have been studied by means of the adsorption of carbon tetrachloride. The density of the gel after these heat treatments has also been measured at 30°. Adsorption is unchanged until the pure gel has been heated above 900°, after which it decreases rapidly to a minimum at 1000°. With a gel containing 0·28% of sodium sulphate, the decrease in adsorption begins at about 600°, is more gradual, and reaches a minimum (in this case zero) at 1000°. The density changes correspond qualitatively with the changes in adsorption, increasing at 800° to a maximum value at 1100°. Heating the gel for 2 hrs. at 1000° apparently closes the capillaries of the gel, and on heating at 1100° for 3 days the gel changes definitely to the crystalline form, as the *X*-ray patterns show. This is not in agreement with the findings of van Bemmelen (A., 1899, ii, 84) or of Berl and Urban (B., 1923, 350). An explanation of this structural change is given. L. S. THEOBALD.

Refractometric measurements on colloidal solutions. BOUTARIC and (MLLE.) G. PERREAU (Compt. rend., 1927, **185**, 892—893).—The interference refractometer is used to study the effects on hydrosols of the intermicellular liquid and of the micelles. For the former, which was separated by ultrafiltration, n is similar to that of water. For the sol, n does not alter appreciably during the addition of sufficient electrolyte to produce coagulation, but falls sharply once this has occurred. Adsorption isotherms of the micelles were obtained from a comparison of the value of n for the clear liquid after coagulation with that for a solution containing the coagulating electrolyte in the same concentration. J. GRANT.

Influence of hydrophilic colloids on the conductivity of acids and bases. H. BRINTZINGER (Kolloid-Z., 1927, **43**, 93—106).—The conductivity of solutions of strongly dissociated acids is progressively reduced by increasing amounts of gelatin, gum arabic, salep mucilage, and dextrin. The order of influence of the colloids is that given above, dextrin exerting little effect. The colloids which have a slight effect on the conductivity of strong acids lower the conductivity of sodium hydroxide solutions in a striking manner. This is said to be due to the formation of chemical compounds. The conductivity of acetic acid solutions is raised by the addition of hydrophilic colloids, in consequence of the further dissociation of the acid due to the adsorption of hydrogen ions by the colloid. The hydrogen-ion concentration of all acids and the hydroxyl-ion concentration of bases are diminished by the presence of hydrophilic colloids, the order of influence here being:

gelatin, salep mucilage, gum arabic, dextrin. Dextrin has only a very slight effect on the reaction of acids. The alteration of the conductivity of acids and bases approximates to a linear function of the hydrogen-ion or hydroxyl-ion concentration. The equivalent conductivity of such a system can be represented by the formula $\Lambda=\{(\Lambda'-c)\cdot[H^{\cdot}]+[H^{\cdot}]'\cdot c\}/[H^{\cdot}]'$, where Λ' and $[H^{\cdot}]'$ are respectively the equivalent conductivity and hydrogen-ion concentration of the colloid-free acid, $[H^{\cdot}]$ is the hydrogen-ion concentration of the system, and c is a constant characteristic of the colloid. E. S. HEDGES.

Emulsification by solid powders. A. J. SCARLETT, W. L. MORGAN, and J. H. HILDEBRAND (J. Physical Chem., 1927, 31, 1566—1571).—Photomicrographs of emulsions stabilised by various solids in the form of powder are reproduced and support the explanation previously given by Finkle, Draper, and Hildebrand (A., 1924, ii, 97) that the type of emulsion depends on the angle of contact of the interface with the solid. It is further suggested that in forming the emulsion, droplets having the particles mainly on the outside of the interface would be better protected from coalescence than those having the particles more on the inside. The difficulties encountered in determining angles of contact between solids and liquid interfaces are discussed. L. S. THEOBALD.

Coagulation of smokes and the theory of Smoluchowski. G. NONHEBEL, J. COLVIN, H. S. PATTERSON, and R. WHYTLAW-GRAY (Proc. Roy. Soc., 1927, A, 116, 540—553; cf. Whytlaw-Gray and Speakman, B., 1923, 211).—The use of the Zsigmondy slit ultramicroscope for determining the number of particles in a smoke is criticised and shown to give inaccurate results. A new method, claimed to be free from any serious experimental error, is described, involving the use of a special wedge-shaped cell in which the depth of the observed volume of smoke is limited by the walls of the cell itself. The coagulation of clouds of varying concentrations of ammonium chloride has been investigated, using different types of heater, with a view to discover some method of quantitatively reproducing a cloud; also smokes of antipyrin and arsenious oxide (prepared by sublimation), and of cadmium oxide (prepared by striking an arc between cadmium electrodes). In all cases straight-line graphs of σ, the particulate volume, or the volume containing a single particle, against t, the age of the cloud, were obtained. The constants of the equation $\sigma=\sigma_0+Kt$, calculated by the method of least squares, are tabulated, and it is believed that the results are accurate to about 10%. The experimental data agree as closely as those obtained for sols with the theory of Smoluchowski. The reasons for the fact that K is not a constant, but varies from cloud to cloud, are discussed. L. L. BIRCUMSHAW.

Electrokinetic potential of silica gel. I. Influence of structure of the diaphragm. S. GLIXELLI and J. WIERTELAK (Kolloid-Z., 1927, 43, 85—92).—A method is described for the measurement of the velocity of electro-osmosis through powdered or gelatinous substances in an apparatus which is a modification of that used by Perrin, and experiments were carried out to demonstrate its applicability. A study was made of the electrokinetic potential of silica gel and of ignited silica in dilute nitric acid, and it was established that mechanical deformation of the gel did not affect the values obtained. Although quartz powder and ignited silica gave the usual value for the electrokinetic potential, an abnormally low result was obtained on using silica gel in $10^{-3}N$- and $10^{-4}N$-nitric acid. The low value depends on the silica concentration of the gel, and rises for lower concentrations of silica. This effect is related to the extreme fineness of the capillaries in the stronger gels, which may be less than the width of the electric double layer. E. S. HEDGES.

Molecular association in the liquid state. K. M. STACHORSKI (Ukraine Chem. J., 1926, 2, 408—413).—An expression for the determination of the association factor of liquids has been worked out based on Pavlov's "capillary-chemical law of equimolecular surfaces" (A., 1917, ii, 125). Association factors for various organic liquids have been calculated by means of this expression; the results are found to be in good agreement with those obtained from the equation of Ramsay and Shields. A. RATCLIFFE.

Chemical equilibrium in a mixture of paraffins. H. A. WILSON (Proc. Roy. Soc., 1927, A, 116, 501—515).—Theoretical. The theory of chemical equilibrium is applied to the hypothetical reaction $C_{n-1}H_{2n}+C_{n+1}H_{2n+4}=2C_nH_{2n+2}$, and it is shown that the equilibrium composition of the vapour and liquid phases can be approximately calculated at any given temperature and pressure. Tables are given of values of the equilibrium pressure at different temperatures and for different values of x (CH_x being the composition of the vapour), and of values of x' ($CH_{x'}$ being the composition of the liquid in equilibrium with the vapour) for different values of x and the temperature, and from these a chart is drawn showing the values of x and x' corresponding with any temperature and pressure. The chart may be used for approximate calculations on vapour at temperatures down to about 260°, provided the vapour was originally produced above 370° or 430° and kept hot long enough for equilibrium to be approximately established between the hydrocarbons present. The theory is compared with the results obtained in large-scale operations on paraffin oils, and gives results which agree approximately with those obtained at temperatures above 320°. L. L. BIRCUMSHAW.

Determination of the dissociation constants of dihydric mono- and di-nitrophenols electrometrically and colorimetrically. F. L. GILBERT, F. C. LAXTON, and E. B. R. PRIDEAUX (J.C.S., 1927, 2295—2308).—Owing to oxidation reactions and tautomeric changes on dilution, some of the dissociation constants show irregularities, but the values for 3 : 5-dinitropyrocatechol, 4 : 6-dinitroresorcinol, 3-nitropyrocatechol, 2-nitroresorcinol, and 4-nitroresorcinol remain fairly constant. When the phenolic form is predominant the dissociation constant may be corrected for the presence of the quinonoid ion by the equation $p_{K'_a}=p_H-\log(\alpha-x)+\log(1-\alpha)$, where x is the degree of transformation into the quinonoid form as shown by the colour change, if it is assumed

that the quinonoid form is completely ionised. Similarly when the *aci*-form is present in excess, the dissociation constant of this form can be corrected by the equation $p_{K'_o}=p_H+\log(x-\alpha)/\alpha$, if it is assumed that all the ion present is quinonoid. The relation between the dissociation constants and the position of the substituents is generally in accord with the alternate polarity theory. F. S. HAWKINS.

Ionisation of sodium acetate. M. MEYER (Chem. News, 1927, **135**, 280—281).—The degree of dissociation of sodium acetate in half-neutralised acetic acid is given approximately by the ratio [AcO']/[AcOH], since the free acid is very slightly dissociated. Measurements of the dissociation of the salt and of the p_H of the solution suffice, therefore, to determine the dissociation constant of acetic acid, or if this is known the degree of dissociation of the salt may be obtained. Data are given which show that values of p_H calculated from the Nernst equation are much too low for concentrations greater than $0{\cdot}1N$. G. A. ELLIOTT.

Formation and ionisation of compounds of casein with alkali. VI. Effect of temperature and concentration on the transport numbers of alkali caseinate solutions. D. M. GREENBERG (Univ. Calif. Pub. Physiol., 1927, **7**, 9—24).—The electrochemical equivalent of casein is, within certain limits, independent of the temperature. The influence of temperature on the mobility of the casein ion or micelle is linear between 5° and 50°; the Kohlrausch temperature coefficient of mobility at 18° is higher than that of any other ion. Solutions of alkali caseinates containing up to 8·65% of casein are to be regarded as completely ionised electrolytes. CHEMICAL ABSTRACTS.

Determination of ionic hydration. (Modification of Remy's method.) G. BABOROVSKY (Z. physikal. Chem., 1927, **129**, 129—160).—In order to investigate ionic hydration, transport experiments have been made, in which solutions of sodium, potassium, and lithium chlorides of concentrations from $0{\cdot}1N$ to N, N-solutions of the corresponding bromides, and $0{\cdot}1N$- and N-solutions of hydrogen chloride were electrolysed in an apparatus in which one electrode section was separated from the remainder of the apparatus by means of a diaphragm of parchment-paper. From the weight and composition of the contents of this section before and after electrolysis the amount of water transported may be calculated (cf. A., 1923, ii, 289). The values for the water transport and transport numbers obtained in this way are, however, affected by electro-osmosis at the membrane. Attempts to eliminate this effect have been unsuccessful, but experiments in which no membrane was used indicate that it may be neglected for N-solutions, so that in this case the electrolytic transport of water is given by the total transport. In this way, the following absolute hydration numbers, in molecules of water, have been derived: $H^{\cdot}$, 1; $K^{\cdot}$, 5; $Na^{\cdot}$, 8—9; $Li^{\cdot}$, 13—14; Cl', 4; Br', 3. The lack of agreement between these numbers and those calculated from activity data may be due to the present method yielding the dynamic, as distinct from the static, hydration. R. CUTHILL.

Activity coefficients of electrolytes. I. Bivalent salt and the ion attraction theory. U. B. BRAY (J. Amer. Chem. Soc., 1927, **49**, 2372—2380).—The activity coefficients of zinc sulphate were determined by measuring the *E.M.F.* at 25° of cells of the type Zn,Hg(two phase)|M-$ZnSO_4$soln.|$PbSO_4$(solid),Pb,Hg(two phase), where M varies from 0·0006 to 3·4. Lead–lead sulphate electrodes are reproducible only in the complete exclusion of oxygen; a definite crystalline form of lead sulphate is essential, which should attain equilibrium with the solution before the electrode is set up. The use of two-phase amalgams, also, is desirable. The preparation of such an electrode is described. The experimental activity coefficients agree with those calculated in accordance with Debye and Hückel's theory within 2% when $M<0{\cdot}005$; for greater values of M the discrepancy increases with great rapidity, indicating that the theoretical equation requires substantial correction before being applicable to ions of higher valency. S. K. TWEEDY.

Influence of a foreign substance on the osmotic pressure. F. A. H. SCHREINEMAKERS (Z. physikal. Chem., 1927, **130**, 120—124).—A mathematical paper in which it is shown that addition of a foreign substance to a solution may either raise or lower the osmotic pressure of the solution; in the latter case the osmotic pressure falls to a minimum and then rises on the addition of further quantities of the substance. If the foreign substance is added to both sides of a semi-permeable membrane with pure water on one side and a binary solution on the other, then the change $d\pi$ in the osmotic pressure depends on the concentration of the substance on both sides of the membrane. S. J. GREGG.

Variations in the b. p. of hydrochloric acid on adding a third substance. A. MAZZUCCHELLI and A. FATTA (Gazzetta, 1927, **57**, 584—592).—The method of Schleiermacher (A., 1891, 873) for the determination of b. p. is adapted to the use of 10 c.c. of liquid by fitting a bulb with a U-tube containing a mercury pellet and with another tube through which liquid can be removed to balance the increase due to expansion. In this way the b. p. of hydrochloric acid solutions of 14—22% concentration, containing in addition 5% of ammonium chloride, 4% of lithium chloride, 7% of zinc chloride, or about 10% of sulphuric acid, are determined. The curve obtained by plotting b. p. against the acid concentration is shifted by the addition of the third substance towards lower concentrations of acid, the maximum remaining at about 110°. With zinc chloride the b. p. falls off less slowly than that of the pure solution when the maximum has been reached; this is attributed to the formation of complexes with hydrochloric acid. Somewhat similar results are obtained with ammonium chloride. Sulphuric acid has an opposite effect, and combination with water is suggested as the cause. E. W. WIGNALL.

Vapour pressure of the binary system methyl alcohol–water. G. BREDIG and R. BAYER (Z. physikal. Chem., 1927, **130**, 1—14).—The method used was the dynamic method of Zawidski (A., 1901, ii, 6), the mixture being heated electrically in a special

flask, the pressure in which was varied until the temperature of the liquid was at the required point. The distillate was collected in a special vessel and analysed pyknometrically. For pressures above atmospheric, a special flask heated in an autoclave was employed. Over the range 40—240°, the total pressure P can be represented by the equation $\log P - J - k/T^n$, where J is a universal constant for all mixtures, and k and n are specific constants for each mixture. With rising temperature, the alcohol content in the vapour over a given mixture decreases, as expected from theoretical considerations.

For mixtures which contain 20—100 mols.-% of methyl alcohol, the isotherms are well represented by Lewis and Murphee's equation (A., 1924, ii, 145). For low alcohol content and low temperatures, the isotherms are straight and follow the equation $x(1-y)/(1-x)y - P_2/P_1'$, where P_2 is the vapour pressure of pure water and P_1' the intercept of the isotherm on the 100% alcohol ordinate. The equation $x(1-y)/(1-x)y = P_2 e^{-\lambda/RT.(1-2x)}/P_1$, where P_1 is the vapour pressure of pure methyl alcohol and λ the differential heat of mixing of the components (*i.e.*, the difference between the respective heats of mixing one component with excess of the other), holds over the same range. S. J. Gregg.

Ionic equilibria. II. Equilibrium between calcium fluoride and dilute hydrochloric acid. M. Aumeras (J. Chim. physique, 1927, 24, 548—571; cf. this vol., 312).—The solubility of calcium fluoride in hydrochloric acid has been studied in presence of excess of hydrofluoric acid or of calcium chloride between 15° and 65°, by a method involving the titration of the liquid containing a suspension of the fluoride with hydrochloric acid until the solution became clear. The saturated solutions were, in general, 0·01N with respect to calcium. The solubility of calcium fluoride in water was found by a chemical method to be 0·018 g. per litre at 25°, a result in close agreement with the conductivity measurements of Kohlrausch (A., 1905, ii, 152). On the assumption that the calcium chloride and hydrochloric acid are completely dissociated, the solubility of calcium fluoride has been calculated from mass law considerations and found to be in agreement with experiment. The results show that hydrofluoric acid dissociates in a simple manner in dilute solution, and that the dissociation constant is $16{\cdot}7\times10^{-5}$ at 25°. G. A. Elliott.

The ionic equilibrium $Al(OH)_3+6F' \rightleftharpoons AlF_6+3OH'$. A. Travers (Compt. rend., 1927, 185, 893—895).—This reaction is of importance in the detection of alumina in the presence of silver, and in the determination of fluorine or silica in the presence of alumina. The addition of increasing quantities of potassium fluoride to amorphous aluminium hydroxide, or to potassium aluminate, results in the production of hydroxyl ions. Determinations of the p_H value show, however, that they increase with an increase in the concentration of fluoride, to an extent which corresponds with the above equilibrium. Cryolite is stable over a wide range of p_H values, but potassium fluosilicate and fluotitanate are completely decomposed above p_H 6. J. Grant.

Salting out, and the ionic electric field. P. Debye (Z. physikal. Chem., 1927, 130, 56—64).—Mathematical. An attempt is made to predict quantitatively the salting-out effect from the dielectric properties of the substances in question. If the dielectric constant ϵ of a mixture follows the equation $\epsilon = \epsilon_1 c_1 + \epsilon_2 c_2$, where ϵ_1 and ϵ_2 are the respective dielectric constants of the constituents and c_1 and c_2 their concentrations, and if $\epsilon_1 - \epsilon_2$ is positive, then it is shown mathematically that the concentration of each constituent in the neighbourhood of the ions of an added electrolyte is reduced. The formula given is in fair agreement with the experimental results for the salting-out effect of potassium chloride on a water-ether solution. S. J. Gregg.

Equilibrium diagram of the copper-zinc system. D. Jitsuka (Z. Metallk., 1927, 19, 396—403).—A reinvestigation of the system zinc-copper by thermal and micrographic methods has confirmed the shape and position of the liquidus and peritectic lines found by Roberts-Austen and others, except in the case of the lines between 0 and 12% Cu and between 20 and 30% Cu. In the first case the horizontal occurs at 425° with 2—12% Cu and is a peritectic and not a eutectic line, since it is above the m. p. of zinc; in the second case the horizontal is at 695°. Considerable variations from earlier work in the solubility limits in the solid state have been noticed; thus the β phase undergoes a transformation between 475° and 450° and a second transformation below 450°, the maximum temperature of each change being found in the alloy with 53% Cu. The solid solution δ is unstable below 550°, being decomposed into the $\epsilon+\gamma$ eutectoid, and the $\epsilon+\delta$ and $\delta+\gamma$ fields extend from 590° to 560° only. The limit of solubility of ϵ in η is 1·5% Cu and of η in ϵ 14% Cu; the former line is vertical and the latter vertical to 390°, then bending towards the temperature axis. The lines bounding the $\epsilon+\gamma$ field from the ϵ and from the γ fields bend towards one another above 500°. The remaining boundary lines correspond fairly closely with those generally accepted. Zinc is appreciably volatile at 470°, so that the outer surfaces of ingots always contain a smaller proportion of zinc than does the interior. A. R. Powell.

Saturation limit of α-copper–tin solid solution. M. Hansen (Z. Metallk., 1927, 19, 407—409).—As the result of prolonged annealing tests followed by slow cooling and by quenching and tempering, the limit of solid solubility of tin in copper (α solution) is established at 14% Sn at the ordinary temperature, 16% Sn at 518°, and 13·4% Sn at 800°. The curve joining the first and second points is convex to the temperature axis, whilst that joining the second and third is a straight line. A. R. Powell.

Systematic doctrine of affinity. XLIII. System cuprous chloride-cupric chloride. W. Biltz and W. Fischer (Z. anorg. Chem., 1927, 166, 290—298; cf. this vol., 831).—Extension of Sandonnini's f.-p. measurements with the above system (A., 1912, ii, 918) to higher cupric chloride concentrations has given an extrapolated value of 630±10° for the m. p. of this salt, but has failed to yield any indication of compound formation. This result is

confirmed by the fact that cuprous chloride does not affect the dissociation tension of cupric chloride. Density measurements have been made with molten mixtures of the two chlorides, and also with the same mixtures after solidification. Anhydrous cupric chloride has d_4^{25} 3·387. The molecular volumes of both salts are equal to the sum of the zero volumes of the constituents. R. CUTHILL.

Vapour pressure of the ternary system methyl alcohol–methyl acetate–ethyl acetate. G. BREDIG and R. BAYER (Z. physikal. Chem., 1927, **130**, 15—28).—The apparatus is as previously used (this vol., 1140) and the vapour-pressure measurements were made first on the three binary systems methyl alcohol–methyl acetate, methyl alcohol–ethyl acetate, and methyl acetate–ethyl acetate. Both phases were analysed using the Haber–Lowe interferometer with the aid of standard reference mixtures. The first and second systems give vapour-pressure maxima lying for 40° at 33·7 and 67·4 mol.-% of methyl alcohol, respectively. The third system has an almost rectilinear isotherm, and all three follow the Herzfeld equation, the total pressure P being given by $P=P_1xe^{-\lambda(1-x)^2/RT}+P_2(1-x)e^{-\lambda x^2/RT}$, where P_1 and P_2 are the vapour pressures of the constituents, and x and $(1-x)$ their respective molecular fractions, λ being the differential heat of mixing.

In the analysis of the ternary mixtures, the free methyl alcohol was determined by esterifying the mixture at 100° with a mixture of pyridine and acetic anhydride, and titrating the excess of acetic acid with alkali. The combined weight of the two esters in the mixture was then found by difference, and their individual proportions by hydrolysing with alcoholic potassium hydroxide and titrating with sulphuric acid. The shape of the "vapour-pressure surface" was fixed by measurements on a mixture of methyl alcohol (18%) and methyl acetate (82%), the quantity of ethyl acetate being varied.

An examination of the results obtained shows that at 760 mm., and using a perfect column, the ternary mixture could be separated into pure methyl acetate and an azeotropic mixture of the other two; the latter can only be completely separated by altering the pressure or distilling in steam. S. J. GREGG.

Ternary systems. VI. Sodium carbonate, sodium hydrogen carbonate, water. A. E. HILL and L. R. BACON (J. Amer. Chem. Soc., 1927, **49**, 2487—2495).—The isotherms for the above system have been determined at 24·87°, 30°, and 50°. The double salt "Trona," $NaHCO_3,Na_2CO_3,2H_2O$, is stable at all three temperatures and separates out from solutions which contain only 0·16% of sodium hydrogen carbonate at 31·98°; this limiting percentage increases with rise of temperature. Quintuple points are indicated at −3·32°, 21·26°, 31·98°, and 35·17°. The binary eutectic temperatures for sodium carbonate and for sodium hydrogen carbonate with water are −2·05° and −2·33°, respectively, the solid phases in the latter case being sodium hydrogen carbonate and ice. S. K. TWEEDY.

System $Fe(NO_3)_3$–KNO_3–H_2O at 25°. G. MALQUORI (Atti R. Accad. Lincei, 1927, [vi], **5**, 1000—1003).—Neither compounds nor mixed crystals are formed at 25°. The solid phases in equilibrium with solution are KNO_3 and $Fe(NO_3)_3,9H_2O$.

R. W. LUNT.

Systems $MnSO_4$–K_2SO_4–H_2O and $MnSO_4$–$(NH_4)_2SO_4$–H_2O at 0°, and $CuSO_4$–Na_2SO_4–H_2O at 0°, 25°, and 37·5°. R. M. CAVEN and W. JOHNSTON (J.C.S., 1927, 2358—2365).—The double salt $MnSO_4,K_2SO_4,4H_2O$ separates at 0°, although this type of salt is usually hexahydrated. The isotherms at 0° and 25° are similar. The double salt $MnSO_4,(NH_4)_2SO_4,6H_2O$ separates at 0° and 25°, and the double salt curve is more extended than that for the corresponding potassium salt. This is due to the greater solubility of the ammonium sulphate, and to the larger amount of water of crystallisation in the double salt. Copper and sodium sulphates would appear to give no double salts at 0°, but the salt $CuSO_4,Na_2SO_4,2H_2O$ separates over a fairly wide range at 25°, and diminishes in solubility with rise of temperature. At 25° the addition of copper sulphate causes an increase in the solubility of sodium sulphate, but at 37·5° the reverse is true. F. S. HAWKINS.

Equilibria in systems in which phases are separated by a semi-permeable membrane. XXI. Influence of pressure on osmotic systems and on the osmotic pressure. F. A. H. SCHREINEMAKERS (Proc. K. Akad. Wetensch. Amsterdam, 1927, **30**, 521—531).—Theoretical. A continuation of previous work (this vol., 1031). M. S. BURR.

Equilibria in systems in which phases are separated by a semi-permeable membrane. XXII. F. A. H. SCHREINEMAKERS (Proc. K. Akad. Wetensch. Amsterdam, 1927, **30**, 610—618).—The influence of temperature on osmotic equilibria is discussed. J. S. CARTER.

Complete heterogeneous equilibrium. R. WEGSCHEIDER (Z. physikal. Chem., 1927, **130**, 44—48).—The term "complete heterogeneous equilibrium" proposed by Roozeboom (Rec. trav. chim., 1887, **5**, 266) is superfluous, since it is synonymous with "univariant system." It should not be used to designate those systems in which volume alterations can take place without disturbance of the equilibrium.

S. J. GREGG.

Experimental basis of the third law of thermodynamics. N. DE KOLOSOVSKI (Z. Physik, 1927, **44**, 756).—Attention is directed to a fundamental error in the author's recent contribution (this vol., 732) in which it was erroneously stated that if $\lim._{T=0} dp/dT=0$, then $\lim._{T=0} d\log p/dT=0$. Equations 3, 6, and 9 are then invalid, and the analysis is applicable to a degenerated gas only.

R. W. LUNT.

Properties at the absolute zero of temperature of the quantities associated with the reversible mixing of substances. R. D. KLEEMAN (J. Physical Chem., 1927, **31**, 1559—1565).—Mathematical. These properties are deduced from the results already established (this vol., 520, 936).

L. S. THEOBALD.

Standardisation of Richards' thermochemical data. W. SWIENTOSLAWSKI and J. BOBINSKA (J. Amer. Chem. Soc., 1927, **49**, 2476—2478).—The thermochemical data of Richards and his co-workers

are recalculated, taking the heat of combustion of 1 g. of benzoic acid (weighed in air) equal to 6324 g.-cal.$_{15}$, as standard. Data published subsequent to 1915, expressed in g.-cal.$_{18}$, are multiplied by 0·99942; data published previous to 1915, expressed in kilojoules, are multiplied by 238·27. A complete table is appended. S. K. Tweedy.

Correction of Swarts' thermochemical data. W. Swientoslawski and J. Bobińska (J. Chim. physique, 1927, 24, 545—547).—The adoption of more accurate values for the standard substances —benzoic acid and sucrose—indicates that Swarts' values for the heats of combustion of fluorine compounds should be multiplied by 0·9981.

G. A. Elliott.

Systematic doctrine of affinity. XLIV. Heats of formation [and volumes] of ammines, and pyridine compounds. W. Biltz, K. A. Klatte, and E. Rahlfs (Z. anorg. Chem., 1927, **166**, 339—350; cf. this vol., 1141).—The apparent heat of neutralisation of ammonia with excess of hydrochloric acid in aqueous solution increases with increase in the acid concentration and with decrease in the ammonia concentration; this is quantitatively accounted for by the fact that the observed heat effect includes the heat of dilution of the acid by the water in which the ammonia is dissolved. In the action of acids on metal ammines, however, the dilution effect is negligible, so that in deriving from the heat of this reaction the heat of formation of the ammine from ammonia and the metallic salt by means of the values for the heat of dissolution of the salt in the acid, and of ammonia in water, and the heat of neutralisation of ammonia, the value taken for the last quantity should be that for very dilute acid. The previous determinations of the heat of formation of the beryllium halides (A., 1925, ii, 1183), in which the apparent heat of neutralisation of the acid of the particular concentration employed was used, therefore require correction, and the new values then agree satisfactorily with the values derived from fresh determinations of the heat of dissolution of the ammines in more dilute acid. Similar corrections have been applied to the heats of formation of the ammines of mercuric chloride (A., 1925, ii, 1184) and of cupric chloride and bromide (*ibid.*, 1182). The volumes of the ammonia molecules in the beryllium halide ammines are approximately equal to the zero volume, but increase with increase in volume of the halogen. In the compounds of pyridine with calcium iodide, the volume of the pyridine molecule is minimal in the compound $CaI_2,2C_5H_5N$.

R. Cuthill.

Heats of dissolution of acetonitrile in some organic solvents. P. G. Popov (Ukraine Chem. J., 1926, 2, 387—390).—The heat of dissolution of acetonitrile in methyl alcohol, ethyl alcohol, ethyl acetate, acetic acid, and benzene is negative, but not in acetone. The heat charge is greater for ethyl alcohol than for methyl alcohol.

A. Ratcliffe.

Heats of dissolution and dilution of salts from extreme dilutions to saturation. III. Potassium fluoride and potassium fluoride dihydrate. E. Lange and A. Eichler (Z. physikal. Chem., 1927, **129**, 258—300; cf. this vol., 1029).—The integral heats of dissolution of anhydrous potassium fluoride at 25° have been obtained from measurements of the intermediate heats of dissolution at lower concentrations and of heats of dilution at higher concentrations up to saturation, and the intermediate heats of dissolution at high concentrations have been calculated from the results. From the data obtained, the values for the first, last, and entire heats of dissolution are found to be 4244, 185, and 2415 g.-cal./mol., respectively. The heat of hydration to form the dihydrate being found to be 5912 g.-cal./mol., the corresponding heats of dissolution for the hydrate are —1668, —4367, and —3497 g.-cal./mol., respectively. R. Cuthill.

Heats of dissolution and dilution of alkali salts in solutions of electrolytes with the same cation. J. Holluta and H. Werner (Z. physikal. Chem., 1927, **129**, 262—284).—The integral heats of dissolution of potassium chloride in water and in aqueous solutions of potassium nitrate, and of potassium nitrate in water and in aqueous solutions of potassium chloride, have been measured, and by subtraction from them of the corresponding heats of dilution, the entire heats of dissolution have been obtained. With both salts, the integral heats of dissolution are negative, and decrease numerically with increase in the concentration of the salt solution serving as solvent. The relative lowering of the entire heat of dissolution produced by 1 g.-mol. of the electrolyte with a common ion is an approximately linear function of its concentration in the solution employed as solvent. This variation is probably to be ascribed to ionic hydration, and this assumption leads, in fact, to hydration values which approximate to those obtained by the usual methods. R. Cuthill.

Stabilisation of chemical compounds by means of exothermic additive reactions. W. Biltz (Z. anorg. Chem., 1927, **166**, 275—283).—The stability of a chemical compound may be increased by adding to it a substance with which it combines with evolution of heat. In many instances, this involves the conversion of an endothermic into an exothermic compound by such processes as double salt formation, hydration, combination with ammonia, and polymerisation. Exothermic substances, however, may frequently be treated in a similar manner, *e.g.*, silver chloride loses its photochemical sensitivity when combined with ammonia to form the compound $AgCl,3NH_3$. R. Cuthill.

Conductivity of acids of medium strength in methyl alcohol, and their catalytic action. II. H. Goldschmidt, E. Marum, and L. Thomas (Z. physikal. Chem., 1927, **129**, 223—240; cf. A., 1925, ii, 976).—The conductivity of 2 : 4 : 6-trinitro-*m*-cresol and its salts and of certain picrates in methyl alcohol and mixtures of methyl alcohol and water has been measured, and the affinity constants and degree of dissociation have been calculated by application of Bjerrum's theory. In pure aqueous solution, the dissociation of the trinitrocresol is considerable, being much greater than in alcoholic solution. The influence of trinitrocresol and of trichloroacetic acid on the rate of esterification of acetic and phenylacetic

acids in methyl alcohol containing varying amounts of water or free from water has also been examined. In the esterification of a particular acid, the quotient of the velocity coefficient by the hydrogen-ion concentration of the catalyst is somewhat different for different catalysts, so that it appears probable that the rate of esterification is influenced by another factor in addition to the concentration of hydrogen ions and alcoholated hydrogen ions. For water concentrations up to 0·5*N*, the retarding effect of water can be represented satisfactorily by the formula previously proposed (*loc. cit.*). At higher concentrations, however, the velocity coefficient diminishes rather more rapidly than the formula indicates, but for acetic and phenylacetic acids the ratio of the observed to the calculated values is practically the same for all the catalysts. The effect of water on the affinity constant of trinitrocresol in methyl alcohol is much the same as it is with trichloroacetic and trichlorobutyric acid, so that it is primarily the hydrogen ion which is affected, in accordance with the equation (alcohol, H)$^{+}$+water=(water, H)$^{+}$+alcohol.

R. CUTHILL.

Conductivity of salt solutions containing agar. E. IWASE (Kolloid-Z., 1927, **43**, 70—72).—The salt solutions studied were copper sulphate, potassium sulphate, chloride, thiocyanate, and iodide, and sodium chloride. Measurements of the conductivity of these solutions were made at a series of dilutions, and were repeated after 0·5% of agar had been added. A further measurement of conductivity was made when the agar had set to a gel. In every case the conductivity of the salt solution+gel was greater than that of the salt solution+sol. It is concluded that in the process of gelation a decrease in specific volume of the particles of colloid occurs, causing desorption of some of the electrolyte, which thus produces the rise in conductivity. E. S. HEDGES.

Potential of a proposed standard form of copper and the activity of copper sulphate. R. F. NIELSEN and D. J. BROWN (J. Amer. Chem. Soc., 1927, **49**, 2423—2426).—Copper electrodes prepared by Lewis and Lacey's method (A., 1914, ii, 521) do not give reproducible potentials in copper sulphate solution. Two-phase copper amalgam is recommended as an alternative standard electrode material. From the *E.M.F.* at 25° of the cells Cu amalgam|$CuSO_4$,x*M*soln.|Hg_2SO_4|Hg, where x=0·05, 0·1, 0·2, 0·4, and 0·5, and combinations of these cells, the activity coefficients of copper sulphate over a limited concentration range were calculated, Lewis and Randall's value at 0·05*M* being assumed. The results are about 3% lower than those of Lewis and Randall. The standard potential of the amalgam is calculated to be −0·3502 volt, independent of the composition within fairly wide limits.

S. K. TWEEDY.

***E.M.F.* of the cell with transference and theory of interdiffusion of electrolytes.** P. B. TAYLOR (J. Physical Chem., 1927, **31**, 1478—1500).—Mathematical. A general expression for the *E.M.F.* of a cell with transference has been derived in terms of the corresponding cells without transference, and the integral obtained has been extended to include the effect of solvent transfer. The differential equation for the diffusion of electrolytes is derived rigorously, and is shown to depend only on molecular free energies and to be independent of ionic free energies. It is shown from this that the *E.M.F.* of the cell with transference is independent of these latter, which may be chosen for each solution so as to satisfy any single arbitrary function, not a function of molecular free energies, without thermodynamic error. A method of general application is given for finding the distribution of concentrations through a junction. Henderson's formula (A., 1908, ii, 655) for liquid junction *P.D.* is extended to provide for variable mobilities and activity coefficients, and the theory when applied to the tenth-normal HCl|KCl cell, gives better results. The bearing of these results on the determination of p_H is discussed.

L. S. THEOBALD.

Electronic theory of the voltaic cell. O. M. CORBINO (Phil. Mag., 1927, [vii], **4**, 436—446).—With the acceptance of the existence of the Volta effect between two metals a basis is provided for the explanation of the working of a voltaic cell. It is shown that this basis of explanation does not lead to any of the substantial contradictions inherent in the usual theories. A. E. MITCHELL.

Cells with identical, unchangeable electrodes. V. KARPEN (Compt. rend., 1927, **185**, 766—768).—Pairs of electrodes of various types of carbon, or of metals unattacked by alkalis, give an *E.M.F.* when one is completely immersed in a saturated solution of sodium hydroxide and the other only partly. The former electrode is negative, and the *E.M.F.*, which is of the order of 0·7 volt for platinum, decreases with diminution in the concentration of the solution, with agitation of the electrodes, or when the positive electrode is gradually submerged. It also depends on the nature of the electrode surface, but once established, is independent of the time or of the passage of a current. The rapid and almost complete polarisation obtained (99%) supports the evidence for the absence of any reaction in the cell, the *E.M.F.* of which is unexplained. J. GRANT.

***P.D.* in the double layer at the surface of a simple electrolyte and of pure water.** A. BUHL (Ann. Physik, 1927, [iv], **84**, 211—244).—The drop method for measuring the *P.D.* at a liquid surface has been refined and applied to the chlorides of potassium, sodium, and lithium and hydrochloric acid. For the alkali chlorides a maximum *P.D.* is observed at a concentration which is smaller as the mobility of the cation is greater. The diffusion potential is discussed in terms of Nernst's theory. The comparison of experimental data with calculated diffusion potentials leads, especially for hydrochloric acid, to a proof of complete dissociation in dilute solutions of strong electrolytes; it shows also that it is the ionic mobility only which changes with concentration. On the assumption that two separate effects enter into the observations it is calculated that the *P.D.* in the double layer of pure water is 5·5±0·5 millivolts. R. A. MORTON.

Thermodynamic evaluation of the contact potentials of two fused salts. R. LORENZ (Z.

physikal. Chem., 1927, 130, 39—43).—It has been found experimentally that the *E.M.F.* of a Daniell cell containing fused salts is equal to the difference between the *E.M.F.* of the two corresponding "salt formation cells," *i.e.*, cells in which *E.M.F.* is developed by the formation of a salt from its elements, *e.g.*, $Pb|PbCl_2|Cl_2$. Using this fact, it is readily shown that the contact potential – between two fused salts is given by $\pi=[n\mu(Cl')_2-n\mu(Cl')_1]/rF'$, where n is the valency of the metals, $\mu(Cl')_2$ and $\mu(Cl')_1$ the thermodynamic potentials of the chlorine ions in the respective fused salts, and r and F have their usual meanings. S. J. GREGG.

Theory of overpotential. J. HEYROVSKY (Rec. trav. chim., 1927, 46, 582—585).—At cathodes where a large overvoltage is present, molecular hydrogen is formed according to the equation $H'+H'=H_2$, at a rate v_{H_2} given by $v_{H_2}=k[H']c-K'i$, where c is the concentration of the hydrogen ions, i is the current, and k and K' are constants. Sand's objections to this theory (this vol., 735) are refuted, and his modification of it involving the formation of ions H_3''' and H_4''' is criticised as leading to a constancy of overpotential with changing acidity at the mercury dropping electrode, which is contrary to experiment. S. J. GREGG.

Overvoltage in alkaline solution. P. HERASYMENKO (Rec. trav. chim., 1927, 46, 586—587).—The author re-affirms his criticism of Sand and Weeks' investigation of the overvoltage at the antimony cathode in alkaline solution (A., 1924, ii, 152). The experiments of Sand, Grant, and Lloyd (this vol., 317) confirm the validity of the Nernst formula for the relationship between cathode potential and the sodium-ion concentration. S. J. GREGG.

Influence of perchlorate ion on the anodic overvoltage during the electrolysis of sulphuric acid. A. MAZZUCCHELLI and B. ROMANI (Gazzetta, 1927, 57, 574—583).—Experimental evidence is adduced for the view previously suggested (A., 1925, ii, 214) that the increased yield of persulphuric acid obtained by the electrolysis of sulphuric acid in presence of small quantities of perchloric acid is due to an increase in the anode overvoltage. Curves are given showing the variation of the anode potential with the time, before and after the addition of perchloric acid. After the perchloric acid is added there is a small increase of short duration in the anode potential. The addition of small quantities of chloride ion during the electrolysis of sulphuric acid, or of fluoride ion during the electrolysis of potassium hydrogen sulphate, has a similar result. The fluoride ion, however, has an abnormal effect on the electrolysis of pure sulphuric acid and causes a decrease in the anode potential in spite of the fact that the yield of persulphuric acid increases. O. J. WALKER.

Anodic behaviour and passivity of nickel. W. J. MÜLLER (Monatsh., 1927, 48, 559—570).—The development of passivity in nickel immersed in *N*-sulphuric acid is dependent on time, and the behaviour resembles that of iron and chromium in that a close connexion exists between the time effect and the current strength. The initial polarisation observed with nickel is a property of active bivalent nickel which passes into solution, and is due to anodic overvoltage. A voltage–current density diagram is shown which gives a fairly complete account of the behaviour of a nickel anode. The first stage is a superficial passivity bound up with the dissolution of bivalent nickel; later something approaching true passivity sets in at higher current densities and oxygen is liberated, but the passive state is not yet permanent and the nickel is alternately active and passive. At considerably higher current densities the alternation disappears and the nickel remains passive so long as the circuit is complete. The initial polarisation recorded by many observers corresponds with an anodic overvoltage and has nothing to do with passivity as such. R. A. MORTON.

Electrometallurgy of magnesium and its alloys. Pressure of the binary system lithium fluoride–magnesium fluoride. V. P. HYNISKI and P. F. ANTIPINE (Trav. inst. russe chim. appl., 1925, No. 84, 3—8).—Lithium fluoride has m. p. 837°; magnesium fluoride has m. p. 1225°. The eutectic, containing 53% of the latter, has m. p. 718°. Between 0 and 53% of magnesium fluoride there is no eutectic. At 90% of magnesium fluoride there is another eutectic point. All the mixtures contract on cooling. The fused eutectic readily dissolves 10% of magnesium oxide. Crystallisation in the system magnesium fluoride–lithium fluoride–magnesium oxide commences at 753°; hence the magnesium oxide may be electrolysed in the eutectic at 753°. CHEMICAL ABSTRACTS.

Electrolytic decomposition of glass. P. SELENYI (Ann. Physik, 1927, [iv], 84, 111—118).—If glass is electrolysed with an anode consisting of an ionised gas, sodium is set free at the cathode and oxygen at the anode. A feebly-conducting layer of silicic acid is formed on the anode side. W. E. DOWNEY.

Valve effect shown by a silicon anode, and its mechanism. R. AUDUBERT (Compt. rend., 1927, 185, 768—770).—It is shown theoretically and by experiments with cells of the type $Si|10\%\ H_2SO_4|Pb$ that the anodic valve effect (unilateral conductivity) is associated with an oxidation–reduction process. The silicon, which may be in the pure or alloyed state, is probably oxidised by anodic polarisation, and forms a non-conducting layer of silica which is subsequently reduced by cathodic hydrogen. The effect is an exponential function of temperature and occurs in acid or alkaline solutions. J. GRANT.

Theories of the velocity of chemical reactions. F. GIORDANI (Rend. Accad. Sci. fis. mat. Napoli, 1927, [iii], 32, 70—82).—A theoretical discussion of various formulæ and their application to some reactions. M. CARLTON.

Inflammability of hydrogen. V. Influence of tin tetramethyl and lead tetramethyl on the limits of inflammability of hydrogen–air mixtures. Y. TANAKA and Y. NAGAI (Proc. Imp. Acad. Tokyo, 1927, 3, 434—436).—Tin tetramethyl and lead tetramethyl lower the upper limit of hydrogen concentration necessary to cause inflammability. The presence of 0·125% of tin tetramethyl in the

mixtures lowers the upper limit from 71 to 54 mol.-% of hydrogen, whilst 0·5% of lead tetramethyl is necessary to produce the same effect.

W. E. Downey.

[Flame and combustion.] G. I. Finch (Nature, 1927, **120**, 694).—The combustion of the mixture $2CO+O_2$ in a steady high-tension direct-current discharge has been studied. In the cathode zone the rate of combustion is independent of the gas pressure or of the presence of moisture, but is proportional to the current. In the positive column region, however, the presence of moisture greatly accelerates the combustion. The results support Bone's view that moisture is not essential to the combustion of carbon monoxide, and that if it accelerates the process its effect is electrical, and not chemical.

A. A. Eldridge.

Gaseous combustion at high pressures. VIII. Explosion of methane with up to its own volume of oxygen at initial pressures up to 150 atm. D. T. A. Townend (Proc. Roy. Soc., 1927, **A**, **116**, 637—663; cf. Bone, Phil. Trans., 1915, **A**, **215**, 275).—A systematic study has been made of the pressure–time curves obtained by exploding (1) a number of methane–oxygen mixtures of compositions between $5CH_4+2O_2$ and CH_4+O_2, at initial pressures of 6—150 atm., and (2) mixtures corresponding with $CH_4+O_2+3{\cdot}76R$ (where R=N_2, A, or He), at initial pressures of 10, 50, 100, and 150 atm. The results obtained confirm previous observations (*loc. cit.*) and are in agreement with the "hydroxylation" theory of hydrocarbon combustion. It is found that, although at atmospheric pressure it is not possible to explode methane with less than two thirds of its own volume of oxygen, at high pressures mixtures containing much lower proportions of oxygen can readily be exploded. With mixtures containing more than 60% of methane, the effect of increasing the initial pressure is not only to decrease the violence of the explosion, but also to diminish, and in some cases to suppress altogether, carbon deposition. The results are attributed to the influence of pressure in suppressing the thermal decomposition of methane. Contrary to its behaviour in carbon monoxide–air explosions at high initial pressures (cf. A., 1924, ii, 398; 1925, ii, 800), nitrogen is not activated in explosions of $CH_4+O_2+3{\cdot}76N_2$ mixtures, but appears to behave normally as a diluent only. Reasons for this are discussed. The general influence of helium, as compared with argon, as a diluent in the explosion of $CH_4+O_2+3{\cdot}76R$ mixtures, is to hasten the rate of pressure development and to increase the subsequent rate of cooling, effects attributable to the greater mobility of the helium molecule. The corrected P_m/P_i ratios are in most cases, however, about 6 or 9% higher with the argon-diluted mixtures than with the corresponding helium-diluted mixtures.

L. L. Bircumshaw.

Explosions in gaseous mixtures of acetylene, of hydrogen, and of pentane. A. Egerton and S. F. Gates (Proc. Roy. Soc., 1927, **A**, **116**, 516—529; cf. this vol., 318).—An arrangement is described by means of which the velocities of detonation waves can be measured to an accuracy of at least 0·5%, and the velocities and positions of detonation for various mixtures of acetylene, of hydrogen, and of pentane with oxygen, nitrogen, or argon are recorded for initial pressures up to 6 atm. The results are in fair agreement with those obtained previously (*loc. cit.*), and the fact that detonation occurs earlier as the pressure increases up to a certain limiting value is confirmed. Experiments in which the steel explosion tube (diameter 1·5 cm.) was virtually shortened by the insertion of steel rods showed that the length of the tube does not appreciably affect the position of detonation, except in the case of the weak mixture ($1C_2H_2:2{\cdot}5O_2:6N_2$), where shortening the tube caused later detonation. The photographic record of flame travel in a short bomb of large diameter (10·7 cm.) gave some evidence of autoignition during the progress of combustion of a vibratory nature in certain acetylene mixtures. The addition of the "anti-knock" compound, lead tetraethyl, has a definitely delaying effect on the rate of travel of flame in the case of slow-burning pentane mixtures, but with acetylene mixtures the only effect is an accelerating one. The results obtained in general support the inference that "knock" is associated with a vibratory type of combustion, not necessarily involving autoignition, and is not due to the establishment of a detonation wave (cf. Morgan, this vol., 630).

L. L. Bircumshaw.

Gaseous combustion in electric discharges. II. Ignition of electrolytic gas by direct current discharges. G. I. Finch and L. G. Cowen (Proc. Roy. Soc., 1927, **A**, **116**, 529—539; cf. A., 1926, 690).—An investigation of the conditions of ignition of electrolytic gas by direct-current discharges has been carried out, precautions being taken to eliminate as far as possible any conditions favourable to ignition, particularly heat and catalytic combustion at the electrodes, other than those due to ionisation of the gas. Four series of measurements were made with water-cooled platinum electrodes, three over concentrated sulphuric acid with gap-widths of 3·8, 7·5, and 15 mm. respectively, and one with a gap-width of 15 mm., but without sulphuric acid, gas-pressure and igniting current readings being taken simultaneously at the moment of explosion. Ignition occurs without lag immediately on attainment of the igniting current, and it was found that the igniting current varies with the pressure over a considerable range in a hyperbolic manner. The reasons for the observed deviations of the pressure–igniting current curves from rectangular hyperbolæ at the two extremes of the curve are discussed, and it is concluded that the value of the igniting current is raised by either an excess or a deficiency of water vapour in the gas in the ignition zone. The fact that a reduction in the gap-width results in an increase in the igniting current is ascribed to the widening of, and thus the lowering of the ionic concentration in, the two bright positive glows, in the brighter of which ignition probably originates, In an attempt to obtain direct experimental evidence for this, it was found that the velocity of flame propagation was at least ten times as great along the path of the discharge as elsewhere in the explosion vessel. The view is held that, under the given experimental conditions, ignition is determined solely by the attainment in some portion of the gas traversed by the

discharge of a certain definite concentration of suitable ions or electrically charged particles, in the building up of which water vapour materially assists, and that flame propagation is also essentially an electrical phenomenon. L. L. BIRCUMSHAW.

Combustion of mixtures of hydrogen with air or oxygen in a eudiometer. T. TERADA, K. YUMOTO, and U. NAKAYA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1927, 6, 81—128).—In mixtures containing a small percentage of hydrogen, when there is a small volume of gas in the eudiometer tube combustion is complete, but with an increasing volume of gas the proportion burnt becomes less and less until a critical volume is reached, when combustion is again complete. If the original volume of gas be increased still more, combustion may be complete or almost complete until a second critical volume, almost double the first, is reached. After this volume is passed, combustion is only partial, the proportion of gas burnt being the same as before the first critical volume. If the oscillation of water in the bend of the eudiometer tube be stopped, combustion is complete until a certain volume, dependent as before on the size of the tube and the position of the electrodes, is reached, when the gas is only partly burnt. This suggests that the effects at the critical volumes are caused by cooling due to adiabatic expansion of the gas caused by movement of the water column, but photographic studies show that the effect is complicated by the cooling and contraction caused by condensation of moisture in the burnt gas. Experiments with mixtures containing a high percentage of hydrogen showed no evidence of the two critical volumes, but with large volumes of gas the flame was extinguished before combustion was complete. By igniting mixtures in a spherical bulb, it was shown that the volume of gas burnt at each spark was greatly dependent on the construction of the electrodes, and by means of a mathematical analysis, it was shown that the mass velocity of combustion could be assumed to be constant. F. S. HAWKINS.

Ignition of carbon monoxide and oxygen. A. K. BREWER (Proc. Nat. Acad. Sci., 1927, **13**, 689—694).—In a moist explosive mixture of carbon monoxide and oxygen, the ignition at any one pressure is determined by the energy of the spark and not by the voltage, whilst the ignition points at various pressures are related not as the energy ($\frac{1}{2}CV^2$) but as the voltage (V). Using a constant pressure of 14 cm. of explosive gas dried by means of sulphuric acid, and adding known amounts of water vapour, the ignition voltage varied from 262 with a partial pressure of 0·4 mm. of water vapour to 46 at a partial pressure of 20 mm. Addition of argon, nitrogen, carbon dioxide, chloroform, alcohol, *iso*propyl nitrite, and ether showed that these impurities are inert in the explosion except in that they absorb energy, thus increasing the ignition voltage. Other impurities act similarly to water, *i.e.*, they greatly reduce the ignition voltage and cause the oxidation to go to completion. Sufficient oxygen must be added to burn the impurity. It would appear from the partial pressure–voltage curves that the catalytic properties of hydrogen, alcohol, and ether are derived from their ability to furnish water on oxidation, and furthermore, the freshly-formed water must be more potent than ordinary water. It is shown that the two explosive gases in an explosive mixture may ignite more readily than will either gas separately under similar conditions. R. A. MORTON.

Ignition of gases by hot wires. W. C. F. SHEPHERD and R. V. WHEELER.—See B., 1927, 803.

Active nitrogen. R. RUDY (Physical Rev., 1926, [ii], 27, 110).—Argon has little influence on the rate of decay of the afterglow. The decay follows a bimolecular law for the first 100 sec.; the temperature coefficient of the reaction, between 20° and 130°, is much smaller than that of ordinary chemical reactions. Band spectra excited by active nitrogen show vibrational energy as if at high temperature, whereas the rotational energy indicates low temperature. A. A. ELDRIDGE.

Behaviour of oxygen in the reaction between carbon monoxide and chlorine. H. J. SCHUMACHER (Z. physikal. Chem., 1927, **129**, 241—261).—The rate of formation of carbonyl chloride at 160° in the dark from carbon monoxide and chlorine is not affected by the presence of free oxygen, the reaction velocity being given by the equation $d[COCl_2]/dt=k[Cl_2]^{3/2}[CO]$. In light, at the ordinary temperature, however, carbon dioxide is formed to the almost complete exclusion of the formation of carbonyl chloride until the oxygen pressure becomes very small, so that in these circumstances the main reaction is the photosensitised formation of carbon dioxide. The rate of this reaction is represented by the equation $d[CO_2]/dt=k'[Cl_2]^{0\cdot71}[CO]^{1/2}$, the velocity coefficient, k', being independent of the carbon dioxide concentration, but tending to fall somewhat with the oxygen concentration for concentrations below 100 mm., and having a temperature coefficient of 0·95 per 10°. With light of wave-length greater than 405 $\mu\mu$, there are formed about 1000 molecules of carbon dioxide per quantum in a mixture of carbon monoxide, oxygen, and chlorine in which the concentration of each is 0·5 atm., and 3000 molecules of carbonyl chloride in a mixture of carbon monoxide and chlorine, each under 0·5 atm. pressure.
R. CUTHILL.

Chemical kinetics of the reaction between tetrathionate and cyanide. F. ISHIKAWA (Z. physikal. Chem., 1927, **130**, 73—81).—Kurtenacker and Fritsch (A., 1921, ii, 502) give the equations $S_4O_6'' + CN' + H_2O = CNS' + SO_4'' + S_2O_3'' + 2H$ (1); $2H^{\cdot} + 2CN' = 2HCN$ (neutral solution) (2a); $2H^{\cdot} + 2OH' = 2H_2O$ (alkaline solution) (2b). In neutral solution, since reaction (2a) is instantaneous, the velocity of the whole reaction depends on (1), so that $dx/dt=k_2(a-3x)(b-x)$, where a is the initial concentration of potassium cyanide, b the initial concentration of the tetrathionate, and x the number of reacted molecules of tetrathionate per litre during the time t. Hence $k_2=(1/t)[1/(a-3b)]\log_e[b(a-3x)/a(b-x)]$. This has been confirmed by measurements at 0°, the reacting liquids being placed in the respective limbs of a Y-tube and mixed at a given moment; after a definite interval, 20 c.c. were withdrawn and treated with dilute sulphuric acid and the

whole was titrated with 0·1*N*-iodine solution to determine the thiosulphate. The value of k_2 varies linearly with the initial concentration of either reactant, for a constant concentration (*i.e.*, large excess) of the other.

For alkaline solution, from (1) and (2*b*), $k_2 = (1/t)[1/(a-b)] \log_e [b(a-x)/a(b-x)]$. From the experiments, k_2 is found to increase somewhat with increasing concentration of sodium hydroxide; with ammonia, k_2 diminishes with increasing time, probably because ammonia is too weakly basic to neutralise the whole of the hydrogen ions, which therefore react with the cyanide so that excess of the latter is removed. S. J. GREGG.

Conditions controlling oxidation of organic molecules. I. C. FROMAGEOT (J. Chim. phys., 1927, 24, 513—544).—The progress of oxidation of acetic and propionic acids and the corresponding α-amino-acids, of acetaldehyde and propaldehyde and the corresponding alcohols, and of pyruvic acid, by ceric, thallic, and ferric salts and by chloric and permanganic acids has been followed potentiometrically. Pyruvic acid is alone oxidised by the metallic salts, whilst the remaining acids and amino-acids are not sensibly oxidised by any of the agents used. In general there is no relation between the oxidising potentials of the reagents and the occurrence of oxidation, nevertheless for oxidisers of similar type the speed of oxidation increases with the oxidising potential. For chloric and permanganic acids, the order of increasing ease of oxidation is: acid, alcohol, aldehyde. Pyruvic acid, however, is oxidised at approximately the same rate as the alcohols by chloric acid, and almost instantaneously by permanganic acid. G. A. ELLIOTT.

Kinetics of the hydrolysis of vinyl acetate. A. SKRABAL and A. LAHORKA (Monatsh., 1927, 48, 459—473).—The velocity of hydrolysis of freshly-prepared, unimolecular vinyl acetate by acids and alkalis in aqueous solution and by water has been studied at 25°. The velocity coefficient for hydrolysis with hydrochloric acid with the minute as the unit of time is 0·00813, whilst for hydrolysis with sodium borate the value is 620. A much lower value is obtained with sodium carbonate as hydrolysing agent, but this is due to the greater degree of polymerisation in the presence of the stronger alkali, the polymerised ester being hydrolysed much more slowly. The value of the coefficient for hydrolysis by water alone varies from 6·8 to $9·7 \times 10^{-6}$ according to the concentration of sodium acetate present. In all three cases hydrolysis is much more rapid than in the case of the related saturated ester, ethyl acetate. The remainder of the paper is mathematical and it is shown that by integration of the differential equation of the secondary effect of hydrolysis in a buffer solution the values of all three hydrolysis coefficients may be determined. J. W. BAKER.

Velocity of hydrolysis of stearolactone with alcoholic alkali. A. KAILAN and A. BLUMENSTOCK (Monatsh., 1927, 48, 529—536).—The velocity of hydrolysis of stearolactone in concentration of 0·025 mol./litre with sodium hydroxide and ethoxide in aqueous and absolute alcohol at 25° has been measured. Only in alcohol containing relatively large concentrations of water does the bimolecular coefficient approach constancy, and in alcohol containing only 0·036 mol. of water/litre it diminishes rapidly, due to the diminishing concentration of water as the reaction proceeds. In the latter case the termolecular coefficient, based on consideration of the participation of water in the reaction, approaches constancy. As the water content of the alcohol is increased from 0·025 to 1·6 mol./litre this termolecular coefficient decreases to one third of its original value. This may be due either to the alteration in the composition of the medium or to the variation in the relative proportions of sodium hydroxide and ethoxide present as hydrolysing agents. As the water content of the alcohol is increased from 1·6 to 4·8 mol./litre the value of the termolecular coefficient remains approximately constant. J. W. BAKER.

Velocity of hydrolysis of acetonals. A. SKRABAL and F. BILGER (Z. physikal. Chem., 1927, 130, 29—32).—The reaction, which is catalysed by hydrogen ions, was arrested at the required moment by addition of excess of sodium hydroxide; iodine solution was then added in, excess in order to determine the acetonal remaining undecomposed. The excess of iodine was determined by neutralising and titrating with thiosulphate, sodium acetate being added to reduce the hydrogen-ion concentration and thus prevent the reaction of the iodine with the acetone produced by the original hydrolysis. The following velocity coefficients were obtained for unit hydrogen-ion concentration (25°): dimethylacetonal $3·7 \times 10^4$, diethylacetonal $1·35 \times 10^5$. S. J. GREGG.

Dynamic isomerism of the reducing sugars. T. M. LOWRY (Z. physikal. Chem., 1927, 130, 125—145).—The unimolecular form of the mutarotation curves for dextrose has been established for dextrose in water, in pure methyl alcohol, and in aqueous methyl alcohol, and also for tetramethylglucose in aqueous pyridine. This unimolecular form is quite compatible with the occurrence of a chemical change subsequently to mutarotation, provided this is not accompanied by any marked change of rotatory power. The existence of such a change is proved by a comparison of the mutarotation curves, which depend only on the rotatory powers of the isomerides, with the solubility curves, which depend on the concentrations of the products in solution; with aqueous methyl alcohol as solvent, the half-change period calculated from the mutarotation is almost twice as long as that calculated from solubility measurements, showing that concentration changes last much longer than changes of rotatory power. These views are further confirmed by the observations of Riiber and Minsaas (A., 1926, 1228). S. J. GREGG.

Velocity of esterification of nitrobenzoic acids in glycerol. A. KAILAN and L. LIPKIN (Monatsh., 1927, 48, 501—519).—The velocity of esterification of *o*-, *m*-, and *p*-nitrobenzoic acids in anhydrous and moist glycerol with hydrogen chloride as a catalyst at 25° has been measured. In all cases esterification is almost complete, but the velocity of esterification of the *ortho*-acid is so slow that chlorohydrin formation must be taken into account, the value of the

latter coefficient being 5×10^{-5} in anhydrous glycerol. In all cases the unimolecular coefficient is proportional to the concentration of the hydrogen chloride (c). The relationship of the velocity coefficient to the concentration of the water (ω) in each case is expressed by intrapolation formulæ. The velocities in glycerol are compared with those of the same acids in alcohol (Kailan, A., 1907, ii, 242). The effect of water is less in glycerol than in alcohol. When $\omega=0{\cdot}03$ and 0·065 mol./litre the esterification coefficients in alcohol are respectively 41—66% and 24—42% greater than in glycerol. When $\omega=0{\cdot}733$ mol./litre and $c=0{\cdot}66$ mol./litre the velocities in the two media are approximately equal; when $c=0{\cdot}33$ and 0·166 the coefficients in alcohol are, respectively, only 65—68% and 46—48% of the values in glycerol, whilst when $\omega=1{\cdot}346$ and $c=0{\cdot}66$, 0·33, and 0·166, the coefficients in alcohol are respectively only 63—75%, 36—44%, and 25—31% of the values in glycerol. The differences in the velocity of esterification of benzoic acids and the three nitrobenzoic acids are smaller in glycerol than in alcohol. Thus for $\omega=0{\cdot}065$ and $c=0{\cdot}166$ the ratios of the velocity coefficients of benzoic acid and *o*-, *m*-, and *p*-nitrobenzoic acids in glycerol are 1 : 0·068 : 0·63 : 0·80, whilst in alcohol the ratios are 1 : 0·054 : 0·57 : 0·70, the values for *o*-, *m*-, and *p*-nitrobenzoic acids themselves in the two media being, respectively, 1 : 9·27 : 11·7 and 1 : 10·7 : 13·0.

J. W. Baker.

Chemical kinetics in mixed solvents. Velocity of formation of quaternary ammonium salts in mixtures of nitrobenzene and benzene. G. E. Muchin and H. M. Moiseev (Ukraine Chem. J., 1926, 2, 430—436).—Velocity coefficients for the interaction of pyridine and allyl bromide in various mixtures of benzene and nitrobenzene were determined at 25°, 45°, and 55°. The observed coefficients were lower in every case than those calculated from the additive rule, and this difference diminished with rise of temperature when the mixture contained a large proportion of nitrobenzene. The curve showing the change of velocity coefficient as a function of the percentage composition of the solvent was continuous; no definite compounds were formed.

A. Ratcliffe.

Chemical kinetics in mixed solvents. Velocity of formation of quaternary ammonium salts in mixtures of nitrobenzene and heptane. G. E. Muchin, L. E. Karlson, and L. M. Stein (Ukraine Chem. J., 1926, 2, 437—442).—Velocity coefficients for the interaction of allyl bromide with pyridine in a mixture of heptane and nitrobenzene were determined; the results were analogous to those obtained when benzene was used instead of heptane (cf. preceding abstract).

A. Ratcliffe.

Chemical kinetics in mixed solvents. Influence of various substances on the velocity of formation of quaternary ammonium salts. R. B. Ginsburg and G. E. Muchin (Ukraine Chem. J., 1926, 2, 443—458).—The effect of compounds containing electro-negative groups, *e.g.*, phenol and nitronaphthalene, and indifferent solids, *e.g.*, paraffin and naphthalene, on the velocity of reaction of (1) triethylamine and allyl bromide and (2) pyridine and allyl bromide in solution in benzene was studied. The addition of the solids gave results from which no conclusions could be reached. The presence of the electro-negative groups caused an increase in the velocity of reaction. Fairly conclusive evidence has been obtained showing that this influence is due to the formation of an unstable intermediate compound between the base and the substance containing the electro-negative group.

A. Ratcliffe.

Rate of absorption of hydrogen chloride in aqueous solutions. H. O. Askew.—See B., 1927, 813.

Velocity of oxidation of white phosphorus with gaseous oxygen. J. Zawidski (Z. physikal. Chem., 1927, 130, 109—119).—Russell's results (J.C.S., 1903, 83, 1263) do not fit any one mathematical equation. If x is the original concentration of oxygen and a that at time t, and $(1-x')$ its relative concentration (measured by the ratio, pressure at time t : pressure at zero time), then $dx'/dt=(k_1/a^2)/(1-x')$ for oxygen dried over sulphuric acid. For oxygen dried over calcium chloride, $dx'/dt=(k_2/a^{5/2})[1/(1-x')(x')^{\frac{1}{2}}]$; for very moist oxygen, $dx'/dt=(k_3/a^3)[1/x'(1-x')]$; and for a mixture of dry oxygen and nitrogen, $dx'/dt=k_4\sqrt{a}\sqrt{x'}(1-x')$. Slightly moist oxygen (over 44% sulphuric acid) follows the same equation as the very dry gas.

These apparently contradictory results are difficult to explain.

S. J. Gregg.

Passivity of iron mirrors. II. H. Freundlich, G. Patscheke, and H. Zocher (Z. physikal. Chem., 1927, 130, 289—307; cf. this vol., 1037).—The passivity of iron mirrors, deposited on glass surfaces by thermal decomposition of the pentacarbonyl, has been examined by following the changes in the condition of polarisation of the light reflected from the mirrors before and after exposure to air. The measurements show that the phase-changes and loss of amplitude corresponding with greater or lesser transparency of the iron mirrors were smaller to a greater or lesser degree than with massive iron when the mirrors were brought into contact with air, a diminution in the relative phase change and a small increase in the amplitude ratio resulted. This change occurred instantaneously at the first contact of the surface of the iron with air. Withdrawal of the air to a pressure of 10^{-4} mm. did not lessen the effect. These optical changes can be explained by the formation of a surface layer on the iron, and the close correspondence between the optical and chemical behaviour of iron mirrors before and after the first admittance of air permits the conclusion that these surface layers are layers of oxide which cause passivity.

L. S. Theobald.

Corrosion of iron in tap water. J. Tillmans, P. Hirsch, and W. Weintraud.—See B., 1927, 843.

How do acids attack metals? R. Gaus, A. Eliçabe, and Z. Weinstock (Contrib. estudio Ciencias fys. mat. [La Plata], 1925, 3, 341—357).—Silver–gold alloys containing less than 50 at.-% of silver are not attacked by nitric acid. The rate of dissolution of silver in alloys containing more than 50 at.-% Ag is a function of the time and of the

concentration of the silver; the gold remains as a reddish-brown sponge. On exposure of silver to hydrogen sulphide, the rate of thickening of the sulphide film rapidly decreases, then rises to a constant value. CHEMICAL ABSTRACTS.

Saponification of fats in heterogeneous systems. L. LASCARAY (Anal. Fis. Quim., 1927, 25, 332—348).—The saponification of fats in heterogeneous systems occurs exclusively at the boundary of the phases, and its course agrees with the theories of Harkins and Langmuir on the vectorial structure of such boundaries. The velocity of saponification depends on the degree of dispersion of the system, and is inversely related to the percentage of unsaturated glycerides present. G. W. ROBINSON.

Theory of dislocation from the point of view of thermodynamics and kinetics. J. BOESEKEN (Rec. trav. chim., 1927, 46, 574—581; cf. A., 1926, 806).—Two factors influence the catalysis of reactions, viz., energy and entropy. A molecule decomposes when it has acquired the necessary amount of energy, which may be received in various ways, *e.g.*, by external radiation, collision, etc. However, the mean internal energy of the molecule is insufficient to account for the observed velocity of reactions, since the number of molecules uniting is a negligibly small fraction of the number of collisions. Only those few molecules which have reached the "intermediate" or "critical" state by receiving the necessary amount of energy by a series of collisions, will react. The effect of the two factors is given by the equation of Scheffer and Marcelin, viz., $\log_e k=(\varepsilon_i-\varepsilon)/RT+(\eta_i-$ where k is the velocity coefficient, ε the difference between the mean energy of the reacting molecules and that of the total mass of molecules present, $\eta_i-\eta_{c-1}$ the difference of the corresponding entropies, that of the total mass being calculated for unit concentration. In some cases the addition of a catalyst does not change the first term (energy of activation), so that the acceleration of the reaction must be attributed to change in the second (entropy of activation); this type of catalysis is called "ideal" or "physical" catalysis, whilst "chemical" catalysis is characterised by the formation of intermediate compounds, and change also in the energy of activation. If the intermediate compounds dissociate on heating, then a chemically catalytic reaction will become physically catalytic at high temperature. Thus the catalysis of the reaction $C+2H_2 \rightarrow CH_4$ by nickel is chemical below and physical above 420°, since the intermediate compound nickel carbide is unstable above that temperature.

The processes operative in physical catalysis are termed dislocations. S. J. GREGG.

Neutral salt effect in decomposition of hydrogen peroxide catalysed by iron ions. A. VON KISS and (FRL.) E. LEDERER (Z. physikal. Chem., 1927, 129, 186—198; cf. this vol., 837).—The effect of salts on the catalysed decomposition of hydrogen peroxide in acid solutions in presence of iron ions has been studied. With certain sulphates, the unimolecular velocity coefficient, k, calculated from the equation $dx/dt=k(a-x)$, where a is the initial concentration of peroxide and x the amount decomposed in time t, first falls with increasing salt concentration, then passes through a minimum, and ultimately rises again. Potassium and magnesium chlorides, however, at concentrations up to about N cause k to increase, but at higher concentrations they have the reverse effect, so that a change in the mechanism of the reaction must occur. Potassium nitrate has an accelerating effect at concentrations up to $3N$, but the effect is greatest at about $0{\cdot}5N$. The results as a whole are in harmony with the activity theory, but there are anomalies at lower concentrations. No satisfactory reaction mechanism can be formulated, but the experimental results show that it is not an ionic reaction. R. CUTHILL.

Acid and salt effects in catalysed reactions. XI. Hydrolysis of ethyl acetate and the catalytic catenary. H. M. DAWSON and W. LOWSON (J.C.S., 1927, 2444—2451).—The rate of hydrolysis of ethyl acetate in presence of mixtures of acetic acid and sodium acetate has been investigated. With increasing salt content in $0{\cdot}1N$-acid solutions the velocity falls to a minimum and then rises as a linear function of the salt concentration. The observed effects are connected with the catalytic activities of the undissociated acetic acid molecules, and of the acetate, hydrogen, and hydroxyl ions. The connexion between the hydrogen-ion concentration and the reaction velocity can be represented by a catenary curve. C. W. GIBBY.

Dynamic isomerism. XXIV. Neutral-salt action in mutarotation. T. M. LOWRY and G. F. SMITH (J.C.S., 1927, 2539—2554).—The catalytic catenaries for the mutarotation of dextrose in acid, neutral, and alkaline solutions have been determined at 20°. The reaction is catalysed by acids and bases; definite catalytic activity was detected in the undissociated molecules of a strong or weak acid, the anion of a weak acid, and the cation of a weak nitrogenous base. The velocity is unaffected by neutral salts.

The following catalytic coefficients are recorded: [HCl] about 0·5, [NH_4^+] 0·0012, [AcOH] 0·0065, [OAc'] 0·069. C. W. GIBBY.

Dynamic isomerism. XXV. Mechanism of catalysis by acids and bases. T. M. LOWRY (J.C.S., 1927, 2554—2565).—An electrolytic theory of catalysis is propounded, involving the formation of a "zwitterion" by addition and subtraction of a proton by an amphoteric molecule. Isomeric change depends on a process similar to electrolysis of the prototropic compound, and involves a displacement of valency electrons between two alternative points of attachment of the proton. This theory is applied to catalysis in isomeric change by water, acids, and bases. C. W. GIBBY.

Catalytic synthesis of water vapour in contact with metallic gold. A. F. BENTON and J. C. ELGIN (J. Amer. Chem. Soc., 1927, 49, 2426—2438; cf. this vol., 118).—The kinetics of the above catalytic synthesis were investigated at 130—150°. When oxygen is in excess the "steady state" is reached after a much longer time than when hydrogen is in excess. Neither gas is continuously taken up and

retained by the catalyst in any considerable amount. The rate of the reaction varies as the square of the hydrogen pressure and the first power of the oxygen pressure, and is approximately inversely proportional to the pressure of water vapour. The average temperature coefficient is about 1·9 per 10°. The maximum yield occurs when the mixed gases are approximately in stoicheiometric ratio. Preliminary heating of the catalyst in oxygen produces a large but transitory increase in yield. Gold adsorbs considerable amounts of oxygen at a very slow rate which decreases with falling temperature and is practically independent of the gas pressure (cf. Sieverts, A., 1907, ii, 741). The quantity adsorbed increases with rising temperature but is almost independent of the gas pressure. No simple mechanism will account for the observed facts; possibly two gaseous hydrogen molecules must strike an adsorbed oxygen molecule simultaneously for combination to occur. Bone and Wheeler's observations that the kinetics of the reaction is independent of the oxygen pressure and that previous oxygen treatment of the catalyst decreased the reaction rate are probably to be attributed to the higher temperature at which they worked (cf. A., 1906, ii, 434). S. K. TWEEDY.

Catalytic combination of ethylene and hydrogen in presence of metallic copper. IV. Kinetics at 100° and 200°, temperature coefficient between 0° and 220°, and summary. R. N. PEASE and C. A. HARRIS (J. Amer. Chem. Soc., 1927, **49**, 2503—2510; cf. A., 1923, ii, 842, 862).—The above reaction is very nearly bimolecular at 220°; at 100°, between the ethylene partial pressures of $\frac{1}{4}$ and atm., it is unimolecular with respect to hydrogen and of zero order with respect to ethylene. The reaction rates were measured between 0° and 220°; the conventional expression for the heat of activation applies from 0° to 100°, but above this the temperature coefficient and therefore the heat of activation decreases. The kinetics of the reaction, which is interpreted on the basis of Langmuir's adsorption theory, is similar to that of the hydrogen–oxygen reaction in the presence of platinum (Langmuir, A., 1922, ii, 629). S. K. TWEEDY.

Methyl alcohol catalysts. I. H. S. TAYLOR and C. B. KISTIAKOWSKY (J. Amer. Chem. Soc., 1927, **49**, 2468—2476).—The methyl alcohol catalysts, zinc oxide and especially zinc oxide mixed with chromium oxide, adsorb very large quantities of hydrogen, carbon monoxide, and carbon dioxide at 0° and 100° after the surface has been cleaned of adsorbed water vapour and carbon dioxide by evacuation at 400°. The adsorption isotherms are of the type shown by metal catalysts in hydrogenation reactions, but the adsorption capacities are many times those of most metal catalysts under the same conditions. Strong adsorption of hydrogen and of carbon monoxide occurs at very low pressures; relative saturation is attained, since there is little increase in adsorption with a many-fold increase in pressure. This implies a considerable active surface per unit weight of material and a corresponding comparative insensitiveness to poisons. The heat of adsorption exceeds the heat of liquefaction of the gases and reaches values characteristic of heats of adsorption on metal catalysts. S. K. TWEEDY.

Catalytic oxidation of hydantoins. O. BAUDISCH and D. DAVIDSON (J. Biol. Chem., 1927, **75**, 247—249).—The rapidity of oxidation of 5-substituted hydantoins in presence of trisodium amminoferropentacyanide varies with the nature of the substituent in the order phenyl > (hydrogen) > methyl > benzyl; oxidation does not take place with 5 : 5-dimethylhydantoin, and therefore probably depends on enolisation on the 4-carbon atom; hydantoic acid, glycylglycine, and glycine anhydride were not oxidised under these conditions. C. R. HARINGTON.

Chain reaction theory of negative catalysis. II. Two stages in auto-oxidation reactions. III. General characteristics of auto-oxidation reactions. H. L. J. BÄCKSTRÖM (Med. K. Vetenskapsakad. Nobelinst., 1927, **6**, Nos. 15 and 16; cf. this vol., 737).—II. Iodometric and acidimetric titrations of benzaldehyde, after shaking with oxygen while exposed to light from a mercury lamp, indicate that perbenzoic acid is at first formed. Previous work has shown that the quantum efficiency of this reaction is high (about 10,000) and that, like the corresponding thermal reaction, it shows strong negative catalysis. The perbenzoic acid subsequently reacts with benzaldehyde, forming benzoic acid. This secondary thermal reaction is pseudo-unimolecular, although the half-life period varied between 30 and 8 min. without apparent cause. It is accelerated by light, but the quantum efficiency of the photochemical reaction is certainly less than 0·5% of that for the primary reaction. The secondary reaction shows little or no negative catalysis. The total reaction, which was studied by measurement of the volumes of oxygen absorbed by the benzaldehyde, shows pronounced auto-catalysis in the absence of light; in presence of light the quantum efficiency decreases during the progress of the reaction. These phenomena indicate that the secondary reaction, although probably less effective than the primary reaction in this respect, causes the activation of benzaldehyde molecules which may then react with oxygen or with perbenzoic acid and so establish reaction chains. This activation probably occurs in both the thermal and the photochemical reaction. The absorption of oxygen by sodium sulphite solutions is considerably accelerated by the addition of potassium persulphate or hydrogen peroxide. This acceleration is attributed to the activation of sulphite molecules during the very rapid pseudo-unimolecular reaction (half-life period, 0·53 min.) between the peroxide and the sulphite.

III. A review of auto-oxidation reactions, including those previously studied by the author, and a discussion of the mechanisms of chemi-luminescence, photo-sensitisation, negative catalysis (inhibition), and certain side-reactions, which are in many cases associated with auto-oxidations, from the point of view of the Christiansen theory of chain reactions. The photochemical and thermal reactions are considered to be identical, except when, as in the case of benzaldehyde, a relatively stable intermediate peroxide is formed. It is concluded that the thermal

reaction produces sufficient energy for the excitation of additional molecules, and that it may be followed by a photochemical reaction, or side-reaction, produced by radiation from these excited molecules. The theory also leads to a new explanation of the maximum oxidation pressure of phosphorus which connects it with the formation of ozone. Experiments are described which show that the reactions previously studied (*loc. cit.*) may be photo-sensitised with respect to ultra-violet light, but the results were negative in the case of visible light; the photo-sensitisation is attributed to the formation of activated molecules during the photochemical oxidation of the sensitiser. The decomposition of ozone is also considered in terms of reaction chains of the Christiansen type. G. A. ELLIOTT.

Inhibition of auto-oxidation of benzaldehyde. M. BRUNNER (Helv. Chim. Acta, 1927, **10**, 707—728; cf. Reiff, this vol., 57).—Reaction between benzaldehyde and gaseous oxygen occurs at the surfaces of the reaction vessel and of the added catalyst (pumice, sand, glass, etc.), and apparently only in presence of traces of water. Oxygen and benzaldehyde activated at a polar water layer on the catalytic surface react to form an unstable ring compound which is rapidly transformed into the more stable perbenzoic acid. The latter then reacts with unchanged benzaldehyde to form benzoic acid. Of the reactions involved only the first is influenced by the catalysts mentioned. The present measurements show that, in general, the rate of absorption of oxygen first increases to a well-defined maximum and then rapidly falls to a value which for a considerable time is roughly constant. The maximum rate is roughly proportional to the amount of catalyst and hence to the catalytic surface. Of this surface only an extremely small fraction is active in promoting oxidation. The shape of the velocity–time curve is markedly dependent on the concentration of benzaldehyde and on its purity. Old samples, *i.e.*, containing benzoic acid, and dilute benzene solutions show periods of induction and a flattened maximum at a much lower value. The duration of the period of induction is primarily dependent on the time taken by benzaldehyde and oxygen to reach the active portions of the catalytic surface. Using *cyclo*hexane as solvent in place of benzene the effect is more pronounced, possibly on account of higher viscosity. The existence of a period of induction when the benzaldehyde contains benzoic acid is due to the fact that the acid is adsorbed on the active surface and is only slowly replaced by oxygen. In all cases where benzene solutions were examined small quantities of phenol were detected amongst the products of reaction. Since the phenol thus formed appears to be without inhibitory effect it is apparently formed at a fairly late stage in the scheme of reactions and is prevented from reaching an active centre on the catalytic surface by oxidation or mechanically.

Inhibitors (iodine, diphenylamine, quinol, etc.) exert their effect when present at extremely low concentrations. They are adsorbed on the active centres and thus retard activation. In all cases a period of induction, the duration of which is primarily dependent on the ratio of the concentration of inhibitor to the area of the catalytic surface, is followed by sudden reaction, the rate of absorption of oxygen rising to a sharp maximum, and then rapidly decreasing. The period of induction is much longer when benzaldehyde which has been exposed to the air is used. Rise of temperature shortens the period. With benzene solutions containing iodine, the colour of the latter disappears on commencement of the reaction and further addition has little or no inhibitory effect. The solutions eventually become colourless and contain iodobenzene. During the induction period some of the adsorbed iodine is displaced by oxygen and formation of peroxide ensues. Iodine molecules at the surfaces and in the solution are converted into less strongly adsorbed iodobenzene etc. and further activation of oxygen follows. Florida earth and blood charcoal have an inhibitory effect. With blood charcoal the duration of the induction period increases with increasing quantity of charcoal and the maximum in the absorption–time curve is considerably flattened. It is suggested that positive and negative catalytic centres are present and evidence is put forward which indicates that the negative centres are progressively poisoned before the positive reaction commences.

J. S. CARTER.

Electrolysis of potassium chloride solutions by alternating currents. A. J. ALLMAND and H. C. COCKS (J.C.S., 1927, 2626—2639).—The electrolysis of potassium chloride solutions by alternating current has been investigated at the ordinary temperature with regard to the efficiency of hypochlorite production. The current efficiency diminishes with decreasing current density to zero at a critical value of the latter, and rises from zero above a threshold value of the frequency. The maximum hypochlorite concentration obtained was about 0·3*N*. Measurements of average electrode potentials were made during electrolysis. The different behaviour of polished platinum and graphite electrodes is investigated.

G. W. GIBBY.

Electrochemistry of beryllium. II. S. BODFORSS (Z. physikal. Chem., 1927, **130**, 82—89).—The beryllium salts were prepared in two ways: (1) commercial beryllium chloride solution was precipitated with ammonia, the hydroxide dissolved in acetic acid, evaporated to dryness, and the salt recrystallised from boiling glacial acetic acid. This was decomposed by refluxing with alcohol and 25% sulphuric acid, when the compound $BeSO_4,4H_2O$ crystallised on cooling. (2) The sparingly soluble, easily crystallisable compounds of ammonium beryllium fluoride with the aromatic amines were decomposed by means of concentrated sulphuric acid.

Measurements of the potential of the cell pure Be|x*N*-$BeSO_4$,y*N*-KCl against the normal calomel electrode were made in an atmosphere of carbon dioxide. The potential of beryllium in such a solution 0·1*N* with regard to beryllium sulphate increased in a negative sense on ten-fold dilution, and was greater (in a negative sense) the greater was the original concentration of the potassium chloride. Thus the potential behaves in a "normal" fashion.

Beryllium passes into solution as a univalent ion, readily forming complex ions, which fact explains the effect of halogen salts, *e.g.*, potassium chloride, on the potential. If the solution of beryllium salt with potassium chloride be diluted with water, the complexes are split up, the concentration of beryllium ions is thus increased, and the potential becomes more positive. If the solution be diluted with a solution of potassium chloride, the formation of the complex ions is promoted and the potential becomes more negative.

The univalency of beryllium ions is supported by the fact that a mixture of beryllium and beryllium iodide reduces aromatic ketones in a similar way to a mixture of magnesium and magnesium iodide, where, as Gomberg and Bachmann (this vol., 245) have shown, magnesium subiodide is formed.

Beryllium stands in the electro-chemical series between cadmium and zinc. S. J. Gregg.

Electrochemical reduction of solid electrodes. K. Fischbeck and E. Einecke (Z. anorg. Chem., 1927, **167**, 21—39).—The cathodic reduction of a number of insoluble powders at a lead electrode in 2% sulphuric acid solution has been studied. Titanium dioxide and tungsten trioxide are reduced to the ter- and quinque-valent condition, respectively. Red lead and lead monoxide yield crystals of lead, from which hydrogen is evolved as the reduction proceeds. Manganese dioxide, although largely used as a depolariser, is reduced to only a slight extent. Neither the crystalline nor the amorphous forms of aluminium, ferric, or chromic hydroxides are reduced to any appreciable extent. Silver cyanide and the silver halides are reduced at the interface between the salt and the electrolyte to silver, without evolution of hydrogen. Mercuric oxide, sulphide, and thiocyanate are reduced at the cathode to mercury. Chromium carbide, Cr_3C_2, yields, not chromic ions, but chromic acid and carbon dioxide; the nitride CrN yields chromic acid and ammonia.

Artificial cuprous, ferrous, cobaltous, nickelous, manganous, cadmium, zinc, calcium, and magnesium chromites have been prepared by heating the appropriate oxide with chromic oxide at 1000—1500°, and extracting the product with acid. Cathodic polarisation of the ferrous, cuprous, calcium, and magnesium compounds produces chromic acid, whilst the other chromites are unaffected. Natural chrome ironstone behaves in a like manner, but other commercial chromites are reduced on cathodic polarisation, and yield chromic acid on anodic polarisation. A study of the conditions of formation of chromic acid and of the increase in the amount of gas evolved at higher current strengths indicates that the chromite behaves as an intermediate electrode. H. F. Gillbe.

Effect of high voltages on tantalum anodes. E. M. Dunham (Science, 1927, **65**, 525).—Tantalum anodes, used with high voltages, sometimes acquire permanent, coloured surface films; similar films have not been reproduced by heating or other means.

A. A. Eldridge.

Electrolysis of copper pyrites. R. Saxon (Chem. News, 1927, **135**, 263—264).—Copper pyrites is regarded as iron thiocuprate (cf. following abstract).

A. A. Eldridge.

Electrolysis of copper pyrites. R. Saxon (Chem. News., 1927, **135**, 310).—The use of lead salts as electrolyte to remove the sulphur from the ore was unsuccessful; thus lead chloride gives a deposit of lead sulphide, lead, and lead chloride, with ferric hydroxide, but no copper. Ammonium, sodium, or potassium chloride gave good results as electrolyte. R. A. Pratt.

Anodes for chromium plating. O. P. Watts.—See B., 1927, 849.

Electrolytic preparation of *p*-aminophenol. D. Caeser.—See B., 1927, 849.

Detection of organic diacyl peroxides at the anode. F. Fichter (Z. physikal. Chem., 1927, **130**, 49—55).—Diacyl peroxides are probably formed as intermediate compounds in the Kolbe synthesis of hydrocarbons by electrolysis of solutions of the alkali salts of the corresponding fatty acids. In order to detect their formation, the following conditions must be fulfilled: (1) the electrolyte and anode must be kept very cool to avoid thermal decomposition of the peroxide, (2) hence the salt must be very soluble so that freezing can be prevented by using a very concentrated solution, (3) the molecule of peroxide must be large enough to withstand thermal decomposition.

Hexoic acid fulfils these conditions, and by covering the solution with a layer of light petroleum to remove the peroxide from the anode, the presence of a small quantity of dihexoyl peroxide, $C_5H_{11}\cdot CO_2\cdot CO_2\cdot C_5H_{11}$, and of perhexoic acid ($C_5H_{11}\cdot CO_2\cdot OH$), giving together about a 0·73% yield, were detected in this layer. A theory explaining their formation is given.

S. J. Gregg.

Electrodeposition of rubber. S. E. Sheppard.—See B., 1927, 852.

Photosensitisation. I. J. R. Bates and H. S. Taylor (J. Amer. Chem. Soc., 1927, **49**, 2438—2456; cf. this vol., 217).—A cooled mercury arc for use in mercury-sensitised and general photochemical reactions is described; by increasing the energy input into a high-pressure hydrogen discharge a continuous ultra-violet spectrum to 1900 Å. can be obtained. The hydrogenation of ethylene does not proceed solely as $C_2H_4+H_2\longrightarrow C_2H_6$, since the reaction does not cease when the original partial pressure of hydrogen is reached. This is due to polymerisation of the ethylene by excited mercury atoms (Berthelot and Gaudechon, A., 1910, i, 349). An initial pressure increase is attributed to the reaction $C_2H_4+Hg'\longrightarrow C_2H_2+H_2+Hg$; this increase is controlled by the diffusion of the products from the zone of excited mercury atoms. Acetylene is polymerised both by excited mercury atoms and by ultra-violet light, but it cannot be hydrogenated by hydrogen activated by excited mercury. The photosensitised reaction between oxygen and excess of hydrogen yields hydrogen peroxide as the sole product if the rate of gas flow is fairly rapid. Many substances (water, ethyl and methyl alcohols, benzene etc.) are decomposed by excited mercury atoms. The decomposition products of ammonia show an excess of hydrogen over the stoicheiometric proportions; a provisional

mechanism is suggested. Leifson's absorption band for ammonia at 2260 Å. (A., 1926, 991) is resolved into two bands at 2266—2262 Å. and at 2262—2259 Å.; the next band begins at 2254 Å. Excited mercury atoms decompose formic acid in two ways: $H{\cdot}CO_2H \longrightarrow H_2O+CO$ and $H{\cdot}CO_2H \longrightarrow H_2+CO_2$.

S. K. TWEEDY.

Photochemical decomposition of hydrogen peroxide solutions. F. O. RICE and M. L. KILPATRICK (J. Physical Chem., 1927, **31**, 1507—1510).—Solutions of hydrogen peroxide in dust-containing and dust-free water decompose at different rates, the rate of decomposition being approximately proportional to the dust content. Removal of dust reduced the rate to 1/18 of that of the control solutions, indicating that the deviation of this reaction from the law of photochemical equivalence is much less than the results of Henri and Wurmser (A., 1913, ii, 819), and of Kornfeld (A., 1921, ii, 670) appear to show. Previous melting of the apparatus used greatly reduces the number of distillations required to produce dust-free water by the method of Martin (A., 1922, ii, 335).

L. S. THEOBALD.

Photochemical studies. V. Photochemical decomposition of ammonia by relatively short wave-lengths. L. S. KASSEL and W. A. NOYES, jun. (J. Amer. Chem. Soc., 1927, **49**, 2495—2503; cf. Noyes and Kouperman, A., 1923, ii, 527).—The above reaction was investigated between 190 and 160 mμ, the light intensity being measured by streaming oxygen through the reaction vessel and determining the amount of ozone produced by a special colorimetric method. On the assumption that two molecules of ozone are produced from oxygen for each quantum absorbed (cf. Warburg, Sitzungsber. Preuss. Akad. Wiss., 1914, 872; 1915, 230) it is found that 1·4 quanta are absorbed per molecule of ammonia (cf. Kuhn, A., 1926, 920). A satisfactory mechanism cannot be suggested, although the consideration of thermal data indicates which reactions might be possible.

S. K. TWEEDY.

Photochemical formation of carbonyl chloride. I. M. BODENSTEIN [with BUTEFISCH, KAHLE, SUSSENGUTH, E. HEISENBERG, and HARTECK] (Z. physikal. Chem., 1927, **130**, 422—448; cf. Bodenstein and Plaut, A., 1925, ii, 135).—The photochemical combination of chlorine and carbon monoxide has been investigated from the ordinary temperature up to 300°. At the ordinary temperature, it takes place according to the equation $d[COCl_2]/dt = kJ_{Abs.}^{\frac{1}{2}}[Cl_2][CO]^{\frac{1}{2}}$ (1), with a yield of the order of magnitude of 3000 mols. per quantum. The reaction is retarded by the presence of oxygen, which appears to be sensitised by the illuminated chlorine. In this case, the principal reaction is the formation of carbon dioxide. The reaction (1) takes place more slowly with rising temperature, until at about 260° it is completely replaced by another, which follows the law $+d[COCl_2]/dt = kJ_{Abs.}[Cl_2][CO]$. The presence of oxygen has now no retarding effect, and does not lead to the formation of carbon dioxide. The same reaction probably occurs at the ordinary temperature in place of reaction (1) if the gases are thoroughly dried. A scheme is suggested for reaction (1), by means of which the absolute reaction velocities can be calculated from the data for the dark reaction (*loc. cit.*). The suggested explanation is modified to bring it into line with the work of Franck (A., 1925, ii, 1077) and others on the connexion between light absorption and the dissociation of the chlorine molecule.

L. L. BIRCUMSHAW.

Similarities in the darkening of photographic plates at various exposures. E. F. M. VAN DER HELD and B. BAARS (Z. Physik, 1927, **45**, 364—368).—From experiments on the relative darkening of photographic plates as a function of the time of exposure it is shown that a constant darkening coefficient is obtained for Ilford rapid chromatic and special rapid plates for exposures in the range 1 : 1000 if "rodinal" (1 : 20) be used as developer.

R. W. LUNT.

Decomposition of silver bromide per quantum of *X*-radiation. J. EGGERT and W. NODDACK (Z. Physik, 1927, **44**, 155).—The authors indicate minor corrections to their recent paper (this vol., 841) necessitated by the more accurate data of Rump (this vol., 706) on the energy density of *X*-rays produced by a tube working under specified conditions.

R. W. LUNT.

Mechanism of formation of the latent photographic image. A. P. F. TRIVELLI (Nature, 1927, **120**, 728).—It appears that high-sensitivity photographic materials contain the system silver, silver halide, silver sulphide, in which the silver and silver sulphide are in contact, representing a photo-electric cell of the Becquerel type. In light, the *P.D.* between the electrodes increases, the conductivity of the silver halide increases, and an electric current flows in the system. Electrolysis of the silver halide results, the cations moving towards the cathode, and the anions losing their charge and remaining in the crystal-substance.

A. A. ELDRIDGE.

Decomposition of hydrogen peroxide and the mechanism of latent photographic image intensification. E. P. WIGHTMAN and R. F. QUIRK (Science, 1927, **66**, 92).—It is considered that when the photographic plate is treated with an acid hydrogen peroxide solution, the trace of bromide formed from the soluble bromide in the plate attacks the silver sulphide of the sensitivity or latent image speck (where it has not all been converted into silver during exposure to light) and thus renders the grain developable.

A. A. ELDRIDGE.

Photo-bromination of *cyclo*hexane. B. J. WOOD and E. K. RIDEAL (J.C.S., 1927, 2466—2477).—The photo-bromination of *cyclo*hexane in the presence of radiation of wave-length 5460 Å. has been investigated at 30°. The thermal and photochemical reactions both conform to the unimolecular law, and the latter has no temperature coefficient between 30° and 40°. The velocity of the photo-reaction is proportional to the light-intensity, independent of the *cyclo*hexane concentration, and reduced by the presence of oxygen. The inhibition by oxygen is independent of the pressure of *cyclo*hexane.

It is concluded that the primary photoactive constituents are excited bromine molecules, and the

mechanism of the reaction is discussed (cf. Pusch, A., 1919, ii, 208; Noddack, A., 1921, ii, 568).

C. W. GIBBY.

Reaction of sodium chloride if added to a solution of litmus and mercuric chloride. W. O. MOOR (J. Amer. Chem. Soc., 1927, 49, 2355—2357).—The addition of 4—5 drops of 2% aqueous mercuric chloride solution causes neutral, violet litmus solution to become reddish; on subsequent addition of 1 c.c. (excess) of saturated (neutral) sodium chloride solution, the mixture turns blue, but regains its original violet colour after a few seconds. The formation of the neutral salt, $HgCl_2,NaCl,H_2O$, fails to explain this reaction, which occurs only when the litmus and mercuric chloride come into contact first. The addition of zinc sulphate to blue litmus solution gives a solution of the same violet colour as neutral tincture of litmus.

S. K. TWEEDY.

Decomposition pressure of cupric metaborate. N. PARRAVANO and G. MALQUORI (Z. physikal. Chem., 1927, 130, 167—169).—Copper metaborate glass changes colour from blue to yellowish-red at 800—900°; this is attributed to its conversion into cuprous salt, boric anhydride, and oxygen. Copper oxide does not appreciably lose oxygen under these conditions. A curve was obtained showing the logarithm of the oxygen tension as a function of temperature for the metaborate prepared by two processes. The (linear) curve differs from that for copper oxide. It is calculated that the affinity for oxygen at the atmospheric pressure is 9027 g.-cal. for the oxide and 1159 g.-cal. for the metaborate.

A. A. ELDRIDGE.

Triple iodides of rubidium and gold with other metals. E. S. BURKSER, S. G. RUBLOV, and A. M. SCHARNOVSKY (Z. anorg. Chem., 1927, 167, 87—96).—Triple iodides containing gold, rubidium, and zinc, copper, silver, mercury, or cadmium have been prepared by adding rubidium iodide and the iodide of the third metal to a solution prepared by dissolving gold in aqueous hydriodic acid containing free iodine and ether as a catalyst. Simple formulæ for the complex salts are obtained only on the assumption that both aurous and auric iodides are present in the molecule. The *silver*, *cuprous*, *zinc*, and *cadmium* salts have the general formula $4RbI,MI$ (or $M_{0.5}I$),Au_4I_6, and, with the exception of the silver salt, which is black, form non-hygroscopic crystals with a golden lustre. The crystals break up under the action of water, and the dry salts begin to decompose with evolution of iodine vapour at 170—190°. *Zinc*, *cadmium*, *mercury*, and *thallium* form a series of bluish crystalline salts, having the formulæ $16RbI,9ZnI_2,4AuI,2AuI_3$; $8RbI,2CdI_2,AuI,3AuI_3$; $9RbI,4HgI_2,2AuI,AuI_3$; $RbTlI_4,RbAuI_4$.

H. F. GILLBE.

Silver subfluoride. A. HETTICH (Z. anorg. Chem., 1927, 167, 67—74).—Electrolysis of concentrated silver fluoride solutions yields at the cathode with high current density pure silver, whereas at low current density pure silver subfluoride is obtained. *X*-Ray investigation of the product shows it to contain neither silver nor silver fluoride. The crystals are decomposed by water into silver and silver fluoride, but are unattacked by concentrated silver fluoride solutions. When heated, silver subfluoride decomposes, even in total absence of water, leaving pure silver; this reaction, therefore, furnishes a basis for the chemical preparation of fluorine. The subfluoride crystals, d 8·57, conduct electricity, and in contact with a silver wire act as rectifiers.

H. F. GILLBE.

Silver sulphate-carbon monoxide. W. MANCHOT and J. KÖNIG (Ber., 1927, 60, [*B*], 2183—2185; cf. A., 1924, ii, 609).—The absorption of carbon monoxide by silver sulphate dissolved in sulphuric acid increases with increasing sulphur trioxide content of the solution, with fall of temperature and increase of pressure of the gas, approximating to but never exceeding that required for the formation of the compound, Ag_2SO_4,CO.

H. WREN.

Purification of beryllia. E. CHAUVENET and E. DUCHEMIN (Compt. rend., 1927, 185, 716—717).—The powdered beryllium oxide is placed between two perforated plates in a silica tube and heated in a current of carbonyl chloride at 450° for 1—2 hrs. This removes the volatile chlorides of iron and aluminium; treatment of the residue with water dissolves the calcium chloride and any beryllium chloride present, leaving 80—85% of the original sample as pure beryllium oxide.

B. W. ANDERSON.

Action of calcium, magnesium, and aluminium on beryllia. C. MATIGNON and (MLLE.) G. MARCHAL (Compt. rend., 1927, 185, 812—814; cf. this vol., 430).—Well-calcined beryllia may be reduced to the metal when heated either with an excess of lime (at about 800°), magnesia (at 675—690° for 3—6 hrs.), or with alumina (at 1270° for 4 hrs. in a vacuum). The yields obtained were 30—33%, 14%, and 0·8%, respectively. With lime or magnesia these yields could be increased by promoting more intimate contact between the reagents (*e.g.*, by means of a flux), but with alumina the small quantity of metal corresponds with the formation of an alloy of low beryllium content. The reduced beryllium was separated from the mixture by means of dilute hydrochloric acid, in which well-calcined beryllia is insoluble.

J. GRANT.

Chemical equivalence of carbon monoxide and nitric oxide. W. MANCHOT and W. PFLAUM (Ber., 1927, 60, [*B*], 2180—2182).—Mutual replaceability of carbon monoxide and nitric oxide is exhibited when nitric oxide, alone or in the presence of methyl alcohol vapour, is passed over the substance $RhCl_2,RhO,3CO$ whereby the *compound* $RhCl_2,RhO,3NO$ is produced. The reverse change is readily effected at 130—140°. The carbonyl and nitrosyl groups in these compounds appear to be attached to the metallic atom by subsidiary valencies.

H. WREN.

Interaction between sodium metasilicate and salts soluble in water. P. N. GRIGORJEV (Z. anorg Chem., 1927, 167, 137—144).—Three groups of water-soluble salts are recognised, in regard to their reactions with sodium metasilicate solution. (1) Solutions of the alkali metals precipitate silica, the action being purely one of coagulation. (2) Calcium, strontium, and barium salts precipitate completely the corresponding metasilicate, but on washing the precipitate

hydrolysis takes place. (3) Salts of more weakly basic metals require for neutralisation of their acid reaction more silicate solution than is theoretically necessary. At moderately high temperatures and pressures the reaction is quantitative, *e.g.*, for aluminium sulphate at 215° and 22 atm. pressure the reaction is expressed by the equation: $Al_2(SO_4)_3+3Na_2O,2SiO_2=3Na_2SO_4+Al_2O_3,3(2SiO_2)$. H. F. GILLBE.

Germanium. XXII. Dihalides of germanium. F. M. BREWER and L. M. DENNIS (J. Physical Chem., 1927, **31**, 1526—1538).—The continued fractionation of the mixture of germanobromoform and germanium tetrabromide, produced by the action of hydrogen bromide on germanium, yields *germanium dibromide*. Reduction of the mixture by zinc, under special conditions, is more effective and gives a colourless, crystalline solid which decomposes when heated, presumably according to the equation $2GeBr_2=Ge+GeBr_4$. The dibromide is insoluble in hydrocarbons, but is soluble in alcohol and acetone: it is hydrolysed by water to yellow, hydrated germanous hydroxide. Bromine is absorbed, but not vigorously, forming the tetrabromide. *Germanobromoform* (m. p. −24° approx.) results from the action of hydrogen bromide on this product. Germanium di-iodide (cf. Dennis and Hance, A., 1923, ii, 172) is prepared by the action of concentrated hydriodic acid on an excess of a mixture of hydrated mono- and di-oxides of germanium below 40°. The yellow solid obtained is crystallographically similar to lead iodide; it is insoluble in hydrocarbons, slightly soluble in chloroform and in carbon tetrachloride, and it can be recrystallised from hydriodic acid. Solutions in dilute acids and in water possess reducing properties. Exposure to air results in slow hydrolysis to the dioxide, and on heating in air, oxidation to the dioxide and tetraiodide occurs rapidly at 210°; in a vacuum, germanium and germanium tetraiodide are formed. Attempts to prepare the dichloride by the reduction of the tetrachloride with various metals and amalgams, and by the removal of hydrogen chloride from germanochloroform, failed. L. S. THEOBALD.

Combinations of zirconium oxychloride with the alkali chlorides. E. CHAUVENET and E. DUCHEMIN (Compt. rend., 1927, **185**, 774—776).—Determinations of the heats of mixture of equimolecular solutions (A., 1920, ii, 757) indicate the existence in solution of the compounds $7ZrOCl_2,5NH_4Cl$, $ZrOCl_2,RbCl$, and $8ZrOCl_2,5CsCl$. The corresponding compounds of lithium, sodium, and potassium do not exist, and the *cæsium* compound only could be isolated. A solution of the mixed salts, evaporated slowly, yielded large crystals containing 64 mols. of water, of which 53 were lost at 80° and the remainder at 100°. J. GRANT.

Reaction of active nitrogen. P. JOLIBOIS and H. LEFEBVRE (Compt. rend., 1927, **185**, 853—855).—The decomposition by a powerful electric discharge of carbon monoxide into carbon dioxide and carbon at low pressures (about 4—5 mm. of mercury) is increased seven-fold by the addition of a large excess of pure nitrogen. This phenomenon, Rayleigh's experiments with nitrogen dioxide, and the formation of ammonia in the electric arc may be explained by the catalytic properties of nitrogen passing from the active to the normal state. J. GRANT.

Preparation of hypophosphoric acid. M. SPETER (Rec. trav. chim., 1927, **46**, 588—589).—When 5 g. of red phosphorus are warmed with 1 litre of 10% filtered bleaching-powder solution, only 1·8 g. of phosphorus remains unoxidised. On filtering and nearly neutralising the solution with solid sodium carbonate crystals, calcium hypophosphate is precipitated, and is dried at the pump. It is dissolved in the least possible quantity of dilute sulphuric acid, and on keeping, calcium sulphate is precipitated, leaving a solution of the hypophosphoric acid in sulphuric acid. This solution, which can be used directly for the thorium test, remains stable for years. The residual phosphorus appears to contain a new allotropic modification. S. J. GREGG.

Tetraphosphorus di-iodide triselenide. J. MAI (Ber., 1927, **60**, [*B*], 2222—2223).—*Tetraphosphorus di-iodide triselenide*, $P_4I_2Se_3$, m. p. 154—155° when rapidly heated, is prepared by the addition of iodine to a solution of phosphorus selenide in carbon disulphide. The isolation of *phosphorus sulphide selenide* is mentioned. H. WREN.

Formation of complexes by the arsenate anion. A. ROSENHEIM and S. THON (Z. anorg. Chem., 1927, **167**, 1—20).—Isotherms at 0° of the system Na_2O–As_2O_5–H_2O do not indicate the existence of complex arsenate anions. In acid and neutral solutions there exist the compounds $As_2O_5,4H_2O$, NaH_2AsO_4,H_2O, and $Na_2HAsO_4,12H_2O$. The solubility curve of disodium hydrogen arsenate has been determined between 0° and 34°; the transition of the dodecahydrate to the heptahydrate occurs at 22°. In presence of alkali hydroxides arsenic pentoxide forms with the hydroxides of aluminium and tervalent iron and chromium complex metalloarsenates analogous to the ferriphosphates; the structure of these compounds is discussed on the assumption of a co-ordination number of two for the anion $HAsO_4''$. The following *ferriarsenates*, *aluminiarsenates*, and *chromiarsenates* are described: $NaH_2[Fe(AsO_4)_2],H_2O$, $KH_2[Fe(AsO_4)_2]$, $Ba_3H_6[Fe(AsO_4)_3]_2$, $NaH_2[Al(AsO_4)_2],0{\cdot}5H_2O$, $BaH_4[Al(AsO_4)_3],H_2O$, $NaH_2[Cr(AsO_4)_2],H_2O$, $KH_5[Cr(AsO_4)_3],7$ and $12H_2O$. The corresponding bismuth, cobaltic, thallic, and lanthanum compounds are not formed under the same conditions. *Tripyrogallolarsenates* of *ammonium* ($3H_2O$), *barium* ($12H_2O$), *pyridine*, $(C_5H_5N)H[As(O_2C_6H_3{\cdot}OH)_3],H_2O$, *cinchonine*, and *strychnine* ($2H_2O$) have been prepared, and are analogous to the tripyrocatecholarsenates (*mercury* salt). H. F. GILLBE.

Active form of oxygen. F. R. BICHOWSKY and L. C. COPELAND (Nature, 1927, **120**, 729).—An active form of oxygen, presumably monatomic, is produced when oxygen, saturated with water vapour, is passed through a discharge tube. A. A. ELDRIDGE.

Stable and unstable molybdenum blues. Analytical applications to the determination of phosphoric and arsenic ions. G. DENIGES (Compt. rend., 1927, **185**, 777—779).—True molybdenum blue ($MoO_2,4MoO_3$) is stable towards heat and dilution,

and is precipitated by ether. Other types may be stable but ether-soluble (this vol., 433) or unstable and ether-insoluble. and of unknown structure. Various methods of preparation of each type are described. The true molybdenum blue may be used as follows for the rapid determination of phosphate and arsenate ions. The reagent, which is stable for a week, is a solution of sulphomolybdic acid (a 10% solution of ammonium molybdate with an equal volume of concentrated sulphuric acid) diluted four-fold, and reduced for 1 hr. by means of copper turnings. Five c.c. of the solution under investigation are boiled with 0·2 c.c. of reagent for 5 sec., allowed to cool, and after 10 min. the blue colour is compared with that of a standard generated under the same conditions. An appreciable colour is produced with 0·15 mg. of the ions per litre. J. GRANT.

Systematic doctrine of affinity. XLV. Increase in reactivity through lattice distension, and ammines of the fluorides. W. BILTZ and E. RAHLFS (Z. anorg. Chem., 1927, **166**, 351—376; cf. this vol., 1143).—By tensimetric measurements, evidence has been obtained of the addition of the following numbers of molecules of ammonia to anhydrous fluorides: antimonious fluoride, 6, 4, 3, 1; mercuric fluoride, 5, 4, 2; cupric fluoride (dihydrate), 5; beryllium fluoride, 1; silver fluoride, 1 (an amine?). Certain other fluorides do not react in the anhydrous state, but their hydrates may be reactive, part of the water being replaced by ammonia. In these cases, it is probable that the reduction in lattice energy consequent on the distension of the lattice produced by the water molecules is responsible for the reactivity. The existence of the following compounds obtained in this way has been detected; silver fluoride monohydrate with 2 mols. of ammonia; zinc fluoride dihydrate with 3, and 4 mols. of ammonia; monohydrates of manganous, ferrous, cobaltous, and nickel fluorides, each with ½, 1, and 5 mols. of ammonia; aluminium fluoride dihydrate with 2 mols. of ammonia. The volume of the fluorine atoms in the pure anhydrous fluorides is, in general, much less than the zero volume, but is very variable, whilst in the hydrated salts the volume of the water molecules is nearly equal to the zero volume. In the ammines, the volume of the ammonia molecules approximates to the zero volume. R. CUTHILL.

Formation of aquopentacyano-iron salts in aqueous solutions of hexacyano-iron complexes and the successive dissociation of the latter. S. IIMORI (Z. anorg. Chem., 1927, **167**, 145—172).—Aqueous solutions of ferro- and ferri-cyanides are gradually converted by light, heat, or excess of hydrogen ions into the corresponding aquopentacyano-compounds. The first stage in the dissociation of the ferro- and ferri-cyanide ions results in the formation of pentacyano-iron ions. The reputed existence of the isomeric β-ferro- and ferri-cyanides is ascribed to the influence of aquopentacyano-iron compounds, formed by dissociation, on the crystal form of the salt. H. F. GILLBE.

Univalent iron, cobalt, and nickel. II. W. MANCHOT and F. KAESS (Ber., 1927, **60**, [*B*], 2175—2180; cf. this vol., 33).—The *compound* Ni(NO)·SEt may be prepared by adding an aqueous solution of potassium hydroxide to aqueous nickel acetate in an atmosphere of nitric oxide followed by introduction of ethyl mercaptan and agitation of the mixture with nitric oxide until the gas is no longer absorbed or, preferably, by passing nitric oxide over nickelous mercaptide at the ordinary temperature. Under the latter conditions, nitrosylethylmercaptide (cf. Lecher and Siefken, A., 1926, 819) is also readily isolated; this can also be obtained according to the first procedure if methyl alcohol and potassium methoxide are substituted for water and potassium hydroxide. Reduction of bivalent to univalent nickel proceeds therefore according to the scheme: $Ni(SEt)_2+2NO=NO\cdot Ni\cdot SEt+SEt\cdot NO$.

[With H. SCHMID.]—These observations suggest that the action between potassium thiosulphate, nitric oxide, and nickel chloride (this vol., 34) may be represented by the equations: $NiCl_2+3K_2S_2O_3+2NO=2KCl+NO\cdot S\cdot SO_3K+Ni(NO)\cdot S\cdot SO_3K,K_2S_2O_3$ and $2NO\cdot S\cdot SO_3K=2NO+K_2S_4O_6$. This view is supported by the detection of potassium tetrathionate in 45—50% yield in the mother-liquors from the precipitate of the nickel salt. H. WREN.

Cobaltic fluoride hydrate. E. BIRK (Z. anorg. Chem., 1927, **166**, 284—289).—Cobaltic fluoride prepared by Barbieri and Calzolari's method (A., 1905, ii, 393) is not the anhydrous salt, but a *hydrate*, $Co_2F_6,7H_2O$. It takes up ammonia at 70—80° with loss of water. luteo- and purpureo-fluorides probably being formed. The *X*-ray diagram closely resembles those of the bimolecular types of chromic fluoride hydrates (Werner and Costachescu, A., 1909, ii, 51), but it is not possible to decide with which type the structure actually corresponds. By addition of alcohol to a very concentrated solution of chromic fluoride, a *pentahydrate*, $CrF_3,5H_2O$, may be prepared. R. CUTHILL.

Ruthenium. X. "Isomeric" chlorides. J. L. HOWE (J. Amer. Chem. Soc., 1927, **49**, 2381—2393).—The reduction of potassium hexachlororuthenate and of Claus' potassium pentachlororuthenite with stannous chloride yields in each case "aquo"-pentachlororuthenite, K_2RuCl_5, showing that the valency of ruthenium in each of the compounds is four. Claus' compound is now proved to be K_2RuCl_5OH, as originally suggested by Charonnat (A., 1925, ii, 586). The hydrated oxide usually considered to be Ru_2O_3,xH_2O is thus, in all probability, really RuO_2,xH_2O, since its solution always yields H_2RuCl_5OH. The "aquo" salts are the ordinary series M_2RuCl_5,H_2O. In all these salts the co-ordination number of ruthenium is six. Claus' view that the blue solution of reduced ruthenium contains bivalent metal is confirmed. S. K. TWEEDY.

Complex salts of iridium containing hydrazine. L. A. TSCHUGAEV (Ann. inst. platine, 1926, No. 4, 52—54).—When heated in aqueous solution, hydrazine hydrochloride and potassium chloroiridate yield the *compound* $[Ir(N_2H_5)Cl_5]H$, which, with tetramminoplatinous chloride or cæsium chloride yields, respectively, the *compounds* $[Ir(N_2H_5)Cl_5]_2[Pt4NH_3]$ and $[Ir(N_2H_5)Cl_5]Cs$. CHEMICAL ABSTRACTS.

Pentammine compounds of quadrivalent platinum. L. A. TSCHUGAEV (Ann. inst. platine, 1926, No. 4, 1—36).—Compounds of the type $[5NH_3PtX]Y_3$ have been obtained from ammonium chloroplatinate and anhydrous ammonia; interaction in aqueous solution takes place in the presence of ammonium carbonate or a soluble phosphate. Hydroxypentammine salts are formed by the interaction of alkali with chloropentammine salts. Evidence is adduced for the existence of the ion $[Pt,5NH_3,Cl]^{\cdots}$. The *compounds* $[5NH_3PtCl]ClSO_4$ and $[5NH_3PtCl]ClPtCl_6,2H_2O$ are described. Reduction with zinc and dilute hydrochloric acid yields salts of bivalent platinum with the loss of 1 mol. of ammonia. Soluble salts of the type $[5NH_3PtCl]X_3$ with potassium iodide form the *compound* $[4NH_3PtI_2]I_2$. *Bromopentammineplatinic* salts, $[5NH_3PtBr]X_3$, have been obtained. CHEMICAL ABSTRACTS.

Mononitrites of bivalent platinum. I. I. I. TSCHERNYAEV (Ann. inst. platine, 1926, No. 4, 243—275).—The base $[Pt(NH_3O)_4](OH)_2$ gives with 10% hydrobromic acid the *trans*-compound $[PtBr_2(NH_3O)_2],2H_2O$, whereas boiling hydrobromic acid (*d* 1·52) yields the compound $(NH_3O)_2PtBr_5$. *cis*- and *trans*-Dihydroxylaminoplatinous nitrite, and the oxalate (yielding with water or sulphuric acid the compound $[Pt(NH_3O)_4][Pt(C_2O_4)_2]$ and with hydrochloric acid the compound $[Pt(NH_3O)_4][PtCl_4]$), together with the *compounds* I (from *cis*-dihydroxylaminoplatinous nitrite and ammonia) and II (from *trans*-dihydroxylaminoplatinous nitrite and ammonia), were obtained.

(I.) $\left[\begin{matrix}NH_3O\\NH_3\end{matrix}Pt\begin{matrix}NH_2O\\NO_2\end{matrix}\right]$ $\left[\begin{matrix}NH_3\\NH_3O\end{matrix}Pt\begin{matrix}NH_2O\\NO_2\end{matrix}\right]$ (II.)

The compound II with hydrochloric acid gives *trans*-$[Pt(NH_3O)_2NO_2,NH_3]Cl$ (*chloroplatinite*). The compound I with hot hydrochloric acid gives III, which with water yields the compound $[Pt(NH_3O)(NH_3)(NO_2)(OH)]$, and on crystallisation from pyridine gives IV, which is undecomposed by acids :—

$\left[\begin{matrix}Cl\\NH_3O\end{matrix}Pt\begin{matrix}NH_3\\NO_2\end{matrix}\right]$ (III.) $\left[\begin{matrix}C_5H_5N\\NH_2O\end{matrix}Pt\begin{matrix}NO_2\\NH_3\end{matrix}\right]$ (IV.)

In I, II, and IV, the acid properties of hydroxylamine are increased by proximity of the nitrite group. *trans*-Diamminoplatinous nitrite with hydroxylamine hydrochloride gives nitrogen and *trans*-diamminoplatinous chloronitrite, a general method for obtaining *trans*-salts of the form (A=amine): $PtAA'ClNO_2$. *trans*-Diamminohydroxylaminonitritoplatinous nitrite gives a red chloroplatinite, the free base being soluble in water; the *cis*-compound gives a dark red chloroplatinite ($+4H_2O$), the free base being slightly soluble in water. The *trans*-compound $[Pt(C_5H_5N)NH_3(NO_2)_2]$, with hydroxylamine, yields compound V. The compound VI, with hydroxylamine,

(V.) $\left[\begin{matrix}NH_2O\\C_5H_5N\end{matrix}Pt\begin{matrix}NH_3\\NO_2\end{matrix}\right]NO_2$ $\left[\begin{matrix}Cl\\NH_3\end{matrix}Pt\begin{matrix}C_5H_5N\\NO_2\end{matrix}\right]$ (VI.

affords hydroxylamineamminopyridinonitritoplatinous chloride; an analogue of III, in which ammonia is replaced by pyridine, gives with ammonia a yellow gel (*chloroplatinite* VII), whereas III with pyridine and potassium chloroplatinite

$\left[\begin{matrix}NH_3\\NH_3O\end{matrix}Pt\begin{matrix}C_5H_5N\\NO_2\end{matrix}\right]_2PtCl_4$ (VII.)

(VIII.) $\left[\begin{matrix}C_5H_5N\\NH_3O\end{matrix}Pt\begin{matrix}NH_3\\NO_2\end{matrix}\right]_2PtCl_4,2H_2O$

yield VIII; hence the four co-ordinated groups are uniplanar. Complex *compounds* are produced by interaction of hydrazine sulphate with *trans*-diamminoplatinous nitrite and *trans*-hydroxylaminoamminoplatinous nitrite. The formation of the compounds en $Pt(NO_2)_2$ and [en $Pt(NH_3)(NO_2)$]OH from $Pt(NH_3)_2(NO_2)_2$ is recorded; the *trans*-compound $[Pt(NH_3)_2Cl(NO_2)]$, however, yields the compound IX.

$\left[\begin{matrix}NH_3\\NO_2\end{matrix}Pt\begin{matrix}en\\NH_3NH_3\end{matrix}Pt\begin{matrix}NH_3\\NO_2\end{matrix}\right]Cl_2$

(IX.)

The ethylenediamine–platinum ring is not formed instantaneously. An analogous dihydroxylamino-derivative was prepared.

The following *compounds* are mentioned : *cis*-$[Pt(NH_2O)_2(C_5H_5N)NO_2]NO_2$ (chloroplatinite), *trans*-$[Pt(NO_2)_2(C_5H_5N)(NH_3O)]$, *trans*-$[PtCl(NO_2)_2(NH_3)(NH_3O)]$, *trans*-$[Pt(NH_3)_2(C_5H_5N)(NO_2)]Cl$ (chloroplatinite); [en$Pt(NH_3)(NO_2)$]$PtCl_4$. The author has thus obtained the first instances of isomerides with 3 and 4 substituents linked to platinum; Werner's assumptions are confirmed, the stability of the nitro-groups and the mobility of chlorine are established, the similarity of complexes to metals is instanced, and cases are disclosed in which cycles are not formed with ethylenediamine or oxalate groups. CHEMICAL ABSTRACTS.

Complex sulpho-acids of platinum. L. A. TSCHUGAEV and S. E. KRASIKOV (Ann. inst. platine, 1926, No. 4, 44—47).—By passing sulphur dioxide into a hot solution of the compound $[Pt4NH_3]Cl$, the *compound* $[Pt,2NH_3,Cl,SO_3]_2[Pt4NH_3]$ is produced, with transient formation of the *compound* $[Pt4NH_3][Pt2NH_3(SO_3)_2]$. Both are *trans*-compounds. CHEMICAL ABSTRACTS.

Quantitative spectral analysis. J. ŠEBOR (Chem. Listy, 1927, 21, 415—421).—The points of maximum and minimum absorption of light in the visible spectrum by solutions of a number of dyes vary according to the concentration of the dye. This is proposed to be used for the determination of such dyes. R. TRUSZKOWSKI.

Calculation of gas analyses. BRUTZKUS (Compt. rend., 1927, **185**, 861—863).—In a gas mixture which undergoes a chemical reaction in which the quantities of the constituents are increased or decreased, determinations of the percentage composition before and after the reaction will not give the amounts of the changes. If, however, one of the constituents takes no part in the reaction, any change in the proportion of it present in the mixture is due only to the change in volume of the latter. Hence, by reducing the quantity of each gas present to the same volume as that of the inert gas, the quantity remaining after the operation, and hence the gain or loss, may be determined in each case. If necessary an inert gas may be added to the mixture. J. GRANT.

Electrolytic analysis with a dropping mercury cathode. J. HEYROVSKY (Bull. Soc. chim., 1927, [iv], 41, 1224—1241).—A general account, with bibliography, of the above analytical method as developed by the author, his co-workers, and others (cf. A., 1926, 590, 1184, etc.) S. K. TWEEDY.

Spot analysis. N. A. TANANAEV (Z. anal. Chem., 1927, 72, 155—157).—Polemical, and a claim for partial priority. F. S. HAWKINS.

Microchemical volumetric analysis. I. II. Separation of small quantities of barium and calcium. W. GEILMANN and R. HOLTJE (Z. anorg. Chem., 1927, 167, 113—127, 128—136).—I. The relative merits of various types of burettes and other apparatus for micro-analysis are discussed. The accuracy of titration of chromate solutions with sodium thiosulphate, of permanganate with sodium oxalate, and of potassium hydroxide with hydrochloric acid has been determined at concentrations between 0·1*N* and 0·001*N*.

II. Quantities of calcium less than 5 mg. may be determined by precipitation with sodium oxalate solution, addition of a slight excess of 0·02*N*-potassium permanganate to the centrifuged solution, and titration with 0·02*N*-sodium thiosulphate. The direct determination, made by dissolving the washed calcium oxalate in dilute sulphuric acid, adding a slight excess of permanganate, and titrating with 0·02*N*-sodium thiosulphate, gives more accurate results, the error when about 5 mg. of calcium is present being ±0·015 mg. Barium, in quantities of the order of 5 mg., may be determined with accuracy by precipitation ith an excess of standard potassium chromate solution and titration of the excess with 0·01*N*-sodium thiosulphate. Direct determination of the barium chromate gives inaccurate results. If, however, a known portion (as much as possible) of the centrifuged solution is withdrawn, the remaining solution together with the precipitate may be treated with hydrochloric acid and potassium iodide and titrated with 0·02*N*-thiosulphate solution, whereby 5 mg. of barium may be determined with an error of ±0·01 mg. In the portion of solution withdrawn calcium may be determined by either of the methods given above. H. F. GILLBE.

Vacuum flask for conductivity determination and for conductometric analysis. I. REMESOV (Biochem. Z., 1927, 189, 33—38).—A new vacuum flask is described and used for the determination of conductivity at constant temperatures without the use of a thermostat and for carrying out conductometric titrations. P. W. CLUTTERBUCK.

Use of mixed indicators in acidimetry and alkalimetry. I. M. KOLTHOFF (Biochem. Z., 1927, 189, 26—32).—A series of 25 mixed indicators is given showing change of colour at p_H ranging from 3·25 to 10·8 and their use is discussed.
P. W. CLUTTERBUCK.

Further buffer solutions for the alkaline range. I. M. KOLTHOFF and J. J. VLEESCHHOUWER (Biochem. 1927, 189, 191—193, and Chem. Weekblad, 1927, 24, 526).—Tables indicate the composition of solutions of p_H 9·2—11·0 obtained with mixtures of 0·05*M*-sodium hydroxide with 0·05*M*-borax, of p_H 11·0—12·0 with mixtures of 0·1*M*-disodium hydrogen phosphate and 0·1*N*-sodium hydroxide, and of p_H 6—9·2 with mixtures of 0·1*M*-potassium dihydrogen phosphate with 0·05*M*-borax. P. W. CLUTTERBUCK.

Water analysis. W. R. ATKIN and D. BURTON.—See B., 1927, 830.

Determination of water in mixtures of benzene and alcohol. D. PETERS.—See B., 1927, 858.

Adsorption method of titration. R. H. BURSCHTEIN (J. Russ. Phys. Chem. Soc., 1927, 59, 521—536).—The adsorption method of titrating silver and halogen ions in the presence of organic dyes according to Fajans is discussed, and the mechanism explained on the theory of electrical adsorption. The colloidal particles of silver halide when once the equivalent point is passed adsorb silver or halogen ions, depending on which is in excess, and form with acid or basic dyes highly-coloured complexes, markedly different from the original dye. To give a sharp colour change, the silver halide–dye complex must be more soluble than the silver halide itself. Mixtures of halides can be titrated by choosing a mixture of dyes of suitable solubility. Thus potassium chloride and potassium iodide can be determined with sodium fluorescein, which gives a change from greenish-yellow to orange-red with the chloride, and rose-Bengal, which changes from bright red to purple with the iodide. The accuracy of the method is diminished by the coagulation of the silver halide sol near the end-point, and the action of such protective colloids as gelatin and egg-albumin was consequently investigated. No marked improvement results, but the concentration of the protective colloid does not affect the accuracy, so that the method can be employed in biochemical analysis, where small concentrations of halogen ions often exist in the presence of large amounts of colloidal proteins. The dyes employed belonged to the fluorescein group (acid) and to the rhodamine and triphenylmethane groups (basic).

The method can be extended to the determination of lead salts by means of potassium ferrocyanide, if mordant dyes, such as sodium alizarinsulphonate, which form brilliantly coloured "lakes" with the colloidal lead complex, are used.

Salts of weak acids cannot be determined, as the hydroxyl ions set free through hydrolysis destroy the colour reaction.

The method, which compares favourably with all other existing methods, is being extended to zinc, mercury, and copper. M. ZVEGINTZOV.

Colorimetric determination of perchlorate in the presence of chlorate. O. S. FEDOROVA (J. Russ. Phys. Chem. Soc., 1927, 59, 509—520).—A criticism and an extension of Hahn's method (B., 1926, 404) of determining perchlorates directly in the presence of chlorates by means of methylene-blue.

Solutions of perchlorates (more concentrated than 0·01%) give a green, bluish-violet, or deep purple precipitate, depending on the concentration. With solutions containing from 0·0008% to 0·01% pale blue to bright reddish-violet colorations are obtained in the presence of a concentrated solution of zinc

sulphate, which greatly increases the sensitiveness of the methylene-blue. Chlorates also give a colour reaction with the dye, and their action must be neutralised by the addition of sodium nitrate solution.

A colorimetric table for varying concentrations of perchlorate is provided, and the amounts of zinc sulphate and sodium nitrate necessary to obtain the desired effect in the presence of different amounts of chlorates are determined. The influence of chlorides on the reaction is also investigated. M. Zvegintzov.

Determination of small quantities of iodine. P. A. Meerburg (Z. physikal. Chem., 1927, **130**, 105—108).—There is no satisfactory method of determining separately the organic and inorganic iodine in water, Fellenberg's method (this vol., 692) giving low results for the inorganic and high for the organic iodine. Total iodine is determined as follows: 3—6 litres of water together with a few c.c. of concentrated potassium carbonate solution are evaporated to dryness in a platinum basin and extracted with alcohol; the residue is heated to redness, moistened with potassium carbonate solution, and extracted with alcohol. The united extracts are evaporated, cautiously heated, extracted three times with alcohol, and the combined extracts evaporated to dryness, the residue being taken up in 1 c.c. of water. The iodine is then determined colorimetrically. S. J. Gregg.

Determination of iodide in mixtures of halides. H. Baines.—See B., 1927, 813.

Determination of sulphide, thiosulphate, and sulphur in insoluble carbonates. H. Brintzinger and F. Rodis.—See B., 1927, 841.

Determination of sulphate in solutions of tervalent chromium. M. N. Pavlov (Ukraine Chem. J., 1926, 2, 353—354).—Precipitation of sulphate in the usual way as barium sulphate is inaccurate in presence of tervalent chromium. Chromium is therefore removed as hydroxide by addition of magnesium oxide or carbonate at the ordinary temperature, the precipitate is filtered off, washed, and the filtrate used for the determination. A. Ratcliffe.

Examination of naturally occurring gases. V. F. Henrich and W. Herold (Ber., 1927, **60**, [*B*], 2047—2053; cf. A., 1920, ii, 767).—Improvements in the apparatus described previously are effected by placing the mixture of calcium and sodium used for the absorption of nitrogen in an iron (instead of glass) tube placed in a protecting tube of quartz or porcelain heated in an electric furnace. The open pneumatic trough is replaced by a eudiometer and levelling tube connected directly to the delivery tube of the mercury pump. Analyses of several naturally occurring gases are recorded and also of gases obtained by heating tectites at about 1000°. H. Wren.

Improved micro-Dumas determination of nitrogen. S. Ogawa (Sci. Rep. Tohoku Imp. Univ., 1927, **16**, 667—670).—The apparatus for the micro-determination of nitrogen by the methods of Pregl and Dubsky has been slightly modified in order to facilitate the removal of oxygen from the apparatus before the combustion is commenced. R. Cuthill.

Detection of nitric acid with ferrous sulphate. P. G. Popov (Ukraine Chem. J., 1926, 2, 391—394.)—The sensitivity of the brown ring test, and the difficulties arising when nitrites present are destroyed by the addition of carbamide, are discussed. A. Ratcliffe.

Reactions of nitrous acid. J. V. Dubsky and A. Okac (Publ. Fac. Sci. Univ. Masaryk, 1927, No. 83, 1—84).—The changes in colour produced in dyes by further diazotisation and coupling with a large number of reagents under specified conditions have been studied, and exhaustive tables have been drawn up to show the colour changes and the sensitiveness of the various reactions. Changes of colour from yellows and reds to reds and blues are more readily observed and measured than the development of the original yellow or red coloration, whilst the stability of the colours during treatment makes the tests more definite. The possibility of two colour changes in some cases, one on diazotisation and another on coupling, is a further advantage of this method of testing. Some 600 substances have been examined for this purpose, and those suitable for detection of nitrites are enumerated. S. I. Levy.

Colorimetric determination of minute quantities of dissolved phosphorus in oil. C. Stich.—See B., 1927, 851.

Use of amalgams in volumetric analysis. VII. Determination of phosphoric acid. S. Hakomori (Sci. Rep. Tohoku Imp. Univ., 1927, **16**, 719—722; cf. A., 1922, ii, 721).—Ammonium phosphomolybdate, precipitated by Woy's method, is dissolved in 2*N*-ammonia solution, reduced with 200 g. of zinc amalgam or cadmium amalgam and an amount of 1 : 1-sulphuric acid equal to 0·1 of the volume of the solution, and finally titrated with permanganate. The results are about 1% higher than those of the magnesium pyrophosphate method. R. Cuthill.

Simple mercury cathode for arsenic determinations. F. S. Aumonier.—See B., 1927, 813.

Volumetric determination of antimony and arsenic. P. E. Winkler (Bull. Soc. chim. Belg., 1927, **36**, 491—501).—Although the equilibrium $M^{\cdots\cdots}+2I' \rightarrow M^{\cdots}+I_2$, where M represents antimony or arsenic, is completely displaced to the right in media which are sufficiently acid, direct titration of the liberated iodine is not possible because of oxidation of hydriodic acid by the air. Accurate results are, however, obtained by passing a stream of carbon dioxide through the boiling solution until all the iodine is expelled and after neutralisation and addition of sodium hydrogen carbonate, titrating with a solution of iodine.

For antimony the precipitated sulphide is dissolved in a mixture of 10 c.c. of 20% tartaric acid solution with 20 c.c. of 20% sodium hydroxide solution and 20 c.c. of hydrogen peroxide (20 vol.). The resulting solution is boiled for about 20 min., neutralised with hydrochloric acid, and diluted to 100 c.c. After addition of hydrochloric acid and potassium iodide, and starch, the iodine is removed. The cooled solution is neutralised (methyl-orange) with sodium carbonate and titrated, after addition of sodium

ydrogen carbonate, with a standard solution of odine.

Arsenic sulphide is dissolved in a mixture of 20 c.c. of 20% sodium hydroxide solution and 20 c.c. of hydrogen peroxide (20 vol.) and subsequent neutralsation is effected by sulphuric acid. Reduction to he arsenious state is effected with sulphuric acid, hydrochloric acid, and potassium iodide.

J. S. CARTER.

Determination of small quantities of carbon onoxide. D. STAVORINUS.—See B., 1927, 834.

Determination of carbon monoxide, hydrogen, and methane in air containing ethylene. J. THORBURN.—See B., 1927, 803.

Determination of carbonic acid by precipitation as barium carbonate and titration of the excess of alkali. J. LINDNER (Z. anal. Chem., 1927, **72**, 135—154).—Consistently high results obtained by this method are not due to the precipitation of basic carbonates, but chiefly to the presence of silica dissolved out of the glass. It exists as a colloidal solution which slowly reacts with the baryta and precipitates barium silicate from the solution. The presence of magnesium salts also causes a considerable positive error, and calcium salts act similarly if present in large quantities. In all cases, owing to the adsorption of alkali by the precipitate, a more accurate titre is obtained by warming the solution at the end of the titration. The determination of a mixture of carbonate and hydroxide by Winkler's method is also affected by the presence of silica.

F. S. HAWKINS.

Electrolytic alkali determination in Drossbach's apparatus. H. GINSBERG (Z. anorg. Chem., 1927, **167**, 183—184).—Accurate results may be obtained by employing the correct current and voltage, pure mercury, and polished nickel wire. The distance between the anode and the mercury surface should not exceed 1—2 cm. H. F. GILLBE.

Determination of lithium in scleron and similar aluminium alloys. E. SCHURMANN and W. BOHM.—See B., 1927, 818.

Micro-chemical determination of rubidium. E. S. BURKSER and S. G. RUBLEV (Ukraine Chem. J., 1926, **2**, 355—364).—Rubidium (up to 0·01 γ) is detected by precipitation with a specially prepared solution of silver iodide, aurous iodide, and auric iodide in hydriodic acid. The black crystals so formed consist of the compound $3AuI,AuI_3,3RbI,2AgI$ or $3AuI,AuI_3,4RbI,AgI$, and their formation is neither hindered nor masked by the presence of even fairly large quantities of sodium, potassium, or ammonium salts. A. RATCLIFFE.

Gravimetric determination of calcium. A. FRANKE and R. DWORZAK (Z. anal. Chem., 1927, **72**, 129—134).—If calcium is determined by precipitating as oxalate and igniting the precipitate, the mass gains in weight when kept in the desiccator. The increase is very marked when the drying agent is calcium chloride mixed with soda-lime, or calcium chloride alone, but is smaller when phosphorus pentoxide or well-burnt lime is used, and is therefore due to the absorption of moisture from the drying agent. The easiest and most accurate method of determination is to precipitate the calcium as oxalate, and weigh it as this salt after drying for 5 hrs. at 100—105°. Otherwise the oxalate, contained in a sintered porcelain crucible, should be ignited at 1000° in an electric furnace and cooled in a desiccator over well-burnt lime. F. S. HAWKINS.

Detection of magnesium, especially in rocks, by means of diphenylcarbazide. F. FEIGL (Z. anal. Chem., 1927, **72**, 113—119).—Magnesium ammonium phosphate or carbonate and all magnesium salts which can be decomposed by treatment with alkali hydroxide are coloured rose-violet when treated with an alcoholic solution of diphenylcarbazide. Magnesite is coloured immediately by the reagent, whereas dolomite is not, suggesting that dolomite is a calcium magnesocarbonate. To detect magnesia in a carbonate rock the powdered substance is boiled for 2—3 min. with a 5% alcoholic solution of the reagent, the liquid decanted, and the substance boiled repeatedly with water until the latter ceases to become coloured; if the residue is coloured magnesia is present. In the case of a negative result a second portion of the rock is heated to redness, cooled, and subjected to the test; if a positive result is obtained the rock contains dolomite. A. R. POWELL.

Detection of lead by the spot method. N. A. TANANAEV (Z. anorg. Chem., 1927, **167**, 81—86).—The reagent is prepared by adding to a concentrated stannous chloride solution sufficient potassium iodide solution to cause the liquid to set to a semi-solid on shaking; a concentrated solution of cadmium nitrate is then added drop by drop until a clear solution is obtained. Either hydrochloric acid or potassium thiocyanate may be used in place of cadmium nitrate but the reagent is less sensitive. The solution oxidises rapidly in the air, and should therefore be freshly prepared for the test. On addition of a solution containing lead ions an orange or a red precipitate is produced, which contains lead, tin, and iodine. If a drop of the solution to be tested is placed on filter-paper and treated with a drop of dilute sulphuric acid, lead, if present, is converted into sulphate, and on washing the spot with a little sulphuric acid from a capillary tube other metals present are carried to the outer edge of the spot. Addition of a drop of the reagent to the centre of the spot produces an orange stain, whilst if both lead and bismuth are present the stain is brown. H. F. GILLBE.

Reaction of aluminium with the ammonium salt of aurintricarboxylic acid ["aluminon"] under different experimental conditions, and its application to the colorimetric determination of aluminium in water. J. H. YOE and W. L. HILL (J. Amer. Chem. Soc., 1927, **49**, 2395—2407).—The use of aluminon as an analytical reagent for aluminium is investigated, including the effect of ageing (decrease of colour intensity with time), the quantities and concentrations of the reagents, the conditions of lake formation, and the influence of foreign ions. The effect of ageing is practically the same in both the light and the dark; the colour intensity passes through a maximum with increasing concentration of hydrochloric acid. In colorimetric analysis iron

must previously be separated from the aluminium. The lower limit of the test is 0·002 mg. By stabilising the lake with a protective colloid (*e.g.*, starch) up to 3 mg. of aluminium may be determined. A standard colorimetric method is developed and applied to the determination of aluminium in potable water.

S. K. TWEEDY.

"Potassium chlorate method" of determining manganese. M. MARQUEYROL and L. TOQUET (Ann. Chim. analyt., 1927, [ii], 9, 289—295).—Errors arising in the determination of manganese by oxidation in concentrated nitric acid solution with potassium chlorate are attributed to the solubility of the resulting manganese dioxide in nitric acid. The presence of potassium chlorate diminishes this solubility considerably; less chlorate is required for concentrated than for more dilute nitric acid, although the solubility of manganese dioxide in nitric acid alone increases with the concentration. The procedure should therefore involve operation at a temperature sufficiently low to prevent the disappearance of the chlorate from solution, and the use of a small amount of potassium chlorate and of highly concentrated nitric acid. G. A. ELLIOTT.

Determination of cobalt and other alloyed elements in cobalt, cobalt steel, and high-speed tool steels. E. SCHIFFER.—See B., 1927, 845.

Volumetric determination of tin. B. S. EVANS (Analyst, 1927, 52, 590—591).—The solution of tin in about 250 c.c. of dilute hydrochloric acid and a strip of sheet lead (about 20×2 cm. bent into a coil) are placed in a conical flask carrying a tube bent twice at right angles capable of being moved vertically in the stopper, another tube connected to a Kipp apparatus, and a separating funnel. Before inserting the stopper the doubly bent tube is drawn up and the funnel tap closed. A steady stream of carbon dioxide is then passed through the solution, which is boiled for 1 hr.; the outlet tube is then closed and the flask cooled under pressure from the Kipp apparatus. The outlet tube is pushed down into the solution and its free end placed in a flask containing 20 g. of sodium oxalate and a measured excess of 0·1*N*-iodine solution. The liquid is then blown over under the carbon dioxide pressure and 50 c.c. of rinsing water are passed through. The unreduced iodine is titrated with sodium thiosulphate.

D. G. HEWER.

Analysis of niobium and tungsten groups. I. WADA and S. KATO (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1927, 6, 227—263).—The original solid is dissolved by heating with nitric acid, followed by similar treatment with hydrofluoric acid. The latter solution contains the niobium and tungsten groups, and is acidified with sulphuric acid and treated with hydrogen sulphide to remove arsenic, antimony, selenium, tellurium, and part of the molybdenum. Ammonia and ammonium sulphide are added to the residual solution, thereby precipitating the niobium group, together with titanium, zirconium, and iron, and leaving the tungsten group in solution. The precipitate is boiled with sodium salicylate, when any titanium, iron, and vanadium present dissolves, leaving a residue of niobium, zirconium and tantalum; this is dissolved in hydrofluoric acid and tantalum, together with part of the zirconium, is precipitated as the potassium double fluoride. The tantalum is then separated from zirconium by hydrolysis of a sulphuric acid solution, and any zirconium left in solution with the niobium is removed by precipitation as its basic phosphate. To effect the separation of tungsten, the solution left after treatment with alkaline ammonium sulphide is acidified with hydrochloric acid, and the precipitate is evaporated with nitric acid. In the presence of tin or tungsten a residue insoluble in water is obtained. The residue is dissolved again in ammonium sulphide solution; on addition of excess of hydrochloric acid, tungsten alone is precipitated. F. S. HAWKINS.

Separation of platinum and iridium. B. G. KARPOV (Ann. inst. platine, 1926, No. 4, 360—363).—When a mixture of ammonium chloroplatinate and chloroiridate in aqueous solution is reduced at 100° with mercury, the precipitate on ignition yields platinum containing 0·04—0·11% of iridium; the iridium is obtained as oxide from the liquid and washings by evaporation with nitric acid and conversion into the tartrate. CHEMICAL ABSTRACTS.

Determination of platinum, palladium, and rhodium. V. N. IVANOV (Ann. inst. platine, 1926, No. 4, 331—338).—Thiocyanates precipitate the *compound* $Pd_3S_2(CSNH_2)_2$ from solutions (1% or less) of palladium salts; platinum salts and sodium thiocyanate yield *platinous thiocyanate*, hydrolysed by boiling water to the *compound* $Pt_4(OH)_4S(CSNH_2)_2$, whereby platinum may be rapidly determined; the presence of copper or iron produces slightly high results. Osmium and ruthenium do not give similar compounds, iridium gives an unsuitable precipitate, but palladium and rhodium behave similarly to platinum. When heated, the compounds yield the respective metals. CHEMICAL ABSTRACTS.

Rapid determination of palladium in platinum. O. E. ZVJAGINSTSEV (Ann. inst. platine, 1926, 364—366).—Solutions (1%) of palladium and platinum salts, respectively, give reddish-brown and dark brown colorations with potassium iodide. The solutions, which must be slightly acid, can, however, be compared colorimetrically 30—40 min. after preparation. The method is accurate to 0·0002 g. of palladium in 1 g. of platinum when 1 c.c. of potassium iodide solution (1 in 10^3) is used with 10 c.c. of the platinum solution. CHEMICAL ABSTRACTS.

Detection of iridium, and colorimetric determination of small quantities of iridium in platinum. V. G. CHLOPIN (Ann. inst. platine, 1926, No. 4, 324—330).—Quadrivalent iridium in aqueous solution (0·001%) gives with benzidine a sky-blue coloration; other ions react as follows: $Pt^{\cdot\cdot}$ none, concentrated $Pt^{\cdot\cdot\cdot\cdot}$ rose precipitate, $Ir^{\cdot\cdot\cdot}$ green, $Rh^{\cdot\cdot\cdot}$ rose-yellow precipitate, $Pd^{\cdot\cdot}$ none, $Os^{\cdot\cdot\cdot\cdot}$ yellow precipitate. Osmic acid gives a blue colour.

CHEMICAL ABSTRACTS.

Ruthenium. XI. Volumetric determination of ruthenium. J. L. HOWE (J. Amer. Chem. Soc., 1927, 49, 2393—2395).—Volatile ruthenium tetroxide is condensed in concentrated hydrochloric acid, the

solution is boiled and then standard stannous chloride solution is added, the excess being determined by titration with iodine solution. The amount of stannous chloride required is always somewhat less than that required theoretically for reducing the ruthenium to the tervalent state, so that the method is applicable only when small amounts of ruthenium are present or when only an approximate result is required. S. K. TWEEDY.

Light source for continuous spectrum. V. D. SNYDER (J. Amer. Chem. Soc., 1927, 49, 2510—2511).—A lamp is described and figured in which a Tesla spark is maintained under water. S. K. TWEEDY.

Nickel electrical resistance thermometers. W. DEL REGNO (Rend. Accad. Sci. fis. mat. Napoli, 1926, [iii], 32, 194—201).—Platinum can be replaced by nickel in electrical resistance thermometers for measuring temperature differences below 500°, and for measuring temperatures directly below 360°, with a notable increase in sensitivity, nickel having a high thermal coefficient of electrical resistance. The latter may be expressed by $R_t=R_0+at+bt^2+ct^3$, where a, b, and c are constants characteristic of the threads employed, and have the respective values in a sample examined of $3{\cdot}085\times10^{-3}$, $7{\cdot}7\times10^{-7}$, and $1{\cdot}06\times10^{-8}$. The oxidation of nickel is negligible below 500°, the tensile strength is higher than that of platinum, the change of resistance with temperature shows no hysteresis, and the influence of traces of impurities is, in contrast with platinum, very slight. E. W. WIGNALL.

Copper–constantan thermocouples and the hydrogen thermometer compared from 15° to 283° Abs. W. F. GIAUQUE, R. M. BUFFINGTON, and W. A. SCHULZE (J. Amer. Chem. Soc., 1927, 49, 2343—2354).—The construction of a sensitive copper–constantan thermocouple is described and a method of testing for inhomogeneities in metallic wires intended for use in such low-temperature couples is outlined. A hydrogen thermometer is also described which can be maintained at any temperature between the b. p. of hydrogen and 290° Abs. to within 0·01°; it is designed for the calibration of thermocouples. Calibrations below 25° Abs. are in error, presumably because of adsorption of hydrogen by the glass thermometer bulb (cf. following abstract). The calibrated thermocouple gives 234·18° Abs. for the m. p. of mercury, and the vapour pressure of hydrogen chloride, measured with reference to such a thermocouple as a temperature standard, is stated to agree with the precision measurements of Henning and Stock to 0·01—0·02° (Z. Physik, 1921, 4, 226). S. K. TWEEDY.

Hydrogen gas thermometer compared with the oxygen and hydrogen vapour-pressure thermometers by means of a copper–constantan thermocouple. W. F. GIAUQUE, H. L. JOHNSTON, and K. K. KELLEY (J. Amer. Chem. Soc., 1927, 49, 2367—2372).—A copper–constantan thermocouple, calibrated as previously described (cf. preceding abstract), was compared with the Leiden temperature scales of the oxygen and the hydrogen vapour-pressure thermometers. Complete agreement was found with the former scale; a discrepancy below 25° Abs. with the latter scale indicated adsorption of gas at these temperatures in the hydrogen thermometer used for calibrating the couple. The triple point pressure of hydrogen is 5·370 international cm. of mercury, and the temperature is 13·92° Abs. The equation $\log p(\text{cm.})=-39{\cdot}2/T+2{\cdot}70\log T+0{\cdot}4584$ is derived for the vapour pressure of solid hydrogen. S. K. TWEEDY.

Adiabatic microcalorimeter for radiological researches. W. SWIENTOSLAWSKI and (MLLE.) A. DORABIALSKA (Compt. rend., 1927, 185, 763—765).—The apparatus consists of a thick copper container, in which the calorimeter proper is suspended, immersed in a controlled thermostat. The alteration in temperature of the inner vessel, owing to the evolution of heat by the substance under investigation, is registered by means of a galvanometer connected with a thermocouple, and is balanced by raising the temperature of the thermostat so that the needle of the galvanometer is always at the zero point. The apparatus has a degree of accuracy of 0·7 for radiological work, and may be used to measure any continuous thermal effect. J. GRANT.

Determination of specific gravity of small amounts of liquids and solids. P. L. DU NOUY (J. Biol. Chem., 1927, 74, 443—448).—By means of a modified form of the author's torsion balance for the determination of surface tension the specific gravity of 1 c.c. of a liquid or of 0·1 g. of a solid can be determined to the third place of decimals. C. R. HARINGTON.

Thermo-hydrometer. A. S. WEBB (J. S. African Chem. Inst., 1927, 10, 14—15).—An ordinary hydrometer is modified by filling the large bulb with a mixture of alcohol and water coloured with methyl-red. This solution, rising or falling in the stem according to the temperature of the liquid in which it is floating, indicates changes of concentration of liquids regardless of temperature changes. The mixture having the correct coefficient of expansion is found by trial. In practice, a constant concentration at varying temperatures may be secured by maintaining the surface of the filling liquid level with that of the solution being prepared. R. A. PRATT.

Vacuum distillation technique. M. DEMONT-VIGNIER (Bull. Soc. chim., 1927, [iv], 41, 1244—1251).—A simple mercury-vapour "ejector" which is not fragile and is capable of producing a stable vacuum down to 1 mm. (? 0·1 mm.) with a water backing-pump is described. The degree of evacuation is controlled by the rate of heating of the mercury. A mercury-vapour pump of similar design is figured. An accurate, compact form of the McLeod gauge, capable of measuring pressures between 0·1 and 20 mm., is also described. S. K. TWEEDY.

Burette for the accurate measurement of gas volumes without gas connexion to a compensator. E. R. WEAVER and M. SHEPHERD (U.S. Bur. Stand., Sci. Papers No. 559, 1927, 22, 375—382).—A gas burette embodying a novel compensator to eliminate errors due to diffusion of gas into the manometer is described and illustrated. The burette

proper consists of five 20 c.c. pear-shaped bulbs forming the main stem and a graduated side tube for measuring fractional parts of the bulbs. The lower end of the side tube is connected with a second parallel tube which acts as a mercury seal to the manometer proper and as a balancing intermediate manometer. All the mercury levels are read by means of vernier scales, so that an accuracy of 0·01 c.c. is readily obtained. A. R. Powell.

Colorimeter for precise matching of solutions in Nessler tubes. J. H. Yoe (Ind. Eng. Chem., 1927, **19**, 1131).—Light reflected by a mirror passes upwards through the two tubes for comparison and impinges on two mirrors set at 45°, one of which is half the width of the other. The light from each tube thus occupies half the field as seen through an observation tube with eyepiece and diaphragm. By proportioning these correctly the interference of light reflected from the sides of the Nessler tubes is eliminated. C. Irwin.

Trace of an ancient theory in a modern principle. C. M. van Deventer (Z. physikal. Chem., 1927, **130**, 33—38).—The basic principle underlying the principles of Le Chatelier and van 't Hoff was recognised by Aristotle and Theophrastes. S. J. Gregg.

History of witherite. G. Fowles (Chem. News, 1927, **135**, 309—310).—Witherite, discovered by Withering and described by him (Phil. Trans., 1784, **74**, 293) as a compound of " terra ponderosa " (barium oxide) and " fixed air " (carbon dioxide), was obtained from a lead mine at Alston Moor, Cumberland, whereas the origin of the specimen is variously described in the literature as Scotland and Lancashire. Withering's investigations on this " terra ponderosa aerata " are briefly described. R. A. Pratt.

Mineralogical Chemistry.

Variations in the ozone content of the atmosphere. J. Cabannes and J. Dufay (J. Phys. Radium, 1927, [vi], **8**, 353—364).—Seasonal changes in the thickness of the stratum of ozone in the upper atmosphere were observed at stations at Mount Wilson and at Calama (Chile). The history of the variations in the quantity of ozone in the atmosphere is partly recounted for the period 1908—1920 through a consideration of the monthly means of the factors of transparency of the atmosphere for chosen wavelengths. The results obtained at Mount Wilson are compared with the work of Dobson and Harrison at Oxford. An attempt is made to correlate the results with solar activity, but no relationship is found to exist between the monthly values of the thickness of ozone and the number of sunspots seen during the same months, or between these values and the solar constant, thus confirming the records of Dobson and Harrison. The thickness of the ozone stratum is subject to seasonal variations and is to a certain extent associated with local climatic conditions. R. A. Pratt.

Gases of the Mt. Pelee lavas of 1902. E. S. Shepherd and H. E. Merwin (J. Geol., 1927, **35**, 97—116).—Detailed analyses are given of five specimens of hypersthene-andesite and of the gases evolved when chips are heated in a vacuum. The volatile matter includes carbon dioxide, carbon monoxide, hydrogen, nitrogen, argon, sulphur, chlorine, fluorine, and water, and the amount ranges from 4·3 to 26·5 c.c. (at 1200° and 760 mm.) per g. of rock, being higher in the glassy varieties. On the average, 80% consists of water, and 9% of carbon dioxide. Analysis of the finely-powdered rock may show as much as ten times as much water as the rock actually contains. The formation of pumice and the glassy surface of " bread-crust " bombs is discussed. L. J. Spencer.

Yellow incrustation of the Vesuvian lava of [the eruption of] 1631. F. Zambonini and G. Carobbi (Rend. Accad. Sci. fis. mat. Napoli, 1927, [iii], **32**, 124).—The " vesbium " thought by Scacchi to be present in lava from the Vesuvian eruption of 1631 is vanadium. Vesbina has the composition $(Cu,Pb)_3(VO_4)_3,Cu(OH)_2,5H_2O$, in which lead is also partly replaced by rare-earth metals, including lanthanum, cerium, neodymium, yttrium, and erbium. Vesbina was formed by the action of water on the cooling lava. E. W. Wignall.

Pyromorphite from Leadhills, Lanarkshire, Scotland, and mimetite from Santa Eulalia Chihuahua, Mexico. G. Carobbi (Rend. Accad. Sci. fis. mat. Napoli, 1927, [iii], **32**, 54—69).—The presence of chromium partly, at least, as lead chromate in pyromorphite from Leadhills, Lanarkshire, has been proved and also of manganese, calcium, strontium, barium, as well as cerium, lanthanum, neodymium, yttrium, europium, gadolinium, dysprosium, and erbium. The spectrograph indicates the presence of traces of ytterbium and holmium.

In mimetite from Santa Eulalia, chromium, manganese, zinc, calcium, barium, and strontium have been found. Spectroscopic examination indicates the complete absence of the rare earths. M. Carlton.

Composition and properties of rodonites. P. Aloisi (Atti R. Accad. Lincei, 1927, [vi], **5**, 1017—1021).—Crystallographic and optical characteristics of three samples of rodonite of different origin and composition are discussed with reference to the relationship between these properties and the composition of the mineral. R. W. Lunt.

Metaxite [serpentine] from Liubotina, Banat. M. Savul (Bull. Sci. Acad. Roumaine, 1927, **10**, No. 8—9, 32—35).—The dark-green serpentine, derived from gabbro, readily breaks up into columns and grinds to fine fibres. On account of the columnar structure it is referred to the variety metaxite: d 2·618, H 3—4, n 1·565, $\gamma-\alpha$ <0·008. The fibres give straight extinction with positive elongation. Analysis gave: SiO_2 41·69, TiO_2 nil, Al_2O_3 2·08,

Fe_2O_3 1·48, Cr_2O_3 0·006, FeO 4·31, MnO trace, MgO 37·40, CaO nil, H_2O (−110°) 0·48, H_2O (+110°) 12·34, total 99·786. The serpentine is veined with aragonite. The frequent presence of aragonite, rather than calcite, in serpentines is attributed to the presence of magnesia in the solutions. L. J. SPENCER.

"Blythite" and the manganese garnet from Amelia, Virginia. E. V. SHANNON (J. Wash. Acad. Sci., 1927, **17**, 444—452).—To explain the composition of some manganese garnets Fermor (Rec. Geol. Surv. India, 1926, **59**, 191) has assumed the presence of the molecule $3MnO,Mn_2O_3,3SiO_2$, which he termed "blythite." A new analysis of the reddish amber-coloured garnet (d 4·153, n 1·794) from Amelia, Virginia, gave: SiO_2 35·76, TiO_2 trace, Al_2O_3 17·38, Fe_2O_3 0·92, FeO 4·90 MnO 37·98, MgO 0·22, CaO 1·66, H_2O 0·58, total 99·40. Agreement with the garnet formula is obtained if the manganese is reckoned as MnO 34·86 and Mn_2O_3 3·47%. The composition then corresponds with spessartine 70·41, "blythite" 12·13, almandine 11·47, andradite 3·05, grossular 1·81, pyrope 0·81%. The existence of the "blythite" molecule could, however, only be established if a trustworthy method were available for the determination of manganic manganese in garnet. The low alumina and high manganese oxide shown in an earlier analysis of the Amelia garnet is evidently due to the faulty precipitation of alumina as acetate. L. J. SPENCER.

Structure of the orthoclase molecule. O. K. BOTWINKIN (Z. anorg. Chem., 1927, **167**, 190—192).—The orthoclase molecule is very stable towards water and aqueous solutions of carbon dioxide, although with rise of temperature some decomposition occurs. Increase of pressure up to 120 atm. has but little influence on the amount of decomposition. H. F. GILLBE.

Analyses of three Australian rocks. M. AUROUSSEAU (Proc. Linnean Soc. N.S. Wales, 1926, **51**, 614—626).—Detailed analyses are given of nepheline-basanite (previously described as fayalite-basalt and melilite-basalt) from Tasmania, a micrographic granite from New South Wales, and an amphibolite from Western Australia. The chemical composition of the granite as deduced by micrometric analysis of thin sections is discussed. L. J. SPENCER.

Organic Chemistry.

Catalytic hydrogenations in liquid media by platinum and palladium. G. VAVON (Bull. Soc. chim., 1927, [iv], **41**, 1253—1290).—A lecture.

Catalytic oxidation of methane to formaldehyde. I. S. S. MEDVEDEV (Trans. Karpov Inst. Chem., 1924, No. 3, 54—65; cf. A., 1926, 1012).—Using gold, platinum, manganese sesquioxide (most active), copper oxide (least active), silver oxide, lead oxide, or cerium dioxide on asbestos, and 1 litre per 20 min. at 250—350°, only carbon dioxide is obtained; with 1 litre per min. at 500°, copper oxide yields traces of formaldehyde and carbon monoxide. Glass at 600° gives a large yield of formaldehyde owing to the smaller chemical activity of the surface in not forming peroxides. With methane containing 3—7% of hydrogen, lead catalysts at 500—700° give the highest yields of formaldehyde. The presence of lead chloride or hydrogen chloride (0·13%) raises the relative yield of formaldehyde. With a mixture of methane (13·8%) and oxygen (17·98%) at 0·23 litre per min., at 600°, the yield of formaldehyde was 5·02% of the methane taken. CHEMICAL ABSTRACTS.

Rearrangement of *iso*propylethylene to trimethylethylene and the pyrogenic decomposition of Δ^{β}-pentene and trimethylethylene. J. F. NORRIS and R. REUTER (J. Amer. Chem. Soc., 1927, **49**, 2624—2640; cf. this vol., 440).—When γ-methyl-Δ^{α}-butene is passed over alumina at 450°, the time of contact being 15 sec., 10% of the hydrocarbon is converted into β-methyl-Δ^{β}-butene. This proportion is increased if phosphoric acid is used as catalyst, whilst with aluminium sulphate 47% of the hydrocarbon undergoes this rearrangement. When *iso*amyl alcohol is passed over alumina at a similar rate at 375°, 48% of the alcohol is decomposed, but rearrangement of the resulting hydrocarbon is not observed. With aluminium sulphate, 90% of the alcohol is decomposed, and 70% of the hydrocarbon is rearranged. With phosphoric acid, a higher temperature (405°) is necessary to effect dehydration, and the proportion of the hydrocarbon rearranged is less. Treatment of γ-methyl-Δ^{α}-butene with 84% sulphuric acid at 35° for 10 min. affords a *polymeride*, b. p. about 150°. With 60—69% sulphuric acid, a small amount of *tert.*-amyl alcohol is produced, indicating rearrangement of the hydrocarbon as above. When Δ^{β}-pentene is passed through a carbon-coated silica tube at 600°, it yields, per 100 pts.: hydrocarbons of higher mol. wt., apparently saturated, 15 pts.; methane, 7·8 pts.; butadiene, 8 pts.; butene, 8 pts.; propylene, 4 pts.; ethylene, 2 pts., and unchanged hydrocarbon, 33 pts. At 650°, trimethylethylene is decomposed as above to about the same extent as is the Δ^{β}-pentene at 600°. Rearrangement to γ-methyl-Δ^{α}-butene was not observed, and the products again contained 33% of higher hydrocarbons. The pyrogenic decomposition of both hydrocarbons appears to proceed by removal of the terminal methyl group, with subsequent hydrogenation of the two radicals thus formed, the hydrogen being derived from the total breakdown of a portion of the hydrocarbon, as indicated by the deposition of carbon. Δ^{β}-Pentene has m. p. −138±2°, b. p. 36·39±0·04°/760 mm., d_4^{15} 0·65551, n_D^{15} 1·3839. γ-Methyl-Δ^{α}-butene is viscous at −180°, and has b. p. 20·10±0·05°/760 mm., d_4^{15} 0·63197, n_D^{15} 1·3675. Trimethylethylene has m. p. −123±2°, b. p. 38·42±0·04°/760 mm., d_4^{15} 0·66708, n_D^{15} 1·3906. *tert.*-Amyl alcohol has m. p. −11·9±0·5°, b. p. 101·76±0·04°/760 mm., d_4^{15} 0·81382, n_D^{15} 1·4078. F. G. WILLSON.

Preparation of tetraiodomethane. J. F. DURAND (Bull. Soc. chim., 1927, [iv], **41**, 1251—1252).—Tetraiodomethane is prepared in 75% yield by the action of a potassium hydroxide solution of iodine on iodoform at 90° (cf. Dehn, A., 1909, i, 867). G. A. C. GOUGH.

Action of ultra-violet rays on chloropicrin. A. PIUTTI and F. P. MAZZA (Gazzetta, 1927, **57**, 610—614).—When chloropicrin is exposed to ultra-violet light it decomposes slowly to give nitrosyl chloride and carbonyl chloride, which itself decomposes to the extent of 5%. The proportions of the products are determined by absorbing carbon monoxide in ammoniacal cuprous chloride, after other substances have been condensed by liquid air; the latter are transferred to a pipette containing mercury and amalgamated copper, which absorbs chlorine and decomposes nitrosyl chloride, liberating nitric oxide. Finally the carbonyl chloride is absorbed in alcohol, and the nitric oxide is determined. E. W. WIGNALL.

Reactivity of atoms and groups in organic compounds. II. Relative reactivities of the hydroxyl hydrogen atoms in certain alcohols. J. F. NORRIS and F. CORTESE (J. Amer. Chem. Soc., 1927, **49**, 2640—2650; cf. A., 1925, i, 626).—The values of the (second order) reaction constants for the reaction between *p*-nitrobenzoyl chloride and 18 alcohols, under the conditions previously laid down, have been determined. From the results obtained, together with those previously reported, the following conclusions are reached: (1) in normal primary alcohols, the reactivity of the hydroxyl hydrogen decreases progressively in the first three members, increases progressively for the next three, and then decreases again; the same applies to secondary alcohols with the hydroxyl group in the β-position; (2) the introduction, into a primary alcohol, of a methyl group as a side-chain is of greater effect than a corresponding increase in the length of the carbon chain; this effect is greatest in the α-position, decreases progressively in the β- and γ-positions, and then begins to increase again; (3) the percentage reduction in reaction constant effected by the introduction of a methyl group as a side-chain is of the same order of magnitude whatever the length of the chain, for the same position of substitution; the relative effect is less in the β- than in the α-position; (4) the values of the constants of the secondary alcohols containing 3, 4, 5, and 6 carbon atoms are, respectively, 15·8, 10·0, 7·5, and 7·6% of those of the primary alcohols containing the same number of carbon atoms, the effect in this case increasing with increasing mol. wt. in the first three members of the series; (5) the constants of tertiary alcohols containing four and five carbon atoms are, respectively, 3·7 and 3·2% of those of the corresponding primary alcohols; (6) the reactivity is markedly dependent on the position of the hydroxyl group in a straight chain, the constants of α-, β-, and γ-hydroxy-*n*-pentanes being in the ratio 1 : 0·075 : 0·045; (7) with aromatic alcohols, there is an alternation in the value of the constant as the phenyl radical is removed from the hydroxyl group, but the phenyl group depresses the reactivity in all cases examined. With all the alcohols so far examined, the value of the reaction constant decreases slowly after a certain proportion of the alcohol has been esterified. With primary alcohols, this drift sets in after 20—35%, with secondary alcohols after 4—7%, and with tertiary alcohols after still smaller percentage conversions. F. G. WILLSON.

Decomposition of pentaerythrityl tetraformate by heat. P. VAN ROMBURGH (Z. physikal. Chem., 1927, **130**, 334—336).—Pentaerythrityl tetraformate, m. p. 57°, formed by heating 1 mol. of pentaerythritol with 8 mols. of concentrated formic acid, decomposes quantitatively when heated at 220°: $C_5H_8(CO_2H)_4 \longrightarrow C_5H_8(OH)_4 + 4CO$. The formates of other αγ-glycols undergo a partial decomposition at considerably higher temperatures. L. L. BIRCUMSHAW.

Polymerisation products of propylene oxide and of glycidol. P. A. LEVENE and A. WALTI (J. Biol. Chem., 1927, **75**, 325—336).—On distillation of propylene glycol with sulphuric acid, or on distillation of dihydroxypropyl ether (see below), there was obtained the *substance* $CHMe<^{CH_2-O}_{O\cdot CHMe}>CH_2$, b. p. 117—125°; this compound was also obtained by heating propylene oxide for 4 weeks at 165—170°. Propylene oxide, $[\alpha]^{20}$ +10·3°, on prolonged heating with potassium hydroxide, gave a termolecular condensation *product*, $C_9H_{20}O_4$, b. p. 128—130°/2·4 mm., $[\alpha]_D^{20}$ −43·0°, and a quadrimolecular *product*, $C_{12}H_{26}O_5$, b. p. 130—140°/2·4 mm., $[\alpha]_D^{20}$ −49·19°; these products, together with dihydroxypropyl ether, were formed on prolonged heating of propylene oxide with propylene glycol, the reaction proceeding at a lower temperature and more rapidly in presence of sulphuric acid; thus propylene oxide, $[\alpha]^{20}$ −10·3°, with optically active propylene glycol gave *dihydroxypropyl ether*, b. p. 129—132°/30 mm., $[\alpha]_D^{20}$ −36·4°. Glycidol, on heating at 100° for 42 hrs., gave a compound which, on hydrolysis with sulphuric acid, yielded diglyceryl ether and, on treatment with ammonia, took up less than one amino-group; it is regarded as $OH\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot O\cdot CH_2\cdot CH<^{O}_{CH_2}$; on stronger and more prolonged heating a compound with the same empirical formula and mol. wt. 444 was obtained. C. R. HARINGTON.

The supposed dimethiodide of trimethylene sulphide. G. M. BENNETT and A. L. HOCK (J.C.S., 1927, 2496—2499).—This substance, hitherto regarded as possessing the unique structure $\left[CH_2<^{CH}_{CH_2}>S<_{Me}\right]I_2$ (A., 1917, 153), actually contains only one ionised iodine atom and yields a *chloroaurate* and a *chloroplatinate* both containing iodine. It is really dimethyl-γ-iodopropylsulphonium iodide. The trimethylene sulphide ring of the intermediate monomethiodide ruptures to give methyl γ-iodopropyl sulphide, which then reacts with methyl iodide to give the sulphonium iodide. This view is confirmed by synthesis: γ-hydroxypropyl mercaptan, on methylation with methyl sulphate, yields *methyl γ-hydroxypropyl sulphide*, b. p. 102°/24 mm., d_4^{20} (vac.) 1·030, which in turn is converted into impure *dimethyl-γ-hydroxypropylsulphonium iodide* by methyl iodide.

Treatment of the last-named substance with hydrogen iodide in xylene yields *dimethyl-γ-iodopropylsulphonium iodide*, m. p. 97·5°, identical with the supposed dimethiodide. G. A. C. GOUGH.

Refractivity and dispersivity of normal monobasic aliphatic acids. H. I. WATERMAN and S. H. BERTRAM (Rec. trav. chim., 1927, **46**, 699—702).—The refractivity and dispersivity of the normal aliphatic acids of 2 to 18 carbon atoms (with the exception of the C_4 acid, for which *iso*butylacetic acid was used) have been determined at 70° for the sodium line and the *C*, *F*, and *G'* lines of the hydrogen spectrum. The lower acids were fractionally distilled, and the middle acids also, in a cathodic vacuum; the higher acids were crystallised from acetone. The following are the respective values for n^{70}: C_2, 1·3531; C_3, 1·3662; C_4, 1·3775; C_5, 1·3877; C_6, 1·3967; C_7, 1·4029; C_8, 1·4085; C_9, 1·4130; C_{10}, 1·4170; C_{11}, 1·4203; C_{12}, 1·4225; C_{13}, 1·4249; C_{14}, 1·4268; C_{15}, 1·4287; C_{16}, 1·4303; C_{17}, 1·4319; C_{18}, 1·4332.

The increments in $n_D.M$ in passing from one acid to the next higher form two series, and are at first greater when passing to an acid with an odd number of carbon atoms, but after undecoic acid are greater for the reverse direction. E. W. WIGNALL.

Determination of mixtures of isomeric unsaturated compounds. II. Iodometric methods. R. P. LINSTEAD and C. J. MAY (J.C.S., 1927, 2565—2579; cf. this vol., 445).—A solution of iodine in aqueous potassium iodide reacts with Δ^1-*cyclo*hexenylacetic acid in aqueous sodium carbonate to afford the *γ-lactone* of *1-iodo-2-hydroxycyclohexylacetic acid*, m. p. 58°. The amounts of the components in a mixture of the above acid with *cyclo*hexylideneacetic acid may be determined to within 5% (see also Bougault, A., 1908, i, 537) by the preferential addition of iodine to the βγ-unsaturated acid under standard conditions. A new explanation for the mechanism of the addition is suggested. The method is applied to acids which cannot be separated from their isomerides (dialkylacrylic acids). Measurements are made of the addition of bromine to mixtures of the isomeric ethyl*cyclo*hexenones and of iodine chloride to the ethyl esters of *cyclo*hexylideneacetic, Δ^1-*cyclo*hexenylacetic, and styrylacetic acids and the results used to determine the composition of equilibrium mixtures of these substances.

G. A. C. GOUGH.

Three-carbon system. XIV. Effect of conditions on isomeric change in unsaturated acids. R. P. LINSTEAD (J.C.S., 1927, 2579—2585).—The iodine addition method (preceding abstract) shows that an equilibrium mixture of Δ^1-*cyclo*hexenylacetic acid and *cyclo*hexylideneacetic acid contains 88% of the former acid and that this value is independent of temperature, pressure, and concentration of either the acid or the catalytic alkali. The velocity of interconversion is diminished by dilution and especially by decrease of the concentration of the alkali. The results indicate the optimum conditions for hydrolysis of an ester of an unstable, unsaturated acid without movement of the double linking. G. A. C. GOUGH.

Action of formates on silver acetate. G. GUREVITSCH and E. POKROVSKAYA (Ukraine Chem. J., 1926, **2**, 414—429).—The action of silver acetate on various salts of formic acid, given by the equation, $2AgOAc+H{\cdot}CO_2M \rightarrow 2Ag+CO_2+MOAc+AcOH$, has been studied with the view of determining the effect of various cations on the velocity coefficient, *K*, the latter being calculated from the usual equation for a termolecular reaction. The reaction was carried out at 80°, the concentrations of the silver acetate and the formate being 0·04 and 0·02 g.-mol./litre, respectively. Halving the concentration doubled *K*. The velocity coefficient increases somewhat with the duration of the reaction, but its average value remains constant for the cations, $Na^{\cdot}$, $K^{\cdot}$, $H^{\cdot}$, $Sr^{\cdot\cdot}$, $Zn^{\cdot\cdot}$, $Ca^{\cdot\cdot}$, $Ba^{\cdot\cdot}$. When the concentration of the formate was increased to 100 times that of the silver acetate, and the temperature lowered to 45°, *K* remained constant throughout the reaction, but was greater for a univalent than for a bivalent ion. For ions of the same valency, increase of atomic weight led to an increase of *K*. In the case of formic acid itself, the velocity coefficient was one thirtieth of that for potassium formate. E. ROTHSTEIN.

Metallic derivatives of the enolic forms of monocarbonyl compounds. IX. Condensations of ethyl acetate. X. Preparation and properties of ketenacetals. H. SCHEIBLER and E. MARHENKEL (Annalen, 1927, **458**, 1—39).—The mixture (I) obtained by treating ethyl acetate with sodium, sodamide, or sodium ethoxide at a low temperature contains the "primary reaction product" (II), ethyl sodioacetoacetate, and the additive product $CMe(ONa)(OEt)_2$. The proportion of each (*e.g.*, 13·1%, 34·6%, and 52·3%, respectively) may be determined by comparing the amounts of acetic acid formed when the mixture is treated with water at 60° and with 20% sulphuric acid (cf. A., 1922, i, 426). The behaviour of (II) towards benzaldehyde shows that it cannot have the constitution $COMe{\cdot}CH_2{\cdot}C(OEt)_2{\cdot}ONa$ (A., 1925, i, 1417), and it is now regarded as a quinhydrone-like sodio-derivative of ethyl acetate, $\left[\begin{matrix}CH_3{\cdot}C(OEt){:}O\cdots \\ CH_2{:}C(OEt){\cdot}O-\end{matrix}\right]Na$. When (I) is heated alone or in ethyl acetate (II) evolves ethyl alcohol, forming ethyl sodioacetate. Neither this product nor that obtained by refluxing the latter compound with alcohol yields ketenacetal when decomposed by water. Acetone, ethyl alcohol, and sodium carbonate, as well as ketenacetal, are obtained by treating (I) with water at 80°. The new formula explains simply these and other characteristic reactions of the substance (II). In general, the following steps are postulated in the condensation of two carbonyl compounds, at least one of which forms an enol (Claisen, acetoacetic, aldol, and cinnamic ester condensations): (*a*) formation of a metallic ketyl (with sodium) or of an additive compound (with sodamide or sodium ethoxide), (*b*) conversion into a sodio-enolate with loss of hydrogen or alcohol, (*c*) formation with a further mol. of ketone of a complex of type (II), (*d*) condensation within the complex. The statement of Adickes (A., 1925, i, 1378) that only esters containing adjacent carbonyl groups form alkali alkoxide additive products is shown to be incorrect. Reasons are given for preferring the new

mechanism for the acetoacetic condensation to the older (cf. Swarts, this vol., 132) and newer (A., 1905, i, 258) mechanisms of Claisen.

[With R. Nikolic.]—When the primary reaction product from sodium propoxide and propyl acetate is treated with water and the propyl alcohol removed from the product as the phenylurethane, *keten dipropylacetal*, b. p. 104—106°, d_4^{22} 0·7999, n_D^{22} 1·3769, is obtained. Similarly, using the appropriate ester and alkali alkoxide, *keten diisobutylacetal*, b. p. 110—112°, d_4^{20} 0·8145, n_D^{20} 1·3966; *keten diisoamylacetal*, b. p. 131—133°, d_4^{19} 0·8104, n_D^{18} 1·4021; *ethoxyketen diethylacetal* (*triethoxyethylene*), b. p. 163—165°, d_4^{22} 0·9047, n_D^{22} 1·4038, and *methylketen diethylacetal*, b. p. 78—81°, d_4^{18} 0·8002, n_D^{18} 1·3673, are prepared in 5—10% yield. Ketenacetals are also obtained in slightly smaller yield by treating the primary reaction products successively with phosphoryl chloride and sodium alkoxide. The reaction, which affords evidence in favour of formulæ of the type (II), is represented thus: (II) $\longrightarrow$ $[CH_2{:}C(OEt)\cdot O\cdot]_3PO \longrightarrow$ $CH_3{:}CCl\cdot OEt) \longrightarrow CH_2{:}C(OEt)_2$ (cf. Scheibler, this vol., 338). Unlike those containing negative groups (cf. Reitter and Weindel, A., 1907, i, 748; Staudinger, A., 1922, i, 1015), the above ketenacetals are fairly stable towards water and alkalis. Keten diethylacetal is rapidly oxidised by alkaline permanganate, probably to ethyl hydrogen oxalate, since oxalic acid is formed on hydrolysis. With bromine it yields ethyl bromide and ethyl bromoacetate, and with sodamide in ethereal solution, ammonia, sodium ethoxide, and *sodium ethoxyacetylide*, CNa·C·OEt. The white *silver ethoxyacetylide* decomposes in presence of water, giving metallic silver. Similarly phenylketen diethylacetal and sodamide in benzene give a product, b. p. 100—120°/15 mm., containing ethoxyphenylacetylene, which is converted by water into phenylacetic acid.

H. E. F. Notton.

Interaction of bromine with acetic anhydride. II. K. J. P. Orton, H. B. Watson, and H. I. Hughes (J.C.S., 1927, 2458—2465).—Contrary to previous observations (*ibid.*, 1912, **101**, 1722; 1923, **123**, 3081), it is found that pure acetic anhydride is attacked by bromine at the ordinary temperature in the absence of light. Measurements of the velocity of the reaction indicate that hydrogen bromide, formed in minute amount by direct bromination, reacts with the anhydride to give acetic anhydride and acetyl bromide. The latter is rapidly brominated and then reacts with further acetic anhydride to give bromoacetic anhydride and to regenerate acetyl bromide. Hydrogen, acetyl, propionyl, or benzoyl bromides accelerate the reaction as do ferric chloride, stannic chloride, iodine, iodine chloride, and sulphuric acid; the latter class of substance probably induce enolisation and direct bromination of the anhydride. The reaction is completely inhibited by traces of quinoline (probably contained in the samples used in previous work) and partly by other basic substances and alkali bromides. Nitric acid and acetyl nitrate have powerful inhibitory action. G. A. C. Gough.

Action of acetic anhydride containing sulphoacetic acid on aliphatic double linkings. F. Ebel and M. W. Goldberg (Helv. Chim. Acta, 1927, **10**, 677—680).—When treated with acetic anhydride containing 2% of sulphuric acid, *cyclo*hexene undergoes a condensation of the Friedel and Crafts type, giving Δ^1-*cyclo*hexenyl methyl ketone (cf. A., 1922, i, 1033). An intermediate compound cannot be isolated. The reagent has no action on ethylene, methyl cinnamate, or safrole. *d*-Pinene affords, on gentle treatment at 100°, a mixture from which (*a*) a fraction, b. p. 156—158°/720 mm., d_4^{20} 0·853, n_D^{20} 1·4683, containing hydrocarbons, $C_{10}H_{16}$ and $C_{10}H_{18}$, probably pinene and a monocyclic terpene with one double linking, respectively, and (*b*) a triply unsaturated *diterpene*, b. p. 170°/12 mm., d_4^{20} 0·923, n_D 1·5143, are obtained. Vigorous treatment at 120° gives a *substance*, $C_{10}H_{16}O$, b. p. 215°/727 mm., d_4^{20} 0·956, n_D^{20} 1·4853, probably a monocyclic unsaturated ketone.

H. E. F. Notton.

Halogeno-acylato-compounds of quadrivalent titanium. M. Giua and E. Monath (Z. anorg. Chem., 1927, **166**, 306—310).—By the action of titanium tetrachloride on formic, propionic, butyric, and *iso*valeric acids, respectively, mixtures of substances have been obtained, similar to the compound previously described in the case of acetic acid (A., 1925, i, 531). An analogous bromine *compound*, $Ti_2Br_4(OAc)_4$, is formed by interaction between titanium tetrabromide and a mixture of acetic acid and acetic anhydride. Titanium chloroacetate reacts with alizarin to form a substance which is probably a type of lake.

R. Cuthill.

Derivatives of petroselic and petroselidic acids. A. Steger and J. van Loon (Rec. trav. chim., 1927, **46**, 703—708).—By heating pure petroselic acid (van Loon, this vol., 853) with glycerol and zinc dust (2%), pure tripetroselin, m. p. 26·2°, iodine value 85·9, saponification value 189·8 (cf. Vongerichten and Kohler, A., 1909, i, 454), is obtained; the same product is prepared by crystallisation of the natural glyceride of parsley-seed oil from an ether–alcohol mixture. The product of the action of nitrogen peroxide on petroselic acid, m. p. 52·7° (cf. Hilditch and Jones, this vol., 540), is, by analogy with elaidic acid, named "petroselidic acid"; it yields similarly *tripetroselidin*, m. p. 50·1°. Oxidation by alkaline potassium permanganate yields dihydroxy-acids, m. p. 122·2° from petroselic acid, 117·2° from petroselidic acid. Methyl petroselate is oxidised by perbenzoic acid in chloroform to an $\varepsilon\zeta$-oxidostearic acid, m. p. 59·2°, converted by sulphuric acid into a water-soluble derivative, which on warming in water yields the dihydroxy-acid of m. p. 117·0° (obtained by oxidising petroselidic acid). Methyl petroselidate, m. p. 20·0°, yields similarly an $\varepsilon\zeta$-oxidostearic acid of m. p. 65·4°, converted into the dihydroxy-acid, m. p. 122·0°, obtained from petroselic acid.

E. W. Wignall.

Salts of α-linolic tetrabromide from Philippine Lumbang oil. C. M. Jovellanos and A. P. West (Philippine J. Sci., 1927, **33**, 349—356).—Metallic salts of α-linolic tetrabromide, obtained as previously described (this vol., 304), have been prepared by a general method of conversion into the potassium salt, which then interacts, in alcoholic solution, with the solution of the inorganic salt. The following salts are described: *cadmium*, m. p. 135·7—137·8°; *cobalt*,

m. p. 156·5° to opaque drops stable at 190°; *copper*, m. p. 145·4°; *magnesium*, m. p. 150·1—151·7°; and *manganese*, m. p. 144·9—147·5°. A table of solubilities is given for seventeen organic liquids.

E. HOLMES.

α-Elæostearic acid from tung oil. J. BOESEKEN [with W. C. SMIT, J. J. HOOGLAND, and A. G. VAN DEN BROEK] (Rec. trav. chim., 1927, **46**, 619—634).—In continuation of earlier work (A., 1925, i, 507, 1129), and to confirm the theory that α-elæostearic acid contains three conjugated double linkings between the θ and ν carbon atoms, the action of "peracetic" acid (a mixture of glacial acetic acid and 60% hydrogen peroxide) and of catalytic hydrogenation under pressure on α-elæostearic acid and its partly brominated derivatives has been examined mainly along the line of determining the times necessary for saturation of the various double linkings. All the observed facts are accounted for if the acid has the structure indicated, and if addition occurs according to Thiele's hypothesis. When acted on by Wijs' solution two of the three linkings are saturated, under given conditions, in less than ½ hr., whilst the third requires 6 days, this being in accordance with the behaviour of known conjugated systems. In the case of bromine, two molecules are introduced rapidly, but the third is added only under the influence of ultra-violet light. When tetrabromo-α-elæostearic acid is treated with "peracetic" acid 90% of the theoretical amount of oxygen is absorbed after 8 days. From the reaction product is isolated *tetrabromodihydroxymonoacetylstearic acid*, m. p. 106°. When free α-elæostearic acid is treated with one, two, and three mols. of "peracetic" acid the results are complicated by the fact that it is found impossible to control the reaction so that only one, or only two double linkings are completely saturated before further addition begins, that the hydroxyl groups inserted are so situated that ring closure by loss of water is possible to give a variety of anhydrides, and further that acetylation may also proceed at one or more of the free hydroxyl groups. It is probable that the final substance is a saturated acid having three pairs of carbon atoms bridged through single atoms of oxygen. Catalytic hydrogenation under pressure allows the reaction to proceed at comparatively low temperatures. As before, progressive saturation of the double linkings follows Thiele's hypothesis, and the introduction of two molecules of hydrogen gives an oleic acid having the double linking between the ϰ and λ carbon atoms.

E. HOLMES.

Dehydrogenation of succinic acid. A. HAHN and W. HAARMANN (Z. Biol., 1927, **86**, 523—524; cf. Bach and Michlin, this vol., 591; Thunberg, A., 1918, i, 140, ii, 87; 1920, i, 784).—A preliminary account of experiments on the action of muscle on succinic acid in presence of methylene-blue and in absence of oxygen, in which malic acid and a smaller quantity of fumaric acid were isolated. The evidence favours the view that the succinic acid provides the hydrogen necessary for the reduction of the dye, being itself oxidised to fumaric acid, which rapidly adds water under the influence of a special ferment to form malic acid.

W. J. POWELL.

Stereochemical studies. XIV. Hydrolysis of esters. XV. Alkaline decomposition of monochlorosuccinic acid. XVI. Hydrolysis of the monohalogenosuccinic acids. B. HOLMBERG (Ber., 1927, **60**, [*B*], 2185—2194, 2194—2198, 2198—2211).—XIV. It appears generally valid to consider that during hydrolysis of a carboxylic ester by water without hydrogen-ion catalysis the alkyl group of the ester unites with the hydroxyl from the water: $R'O\cdot CO\cdot R+HO\cdot H=R'\cdot OH+HO\cdot CO\cdot R$. Hence in those esters which are hydrolysed only in the presence of hydrogen ions it is probable that the union between the carbinol carbon and the oxygen atom is so firm that hydrolysis takes place according to the scheme:

$$R'O\cdot CO\cdot R+H(H_2O)_x=R'\cdot OH+HO\cdot CO\cdot R+\overset{+}{H}(H_2O)_{x-1}.$$

The cause of the change lies in the tendency of the alkoxy-radical to unite with hydrogen to form an electrically slightly dissociated compound and the ability of the ion, owing to its hydration, to bring all the elements required for the completion of the change. It is therefore to be expected that other ions containing atoms prone to complex formation with alkoxy-groups will be catalytically active in ester hydrolysis or, more generally expressed, that hydrogen-ion catalysis is only a special instance of a more general complex catalysis. The existence of this new type of catalysis is established by measurement of the rate of hydrolysis of sodium acetoxyacetate in aqueous solution alone and in the presence of copper sulphate (catalyst $CuOH$), barium acetoxyacetate and copper sulphate, sodium acetoxyacetate, sodium acetate, or sodium glycollate and copper sulphate, acetoxyacetic acid and copper sulphate, sodium *dl*-acetylmalate or sodium monohalogenosuccinates and copper sulphate.

XV. The decomposition of monochlorosuccinic acid by alkalis consists of two changes, the first unimolecular, in which the hydroxyl ion reacts with the ion of monochlorosuccinic acid with the production of the ion of fumaric acid and bromine, and the second a bimolecular reaction in which the chlorosuccinic ion forms first the ion of propiolactonecarboxylic acid and the bromine ion and ultimately malic acid. The expressions $C_2=0\cdot444\times[Na^+]^{\frac{1}{2}}=0\cdot80\times[Ba]^{1/3}$ are valid for the bimolecular reaction between sodium chlorosuccinate and sodium hydroxide or barium chlorosuccinate and barium hydroxide, whereas according to Johansson (A., 1913, ii, 126) the corresponding expressions for bromosuccinic acid are $C_2=5\cdot7\times[Na^+]^{\frac{1}{2}}=11\cdot8\times[Ba]^{1/3}$.

XVI. The isolation of (+)-propiolactonecarboxylic acid permits its conversion by ammonia into *d*(+)-β-malamic acid and hence establishes its position in the *d*-series. Since it is transformed by alkalis into *d*(+)-malic acid the change occurs without inversion under the influence of hydroxyl ions. Analogously, the addition of other anions must be supposed to occur without inversion and the lævorotatory halogeno- and sulphur-substituted succinic acids must be regarded as *d*(−)-forms. Conversely, the transformation of an active halogenosuccinic acid into propiolactonecarboxylic acid of the opposite sign occurs without inversion. Hydrolysis of *d*(+)-pro-

piolactonecarboxylic acid in more or less acidic solution gives lævorotatory malic acid and is thus accompanied by inversion. Related to this is the observation that the small quantities of malic acid obtained by the alkaline decomposition of *d*(−)-halogenosuccinic acids are invariably dextrorotatory, whereas decomposition in acid solution generally gives lævorotatory malic acid as shown by Walden's classical experiments and a new series. Inversion during the hydrolysis of propiolactonecarboxylic acid is at first sight surprising, since it is not observed during the hydrolysis of carboxylic esters, acetylmandelic acid, or acetylmalic acid. The reactions do not, however, proceed in the same manner, since, in the first case, hydrogen ions are not generally involved to an appreciable extent. The steric relationships involved in the conversion of a *d*(−)-halogenosuccinic acid into malic acid are expressed by the schemes:

$d(-)\text{-}\bar{C}O_2\cdot CHX\cdot CH_2\cdot\bar{C}O_2 = d(+)\text{-}CO_2\cdot CH\cdot CH_2\cdot CO\cdot O+X$;

$d(+)\text{-}CO_2\cdot CH\cdot CH_2\cdot CO\cdot O+OH = d(+)\text{-}CO_2\cdot CH(OH)\cdot CH_2\cdot CO_2$;

$d(+)\text{-}CO_2\cdot CH\cdot CH_2\cdot CO\cdot O+H_2O = l(-)\text{-}CO_2\cdot CH(OH)\cdot CH_2\cdot CO_2H$;

$d(+)\text{-}CO_2\cdot CH\cdot CH_2\cdot CO\cdot O+H(H_2O)_x = d(+)\text{-}CO_2\cdot CH(OH)\cdot CH_2\cdot CO_2H+H(H_2O)_{x-1}$.

Further possibilities are expressed by the schemes:

$CO_2\cdot CHX\cdot CH_2\cdot CO_2+OH=\bar{C}O_2\cdot CH(OH)\cdot CH_2\cdot CO_2+X$

and $CO_2\cdot CHX\cdot CH_2\cdot\bar{C}O_2+H_2O=CO_2\cdot CH(OH)\cdot CH_2\cdot CO_2+H+X$, but since the yields of fumaric acid are greater and of malic acid smaller as the acidity or alkalinity of the solution increases it appears that in these cases the reactions $CO_2\cdot CHX\cdot CH_2\cdot CO_2+OH=\bar{C}O_2\cdot CH{:}CH\cdot CO_2+H_2O+X$ and $CO_2\cdot CHX\cdot CH_2\cdot CO_2=CO_2\cdot CH{:}CH\cdot CO_2+H+X$ almost completely dominate. Complication due to the formation of compounds of the type $\bar{C}O_2\cdot CH(CH_2\cdot CO_2)\cdot O\cdot CO\cdot CHX\cdot CH_2\cdot CO_2$ do not appear to occur in dilute solution (cf. Senter, A., 1912, i, 828). The above deductions do not appear to be in harmony with Walden's observations as far as experiments with the hydroxides of tin, lead, cadmium, and copper are concerned. The nature of the metals indicates that hydrolysis in these cases is not due to hydrogen or hydroxyl ions, but to metallic ions as a consequence of complex catalysis. This view is confirmed by a lengthy series of experiments in which it is shown that the cupric ion favours the production of *d*(+)-malic acid so pronouncedly that the action is appreciable in acid solution. A similar effect is produced by beryllium and aluminium ions which have a marked tendency to form complexes with hydroxy-acids, whereas the magnesium ion does not differ appreciably from the calcium ion. In agreement with the influence of the cupric ion on the hydrolysis of propiolactonecarboxylic acid, inversion is not observed when copper hydroxide acts on *l*(−)-acetylmalic acid. H. WREN.

Methylpolymethylenedicarboxylic acids connected with the investigation of muscone. L. RUZICKA. I. [with R. STEIGER] **Syntheses from citronellal.** II. [with M. STOLL] **Synthesis of β-methyltridecane-αν-dicarboxylic acid** (Helv. Chim. Acta, 1927, **10**, 680—694).—Citronellideneacetic acid is readily prepared in quantity by the method of Rupe and Lotz (A., 1903, i, 841). The ethyl ester, obtained almost pure by using 1% alcoholic sulphuric acid, is reduced by sodium and alcohol, first to *citronellylacetic acid* (*δθ-dimethyl-Δ$^{\eta}$-decenoic acid*) (I), b. p. 168—169°/12 mm., d_4^{18} 0·9211, n_D^{18} 1·4595 (*ethyl* ester, b. p. 145—155°/12 mm., $[\alpha]_D$ −2·0°); then to *ει-dimethyl-Δ$^{\theta}$-decen-α-ol*, b. p. 140—150°/12 mm., d_4^{15} 0·865, $[\alpha]_D$ −1·25°. This is converted by dry hydrogen bromide into *α-bromo-ει-dimethyl-Δ$^{\theta}$-decene*, b. p. 145—150°/15 mm., d_4^{15} 1·06, which condenses with ethyl malonate giving ethyl *-dimethyl-Δ$^{\iota}$-undecene-αα-dicarboxylate*, b. p. 160—165°/0·5 mm., $[\alpha]_D$ −2·0°, converted by hydrolysis and distillation into *ζκ-dimethyl-Δ$^{\iota}$-dodecenoic acid*, b. p. 178—180°/12 mm., $[\alpha]_D$ −1·6° (*ethyl* ester, b. p. 155—165°/12 mm., $[\alpha]_D$ −1·6°). By repeating these operations the following series of compounds is prepared: *ηλ-dimethyl-Δ$^{\kappa}$-dodecen-α-ol*, b. p. 160—165°/13 mm., $[\alpha]_D$ −1·0°; *α-bromo-ηλ-dimethyl-Δ$^{\kappa}$-dodecene*, b. p. 155—160°/12 mm., *ethyl θμ-dimethyl-Δ$^{\lambda}$-tridecene-αα-dicarboxylate*, b. p. 180—185°/1 mm., $[\alpha]_D$ −1·0°; *θμ-dimethyl-Δ$^{\lambda}$-tetradecenoic acid* (II), b. p. 160—165°/1 mm. (*ethyl* ester, b. p. 185—190°/12 mm., $[\alpha]_D$ −1·0°); *ιν-dimethyl-Δ$^{\mu}$-tetradecen-α-ol*, b. p. 178—182°/12 mm., $[\alpha]_D$ −0·85°; *α-bromo-ιν-dimethyl-Δ$^{\mu}$-tetradecene*, b. p. 170—175°/12 mm., which is converted through the nitrile into *ιν-dimethyl-Δ$^{\mu}$-pentadecenoic acid* (III), b. p. 170°/0·5 mm.; *ethyl κξ-dimethyl-Δ$^{\nu}$-pentadecene-αα-dicarboxylate*, b. p. 175—180°/0·5 mm., $[\alpha]_D$ −0·6°; *κξ-dimethyl-Δ$^{\nu}$-hexadecenoic acid* (IV), b. p. 175—180°/1 mm. (*ethyl* ester, b. p. 200°/11 mm.); *λο-dimethyl-Δ$^{\xi}$-hexadecen-α-ol*, b. p. 195—200°/13 mm.; *α-bromo-λο-dimethyl-Δ$^{\xi}$-hexadecene*, b. p. 190—200°/10 mm., which is converted through the nitrile into *λο-dimethyl-Δ$^{\xi}$-heptadecenoic acid* (V), b. p. 190°/0·5 mm. The new acids are oxidised by ozone and chromic acid to methylated dicarboxylic acids, from which the second higher homologues may be prepared by standard methods (cf. A., 1926, 499). Thus, from (I) is obtained *γ-methylhexane-αζ-dicarboxylic acid*, m. p. 81°, b. p. 190—210°/12 mm. (*ethyl* ester, b. p. 150—160°/13 mm.); from (II), *γ-methyldecane-ακ-dicarboxylic acid*, m. p. 71° (*ethyl* ester, b. p. 140°/0·5 mm.), and *δ-methyldodecane-αμ-dicarboxylic acid*, m. p. 74—75°; from (III), *γ-methylundecane-αλ-dicarboxylic acid*, b. p. 190—200°/0·5 mm., m. p. 47°, and *δ-methyltridecane-αν-dicarboxylic acid*, m. p. 54—55°; from (IV), *γ-methyldodecane-αμ-dicarboxylic acid*, m. p. 76—77°; *δ-methyltetradecane-αξ-diol*, b. p. 200°/0·4 mm.; *αξ-dibromo-δ-methyltetradecane*, b. p. 165—170°/0·5 mm., and *δ-methyltetradecane-αξ-dicarboxylic acid*, m. p. 75—76°, and from (V), γ-methyltridecane-αν-dicarboxylic acid, b. p. 200°/0·5 mm., m. p. 62—63° (cf. Chuit, Boelsing, and Malet, this vol., 446). All

the dicarboxylic acids prepared in this way, except γ-methylhexane-αζ-dicarboxylic acid, are optically inactive, the γ-methyl derivatives, unlike the corresponding β-methyl derivatives (this vol., 57), being racemised by alkali. Many of these acids when apparently pure exhibit variations in m. p. which are attributed to the presence of allotropic forms.

Regulated hydrolysis of ethyl undecane-αλ-dicarboxylate affords the monoethyl ester, converted by thionyl chloride at the ordinary temperature into *ethyl* λ-*chlorocarbonyldodecoate*, b. p. 185—188°/5 mm., which yields with ammonia *ethyl* λ-*carbamidododecoate*, m. p. 91—92°. The acid chloride reacts with zinc methyl iodide (cf. Blaise, A., 1914, i, 141) forming *ethyl* μ-*ketotetradecoate* (I), b. p. 164—166°/1 mm. (*semicarbazone*, m. p. 105—106°). In the same way ethyl azelate yields *ethyl* η-*chlorocarbonyloctoate*, b. p. 155—158°/15 mm., and *ethyl* θ-*ketodecoate*, b. p. 151—153°/11 mm. (*semicarbazone*, m. p. 102—103°), and ethyl sebacate yields ethyl θ-*chlorocarbonylnonoate*, b. p. 168—170°/15 mm., and *ethyl* ι-*ketoundecoate*, b. p. 161—163°/12 mm. The keto-ester (I) with zinc and ethyl bromoacetate gives a mixture of *ethyl* β-*hydroxy*-β-*methyltridecane*-αν-*dicarboxylate* and *ethyl* β-*methyl*-Δ$^{\alpha}$-*tridecene*-αν-*dicarboxylate*, from which the latter, b. p. 186—187°/2 mm., is obtained by treatment with phosphorus tribromide, hydrolysis with alkali, and re-esterification. It is hydrogenated in presence of platinum-black to *ethyl* β-*methyltridecane*-αν-*dicarboxylate*, b. p. 186—187°/2 mm., from which β-methyltridecane-αν-dicarboxylic acid (this vol., 57, 446) (*dihydrazide*, m. p. 148—152°; *diamide*, m. p. 145—150°; *dianilide*, m. p. 131—133°) is obtained.

H. E. F. Notton.

Condensation products of *d*-tartaric and of malic acid with chloral. F. H. Yorston (Rec. trav. chim., 1927, **46**, 711—714).—*d*-Tartaric acid and chloral hydrate condense in presence of concentrated sulphuric acid to give the *chloralides* I, m. p. 160°, $[\alpha]_D$ +42° to 48°, according to solvent; and II, m. p. 173°, $[\alpha]_{5780}$ −54·6° in benzene, +32·4° in acetone.

One form only of *malic acid chloralide* was obtained, of rotation varying with the solvent.

E. W. Wignall.

Effect of ionisation on optical rotation. III. The βε-anhydro-sugar acids. P. A. Levene and L. W. Bass (J. Biol. Chem., 1927, **74**, 727—737).—In the βε-anhydro-sugar acids, the difference in optical rotatory power between the undissociated acid and the acid ion is less than in the case of the sugar acids themselves (cf. A., 1924, i, 615); in the βε-anhydrodicarboxylic acids the change in rotation on passing from one molecular species to another is roughly proportional to the distance traversed by the ionisable groups.

C. R. Harington.

Lactone formation of galactoarabonic and melibionic acids and its bearing on the structure of lactose and of melibiose. P. A. Levene and O. Wintersteiner (J. Biol. Chem., 1927, **75**, 315—324).—Galactoarabinose was oxidised with barium hypoiodite to give *galactoarabonic acid* (*calcium* salt, $[\alpha]_D$ +33·6°); the free acid, $[\alpha]_D^{31}$ +31·9° at first, showed a diphasic mutarotation, indicating that the galactose is linked to the γ-carbon atom of the arabinose, and therefore, in lactose, to the δ-carbon atom of the dextrose (cf. Levene and Sobotka, this vol., 340). Melibionic acid, $[\alpha]_D^{22}$ +108·8° at first, showed a monophasic mutarotation similar to that of lactobionic acid (*loc. cit.*); in melibiose therefore the linking appears to be on the δ-carbon atom of the dextrose, which is in disagreement with the conclusions of Haworth and Leitch (J.C.S., 1918, **113**, 189) and of Zemplen (this vol., 545).

C. R. Harington.

Walden inversion. X. Oxidation of α-thiolcarboxylic acids to sulphonic acids; Walden inversion in the series of α-hydroxycarboxylic acids. P. A. Levene, T. Mori, and L. A. Mikeska (J. Biol. Chem., 1927, **75**, 337—365).—In every sulphonic acid investigated the difference of rotation between the free acid and its salts is in the same sense as in the corresponding thiol acid; the change in polarity from ·SH to ·SO_3H involves therefore no change in configuration. Tables are given summarising the numerical values of the molecular rotations of α-substituted fatty acids and the occurrence or non-occurrence of Walden inversion in the interconversion of these derivatives. α-Bromo-*n*-butyric acid, $[\alpha]_D^{20}$ +12·9° in water (sodium salt, $[\alpha]_D^{20}$ +1·67°), gave l-α-*thiol*-n-*butyric acid*, b. p. 103—107°/15 mm., $[\alpha]_D^{20}$ −17·66° in ether (*monosodium* salt, $[\alpha]_D^{20}$ +1·38°; *dipotassium* salt, $[\alpha]_D^{20}$ +0·31°), which yielded l-α-*sulpho*-n-*butyric acid*, $[\alpha]_D^{20}$ −3·97° in water (*monopotassium* salt, $[\alpha]_D^{20}$ −2·09°). α-Bromo-*n*-valeric acid, on resolution through the quinine salt, gave d-α-*bromo*-n-*valeric acid*, b. p. 123—124°/15 mm., $[\alpha]_D^{20}$ +20·3° in water (*sodium* salt, $[\alpha]_D^{20}$ +7·28°), which was converted into *l*-α-*xantho*-n-*valeric acid*, $[\alpha]_D^{20}$ −18·1° in ether; this yielded l-α-*thiol*-n-*valeric acid*, b. p. 122—124°/13 mm., $[\alpha]_D^{20}$ −17·1° in ether (*monosodium* salt, $[\alpha]_D^{20}$ +0·44°, *disodium* salt, $[\alpha]^{20}$ +3·55°), which was oxidised to d-α-*sulpho*-n-*valeric acid*, $[\alpha]_D^{20}$ +0·96° (*disodium* salt, +8·81°; *monosodium* salt, $[\alpha]^{20}$ +0·42°). α-Bromo*iso*valeric acid was best resolved by means of cinchonidine in acetone; the *l*-acid, $[\alpha]_D^{20}$ −7·7° in ether, gave d-α-*thioliso*valeric *acid*, b. p. 114—115°/13 mm., $[\alpha]_D^{20}$ +13·3° in ether (*monosodium* salt, $[\alpha]_D^{20}$ +2·24°; *disodium* salt, $[\alpha]_D^{20}$ −4·03°), which was also obtained by direct resolution of α-thioliso*valeric* acid with cinchonidine, and yielded d-α-*sulphoisovaleric acid*, $[\alpha]_D^{0}$ +1·80° (*monosodium* salt, $[\alpha]_D^{20}$ +0·98°; *disodium* salt, $[\alpha]_D^{20}$ −3·57°). α-Bromo-*n*-hexoic acid, resolved with strychnine, gave l-α-*bromo*-n-*hexoic acid*, b. p. 129—130°/14 mm., $[\alpha]_D^{20}$ −22·6° (*sodium* salt, $[\alpha]_D^{20}$ −7·22°), which yielded d-α-*thiol*-n-*hexoic acid*, b. p. 112—115°/1·8 mm., $[\alpha]_D^{20}$ +29·29° in ether (*monosodium* salt, $[\alpha]_D^{20}$ +0·76°; *disodium* salt, $[\alpha]_D^{20}$ −6·05°); this gave l-α-*sulpho*-n-*hexoic acid*, $[\alpha]_D^{20}$ −3·08° (*monosodium* salt, $[\alpha]_D^{20}$ −2·77°; *disodium* salt, $[\alpha]_D$ −14·43°). d-α-*Bromoisohexoic acid*, $[\alpha]_D^{20}$ +29·8° in ether (*sodium* salt, $[\alpha]_D$ +10·37°), gave l-α-*thioliso*-*hexoic acid*, b. p. 126—126·5°/15 mm., $[\alpha]_D^{20}$ −15·6° in ether; d-α-*thioliso*hexoic *acid*, $[\alpha]_D^{20}$ +19·4° in ether (*monosodium* salt, $[\alpha]_D^{21}$ −0·87°; *disodium* salt, $[\alpha]_D^{20}$ −11·68°), was obtained by resolution of α-thioliso*hex*-oic acid with quinine, and yielded l-α-*sulphoisohexoic acid*, $[\alpha]_D^{20}$ −4·22° (*monosodium* salt, $[\alpha]_D^{20}$ −3·38°; *disodium* salt, $[\alpha]_D^{20}$ −16·9°). l-α-*Bromophenylacetic acid*, $[\alpha]^{20}$ −106·4°, gave d-α-*thiolphenylacetic acid*, m. p.

80—87°, $[\alpha]_D^{20}$ +114·5° in ether (*monosodium* salt, $[\alpha]_D^{20}$ +78·9°; *disodium* salt, $[\alpha]^{20}$ +33·2°), which yielded d-α-*sulphophenylacetic acid*, $[\alpha]^{20}$ +1·43° (*monosodium* salt, $[\alpha]_D^{20}$ +1·83°; *disodium* salt, $[\alpha]_D^{20}$ +5·6°). d-α-Bromo-*n*-valeric acid gave, with sodium carbonate, l-α-*hydroxy*-n-*valeric acid*, $[\alpha]_D^{20}$ −1·40° (*sodium* salt, $[\alpha]_D^{20}$ +2·65°); d-α-*hydroxy*-n-*hexoic acid* (from l-α-bromo-*n*-hexoic acid) had $[\alpha]_D^{20}$ +0·72° (*sodium* salt, $[\alpha]^{20}$ −4·02°); l-α-*hydroxy*-n-*hexoic acid*, by resolution of the inactive acid with cinchonidine in chloroform, had m. p. 60—61°, $[\alpha]^{20}$ −3·75° (sodium salt, $[\alpha]_D^{20}$ +14·77°); α-*bromoisohexoic acid*, $[\alpha]^{20}$ 12·1°, gave l-α-*hydroxyisohexoic acid*, $[\alpha]^{20}$ −0·53° (*sodium* salt, $[\alpha]_D^{20}$ −2·81°). C. R. HARINGTON.

Identification and determination of aldehydes and ketones. S. VEIBEL (Bull. Soc. chim., 1927, [iv], **41**, 1410—1416).—The m. p. of semicarbazones are appreciably lower when taken slowly than when determined quickly. For the determination of mol. wt. of semicarbazones, 0·1—0·2 g. is heated under reflux during 30 min. with water (100 c.c.) and concentrated sulphuric acid (10 c.c.) to effect complete dissolution. Potassium iodate (0·4—0·5 g.) is then added, and the mixture boiled until the colour of the iodine disappears. Ammonia is then determined by the usual method. For ten examples quoted the method is accurate to 0·6%, except for *o*-nitrobenzaldehydesemicarbazone. Application of the method to crude semicarbazones gives results which are usually high. H. BURTON.

Affinity, reactivity, and structure in acetal formation. II. W. H. GARTUNG and H. ADKINS (J. Amer. Chem. Soc., 1927, **49**, 2517—2524; cf. A., 1925, i, 784).—Equilibrium constants have been determined for the reactions between ethyl alcohol and amino-, bromo-, cyano-, and imino-acetaldehyde, β-chloropropaldehyde, glycollaldehyde, acraldehyde, crotonaldehyde, heptaldehyde, propaldehyde, acetaldehyde, butaldehyde, and cinnamaldehyde. The values of $-RT \log K$ indicate that the effect of a given substituent on affinity in the acetal reaction is not constant, either qualitatively or quantitatively. The same substituent may increase or decrease the affinity in different cases. Aminoacetal has b. p. 52—53°/2 mm., d^{25} 0·9161, n^{25} 1·4120; diacetalamine has b. p. 127—130°/3 mm., d^{25} 0·9541, n^{25} 1·4210 (cf. Wohl, A., 1888, 443; Wolff, *ibid.*, 809). F. G. WILLSON.

Action of formaldehyde on sodium hydroxide. P. MALVEZIN (Bull. Assoc. Chim. Sucr., 1927, **44**, 441—442).—The reactions described by Mestre (this vol., 960) were studied previously by the author. J. H. LANE.

Effect of dextrose on condensation of formaldehyde. I. Determination of urinary sugar. F. B. KINGSBURY (J. Biol. Chem., 1927, **75**, 241—245).—Polymerisation of formaldehyde to reducing sugars, on heating in alkaline solution, is accelerated by the presence of dextrose or other reducing sugar. The colour developed on heating an alkaline solution of 2 : 4-dinitro-α-naphthol-7-sulphonic acid with sodium sulphite, formaldehyde, and a solution containing reducing sugars, is proportional to the amount of the latter present; on the basis of this observation a colorimetric method for the determination of urinary sugar is described. C. R. HARINGTON.

γ-Chloropropaldehyde dimethyl acetal. R. VOET (Bull. Soc. chim., 1927, [iv], **41**, 1308—1314).—Acraldehyde (1 mol.) and methyl alcohol (1 mol.) in presence of 1% of dry hydrogen chloride react, forming acraldehyde methyl semiacetal, which decomposes on attempted distillation. Similar results are obtained using 2 mols. of the alcohol, but if 1 mol. of hydrogen chloride is employed a good yield of γ-chloropropaldehyde dimethyl acetal is obtained. Excess of hydrogen chloride must be avoided as the chloroacetal is converted by the acid partly into methyl αγ-dichloropropyl ether. Water does not affect the pure acetal, but if a trace of acid is present it decomposes rapidly. With 3 mols. of the alcohol there is obtained *ααγ-trimethoxypropane*, b. p. 148°, d^{20} 0·941, also converted by hydrogen chloride into methyl αγ-dichloropropyl ether. H. BURTON.

***dl*-Glyceraldehyde.** H. G. REEVES (J.C.S., 1927, 2477—2485).—*dl*-Glyceraldehyde, prepared by a modification of Wohl's method (A., 1899, i, 11; cf. Witzemann, A., 1914, i, 1124), is shown to exist in three modifications. The crystalline form, m. p. 138·5°, d_{18}^{18} 1·455, is bimolecular in freshly-prepared aqueous solutions, but on keeping passes to a unimolecular form. The syrup from which the crystalline form is deposited is unimolecular. Titrations of alcoholic solutions of each of these preparations with bromine show that they contain 0·54 and 5·7% respectively of an enolic form, the existence of which in alkaline solutions of glyceraldehyde is demonstrated by colorimetric and refractometric measurements. G. A. C. GOUGH.

Supposed dimeric crotonaldehyde. M. V. IONESCU (Bull. Soc. chim., 1927, [iv], **41**, 1314—1318).—Condensation of the dimeric crotonaldehyde (Delépine, A., 1909, i, 84; 1910, i, 219) with dimethyldihydroresorcinol in presence of piperidine affords a *compound*, $C_{24}H_{34}O_5$, m. p. 190° (*sodium* derivative). In boiling alcohol in presence of piperidine, in boiling acetic acid, or in cold acetic–sulphuric acids this substance loses 1 mol. of water, yielding a *hydroxanthene*, $C_{24}H_{32}O_4$, m. p. 176°, and condenses with 1 : 3-diketohydrindene in alcohol–piperidine solution to give a bisdi-indone derivative. H. BURTON.

Preparation of methyl *n*-alkyl ketones. S. TSURUMI (Sci. Rep. Tohoku Imp. Univ., 1927, **16**, 677—685).—The best conditions for the ketonic decomposition of *n*-alkylacetoacetic esters have been studied. From results obtained in the preparation of the ketones from methyl *n*-butyl to methyl *n*-octyl ketone, it is evident that a 15—20% solution of sodium hydroxide gives the optimum yields. E. HOLMES.

Catalytic condensation of acetone at high temperatures and pressures. II. V. N. IPATIEV and A. D. PETROV (J. Russ. Phys. Chem. Soc., 1927, **59**, 427—430; cf. A., 1926, 1130).—The products of condensation of acetone at constant temperatures (350—400°) and time of heating (10—12 hrs.) at a maximum pressure of 100 atm. in the presence of aluminium oxide were investigated. Among the

products separated by fractionation were identified mesitylene, a sesquiterpene, b. p. 122—127°/10 mm., n^{17} 1·527, mesityl oxide, *iso*phorone, and *iso*xylitone, b. p. 126—128°. On nitration of the fraction of b. p. 122—127°, a yellow, amorphous *compound* which decomposes with incandescence on heating is obtained.

M. Zvegintzov.

Preparation of α-diketones from αβ-unsaturated ketones. C. Dufraisse and H. Moureu (Bull. Soc. chim., 1927, [iv], **41**, 1370—1378).—A more detailed account of work already abstracted (this vol., 246; cf. *ibid.*, 884). H. Burton.

Action of hydrochloric and hydrobromic acids on carbohydrates. H. Colin and E. Ruppol (Bull. Soc. Chim. biol., 1927, **9**, 928—931).—Ketoses and most of their derivatives give a rich purple colour when treated with hydrogen bromide in presence of moisture. Hydrogen chloride gives a similar colour with the free ketoses but not, apart from certain exceptions, with their derivatives (cf. Fenton and Gostling, J.C.S., 1898, **73**, 554; 1901, **79**, 361). W. O. Kermack.

Cryoscopy of carbohydrate acetates. M. Bergmann, E. Knehe, and E. von Lippmann (Annalen, 1927, **458**, 93—101).—The mol. wt. of amylose triacetate (this vol., 342) from potato starch, and of the *triacetate*, $[\alpha]_D^{17}$ +175·1° in chloroform, of a new carbohydrate (to be described later) from potato amylopectin have been determined by cryoscopic measurements at concentrations of 0·1—0·3%, in glacial acetic acid in absence of air, and in phenol. The values in each case approach that required for a hexose anhydride triacetate, and remain sensibly unchanged for periods of up to 27 days. The same results are obtained using lichenin triacetate, $[\alpha]_D^{20}$ +35·2°, prepared by the pyridine method (this vol., 341), and inulin triacetate (cf. A., 1926, 1230). The initial decrease in mol. wt. and subsequent gradual increase to infinity described by Hess (A., 1926, 715; this vol., 753) are not observed. The work of Hess is criticised and it is suggested that cryoscopic results are of value for the determination of constitution only when supported by independent evidence of the homogeneity of the solute particles.

H. E. F. Notton.

1 : 3 : 4 : 6-Tetramethyl-γ-fructose and 2 : 3 : 5-trimethyl-γ-arabinose. Oxidation of *d*- and *l*-trimethyl-γ-arabonolactone. W. N. Haworth, E. L. Hirst, and A. Learner (J.C.S., 1927, 2432—2436; cf. A., 1926, 273, 1025; this vol., 1057).—*l*-Trimethyl-γ-arabonolactone, m. p. 30—32°, $[\alpha]_D$ −44° to 25° (in water; period 20 days), yields a mixture of methyl *d*-dimethoxysuccinate (identified by means of the amide and the methylamide) with the original substance on oxidation with nitric acid followed by esterification of the product. *d*-Trimethyl-γ-arabonolactone yields similarly the corresponding derivatives of *l*-dimethoxysuccinic acid. In neither case was any trimethoxyglutaric acid derivative detected and hence these results support the butylene-oxide formula for *d*-tetramethyl-γ-fructose and *l*-trimethyl-γ-arabinose. G. A. C. Gough.

Structure of the normal and γ-forms of tetramethylglucose. Oxidation of tetramethyl-δ- and -γ-gluconolactones. W. N. Haworth, E. L. Hirst, and E. J. Miller (J.C.S., 1927, 2436—2443).—Oxidation of tetramethyl-δ-gluconolactone affords finally methyl *d*-dimethoxysuccinate and methyl *i*-xylotrimethoxyglutarate alone. The γ-lactone affords similarly methyl *d*-dimethoxysuccinate only. These results confirm the structure assigned to the lactones and to the two forms of glucose (A., 1926, 273).

[With A. Learner.]—2 : 3 : 4-Trimethyl-β-methylglucoside, identical with that prepared from gentiobiose, may be obtained from triphenylmethylglucose by methylation followed by alcoholysis of the product with methyl-alcoholic hydrogen chloride.

G. A. C. Gough.

Condensation products of ethyl acetoacetate. III. Compounds of dextrose. Antiketogenesis. E. S. West (J. Biol. Chem., 1927, **74**, 561—589).—On heating dextrose and ethyl acetoacetate in alcoholic solution in presence of zinc chloride there was obtained a compound, $C_{12}H_{18}O_7$, $[\alpha]_D^{25}$ −19° in methyl alcohol. The substance did not reduce Fehling's solution, but acquired this property when boiled for a short time with dilute acid; on prolonged boiling with acid it lost 1 mol. of carbon dioxide, and with alkali it yielded an *acid*, $C_{10}H_{14}O_7$, m. p. 160—161°, $[\alpha]_D^{25}$ −21·54° in methyl alcohol, −17·08° in water (*sodium* salt, $[\alpha]^{25}$ −14·86°); it is regarded as ethyl dextrose-*cyclo*acetoacetate. On acetylation it gave a *tetra-acetyl* compound, m. p. 84°, $[\alpha]_D^{26}$ −36·85° in chloroform. Dextrose*cyclo*acetoacetic acid when boiled with water gave the *anhydro-acid*, $C_{10}H_{12}O_6$, m. p. 140°, $[\alpha]^{25}$ −111·7° in methyl alcohol, −120·1° in chloroform (*sodium* salt, $[\alpha]^{25}$ −126·6°); on acetylation it yielded a *tetra-acetyl* compound, m. p. 94°, $[\alpha]^{25}$ −38·4° in chloroform, and, on methylation, a *tetramethyl* derivative, $[\alpha]_D^{25}$ −42·2° in chloroform. In the latter preparation evidence was obtained of the formation of a compound with powerful reducing properties, probably tetramethylglucoseacetoacetic acid. Ethyl dextrose*cyclo*acetoacetate, on treatment with cold hydrochloric acid, gave *ethyl anhydroglucose*cyclo*acetoacetate*, b. p. 208°/0·8 mm., $[\alpha]^{25}$ −89·9° in methyl alcohol (*diacetyl* derivative, b. p. 175°/0·6 mm., $[\alpha]_D^{25}$ −67° in chloroform); with hydrochloric acid at 30° it gave *ethyl dianhydroglucose*cyclo*acetoacetate*, b. p. 200°/0·8 mm., $[\alpha]^{26}$ −30·6° in methyl alcohol (*diacetyl* derivative, b. p. 220°/0·8 mm., $[\alpha]_D^{25}$ −59·5° in chloroform); finally, on more prolonged treatment with hydrochloric acid it yielded *ethyl trianhydroglucose*cyclo*acetoacetate*, m. p. 137°, which gave, with phenylhydrazine, a *substance*, $C_{17}H_{20}O_3N_2$, m. p. 177—180° (decomp.).

The fact that certain of the above series of compounds are powerful reducing agents, being more readily oxidised, *in vitro*, than dextrose itself, is discussed in its possible relationship to the mechanism of antiketogenesis in the organism.

C. R. Harington.

Ring structure in normal galactose. Oxidation of tetramethyl-δ-galactonolactone. W. N. Haworth, E. L. Hirst, and D. I. Jones (J.C.S., 1927, 2428—2432).—The amylene-oxide structure of tetramethyl-δ-galactonolactone and hence of normal galactose is confirmed by oxidation of the lactone with nitric acid followed by esterification of the product

with methyl alcohol, whereby methyl *l*-arabotrimethoxyglutarate, b. p. 95°/0·08 mm., is obtained, identified by preparation of the amide and the methylamide. The *phenylhydrazide* of tetramethylgalactonic acid, m. p. 135—137°, is incidentally described.

G. A. C. GOUGH.

Pentamethyl-*d*-mannose, pentamethyl-*d*-galactose, and their dimethylacetals. P. A. LEVENE and G. M. MEYER (J. Biol. Chem., 1927, **74**, 695—699).—Diethylmercaptomannose was converted into *pentamethyldiethylmercaptomannose*, b. p. 155—160°/0·2 mm., $[\alpha]_D^9$ +39·4° in methyl alcohol, which, with mercuric chloride, gave *pentamethylmannose*, b. p. 98—100°/0·1 mm., $[\alpha]^{20}$ +9·1° in *s*-tetrachloroethane, $[\alpha]_D$ +8·0° to $[\alpha]^{20}$ +17·8° in methyl alcohol (*dimethylacetal*, b. p. 112—114°/0·1 mm., $[\alpha]_D^{20}$ +21·2° in methyl alcohol, +19·3° in *s*-tetrachloroethane). *Pentamethyldiethylmercaptogalactose*, b. p. 155—160°/0·2 mm., optically inactive in methyl alcohol, gave *pentamethylgalactose*, $[\alpha]^{20}$ −4·8° in *s*-tetrachloroethane, and 0° to −10° in methyl alcohol (*dimethylacetal*, b. p. 118—120°/0·6 mm., $[\alpha]_D$ 0° in *s*-tetrachloroethane). The above two pentamethylhexoses had similar properties to the pentamethylglucose previously prepared (A., 1926, 1026).

C. R. HARINGTON.

Sucrose. W. D. HELDERMAN (Z. physikal. Chem., 1927, **130**, 396—404).—The densities and heats of dissolution of different preparations of sucrose have been determined, and values ranging from d_4^{30} 1·5860 to 1·5715 and −1095 to −813 g.-cal. (1 mol. in 400 mols. of water) have been obtained. Sugars with different physical properties are prepared by precipitating sucrose with ethyl and methyl alcohol, respectively. In general, the ethyl alcohol preparations have the greater densities and the greater negative heats of dissolution. By treating sucrose of low density with ethyl alcohol or saturated sugar solution at the ordinary temperature, a rise takes place both in the density and the heat of dissolution. These facts are explained by assuming the existence of at least two allotropic modifications of sucrose, of which that prepared by precipitation with ethyl alcohol is the stable form at the ordinary temperature. It is suggested that the deviating values found by different investigators for many of the physical constants of sucrose are to be ascribed to the fact that the measurements were made with undefined mixtures of two or more modifications of the sugar.

L. L. BIRCUMSHAW.

Action of iodine on starch. S. V. GORBATSCHEV and E. N. VINOGRADOVA (J. Russ. Phys. Chem. Soc., 1927, **59**, 433—458).—The adsorption of iodine from aqueous solutions in the absence of iodides at first rapidly increases with the time, then slows down. The final amount adsorbed depends both on the concentration of the solution and on the "history" of the process. The adsorption curve does not obey the equation of adsorption for gases. If potassium iodide is present in excess (up to saturation), the adsorption process is completely reversible, and the adsorption increases with increase of concentration of the iodide. Sodium chloride has a similar effect. Free sulphuric acid up to 1·5*N* had no appreciable effect. Other anions in concentrations from 0·19*N* to 0·2*N* vary in their activity according to the series: $OAc' > I' > Br' > NO_3' > Cl' > SO_4''$, which is similar to that of their facility for adsorption.

The difference in the activity of the various cations is less marked, the series being $Ca'' > K^{\cdot} > Sr'' > Mg'' > Na^{\cdot} > Zn'' > Ba'' > NH_4^{\cdot} > H^{\cdot}$.

Rise of temperature (below 40°, when the starch molecule breaks down), contrary to expectation, favours adsorption, according to a linear function. This cannot be due to the formation of iodide (which acts as a promoter) by reduction, since the effect is unaltered by the presence of an oxidising agent. If a saturated solution of sodium chloride is used, the relation is no longer linear. The property of adsorbing iodine vapour is also shown by perfectly dry starch.

The suggested mechanism of the process is one of electrical adsorption. Starch is negatively charged in colloidal solutions, and it is assumed that the iodine molecule is positive, since it can form the complex ion I_3'. When all the negative charge is neutralised, adsorption ceases, any residual positive charge being due to adsorbed hydrogen ions, as is shown by the removal by starch of hydroxyl ions from alkaline solutions. The addition of easily adsorbed anions to the solution removes the inhibiting hydrogen ions from the starch. The positive temperature coefficient is due to the decrease of adsorption of hydrogen ions with rise of temperature. If these are removed, the coefficient becomes negative, the process being, thus, one of true adsorption.

M. ZVEGINTZOV.

Acyl wandering in partly acylated methylglucosides. B. HELFERICH, H. BREDERECK, and A. SCHNEIDMULLER (Annalen, 1927, **458**, 111—116).—2 : 3 : 4-Triacetyl-6-triphenylmethyl-α-methylglucoside (A., 1926, 274) is hydrolysed by acetic and hydrobromic acids to 2 : 3 : 4-*triacetyl-α-methylglucoside*, m. p. 111° (corr.), $[\alpha]^{20·5}$ +148·8° in chloroform, which mutarotates in 0·001*N*-sodium hydroxide to an end value of $[\alpha]_D^9$ +107·8°. 2 : 3 : 4-Triacetyl-β-methylglucoside (cf. Oldham, A., 1926, 151) (6-p-*toluenesulphonyl* derivative, m. p. 171°, $[\alpha]_D$ +33·1°), prepared similarly from 2 : 3 : 4-triacetyl-6-triphenylmethyl-β-methylglucoside, also changes in presence of alkali to (?)2 : 3 : 6-*triacetyl-β-methylglucoside*, m. p. 114—115°, [α] −64·9° in chloroform [(?)4-p-*toluenesulphonyl* derivative, m. p. 118°, $[\alpha]_D$ −29·7°]. The view that the 1-substituent does not take part in the isomeric change is thus confirmed (cf. this vol., 858).

H. E. F. NOTTON.

Diisopropylideneglucose. IV. α- and β-Isomerides of γεζ-trimethylmethylglucoside and of βγεζ-tetramethylmethylglucoside. P. A. LEVENE and G. M. MEYER (J. Biol. Chem., 1927, **74**, 701—711).—Fractional distillation of larger amounts of γεζ-trimethylmethylglucoside (cf. A., 1926, 1228) gave a *d*-fraction, b. p. 105—109°/0·4 mm., $[\alpha]_D^{20}$ +93° in methyl alcohol, and an *l*-fraction, b. p. 145—150°/0·2 mm., $[\alpha]_D^{20}$ −87° in methyl alcohol. In 0·2% methyl-alcoholic hydrochloric acid the *d*-form mutarotated to $[\alpha]_D^{4·2}$ −13·0° and the *l*-form to $[\alpha]_D^{3·2}$ −12·5° at similar rates. On hydrolysis, the *d*-form yielded a product with $[\alpha]_D^{20}$ −12·3° in methyl alcohol, and the *l*-form one with $[\alpha]^{20}$ −10°; the two trimethyl-

glucoses thus obtained gave, with bromine, acids of which the sodium salts had $[\alpha]_D^{20}$ +31·0° and +31·3°. Further methylation of the trimethylmethylglucosides gave βγεζ-tetramethylmethylglucosides with $[\alpha]^{20}$ +104° and −63°; these mutarotated to $[\alpha]_D^{24\cdot8}$ −22·5° and −17·7°; the tetramethylglucoses obtained on hydrolysis had b. p. 122°/0·4 mm., $[\alpha]_D^{20}$ −20·5° in methyl alcohol, and b. p. 122°/0·05 mm., $[\alpha]^{20}$ −13·5°. The *d*- and *l*-forms of the above tri- and tetra-methylmethylglucosides are therefore to be regarded as α- and β-isomerides.

C. R. HARINGTON.

Bitter principle of Makabuhay, *Tinospora Rumphii*, Boerlage. J. MARANON (Philippine J. Sci., 1927, **33**, 357—361).—The bitter principle of *Tinospora Rumphii*, Boerlage, has been isolated from the dried plant stems by extraction with water, followed by evaporation and extraction of the residue with alcohol, tannin being removed by means of a lead salt. The *principle*, m. p. 154—155°, is obtained as white flakes from chloroform solution, the yield being 0·95% calculated on the dry sample. It is freely soluble in alcohol, slightly soluble in other organic solvents and in water, and is probably a glucoside. E. HOLMES.

Halogenated tertiary amines. C. S. MARVEL and W. H. ZARTMAN.—See this vol., 1064.

Determination of tetrapropylammonium ions as tetrapropylammonium diamminochromithiocyanate, $NPr_4[(SCN)_4Cr(NH_3)_2]$. F. HEIN and F. A. SEGITZ (Z. anal. Chem., 1927, **72**, 119—121).—The ice-cold solution (30 c.c.) of tetrapropylammonium salt is treated drop by drop with 20 c.c. of a 0·05*N*-solution in 10% alcohol of Reinecke's salt (ammonium diamminochromithiocyanate), 10—15 c.c. of a 15% solution of sodium chloride are added, and, after 24 hrs., the light rose-coloured, crystalline precipitate is collected on a porous glass filter, washed free from chlorides with ice-cold water, dried at the ordinary temperature in a vacuum over calcium chloride, and weighed. A. R. POWELL.

Neutral salt additive compounds of alkaline-earth glutamates and aspartates. W. K. ANSLOW and H. KING (Biochem. J., 1927, **21**, 1168—1178).—The following double *salts*, each containing 1 mol. of the organic salt and 1 mol. of the halide, are described: calcium glutamate with calcium chloride ($2H_2O$), calcium bromide ($2H_2O$), calcium iodide ($2·5H_2O$); barium glutarate with barium chloride ($6H_2O$), barium bromide (anhyd. and $4H_2O$), barium iodide ($6H_2O$); strontium glutamate with strontium chloride ($12H_2O$), strontium bromide ($11H_2O$), strontium iodide ($7H_2O$); strontium aspartate with strontium chloride ($2H_2O$). Barium aspartate and barium chloride apparently form a series of mixed crystals. No additive compounds could be obtained from lithium glutamate and lithium halides, calcium chloride and glutamic acid hydrochloride, calcium chloride and glutamic acid, and calcium aspartate and calcium chloride. Calcium, strontium, barium, lithium, and sodium glutamates were also prepared. The specific rotations of the above compounds over a wide range of concentrations were determined. At high concentrations these compounds are dextrorotatory but become lævorotatory in the region of low concentration, the curves showing a tendency to flatten out at 1—2% dilutions; the ionic value for the negative glutamate ion at this region of concentration is about of the same order for all the compounds. Glutamic acid was prepared by hydrolysis of gluten flour with hydrochloric acid and by decomposing the resulting hydrochloride with aniline and alcohol. The constitution of the additive compounds is discussed from the point of view of electron sharing.

S. S. ZILVA.

Separation of arginine and histidine. III. Preparation of arginine. H. B. VICKERY and C. S. LEAVENWORTH (J. Biol. Chem., 1927, **75**, 115—122; cf. this vol., 546).—The purified protein is hydrolysed with hydrochloric acid and most of the latter is removed by evaporation; the solution of the residue is treated with silver oxide and sulphuric acid in excess and then with barium hydroxide to p_H 7·0; the filtrate, after further addition of excess of silver oxide and sulphuric acid, is treated with barium hydroxide until alkaline to phenolphthalein; arginine is recovered from the precipitate by decomposition with hydrogen sulphide and isolated as the picrate. The yield of arginine from edestin was 14·45%. A method of recovering silver from the residues in the above preparation is described. C. R. HARINGTON.

Mercury compound of allantoic acid suitable for the identification of this ureide in the green vegetable of *Phaseolus vulgaris*. R. FOSSE and A. HIEULLE (Compt. rend., 1927, **185**, 800—802; cf. this vol., 1116; Fosse, A., 1926, 548).—Allantoic acid may be conveniently identified by means of its mercury compound, which is formed by the union of 2 mols. of the ureide with 1 mol. of mercuric oxide and is therefore hydrated *mercury allantoate*, $(+H_2O)$. Since products of variable composition may be obtained under certain conditions, the method of preparation is given in detail. From crude dixanthylallantoic acid, which is obtained by treating extracts of *Phaseolus* with xanthhydrol, mercury allantoate may be prepared by treatment with ether and alcoholic hydrogen chloride, the residue after washing with ether being dissolved in water and treated with mercuric nitrate in slightly acid solution.

W. J. POWELL.

Photosynthesis of carbamide from ammonium carbonate. W. R. FEARON and C. B. M'KENNA (Biochem. J., 1927, **21**, 1087—1090).—Carbamide has been produced by exposure of ammonium carbonate to ultra-violet irradiation (200—250 μμ). The effect of accessory reagents such as dextrose, hydroxylamine, formaldehyde, methylene-blue, ammonium nitrate, hydrogen peroxide, copper, iron, uranium, methyl-orange, eosin, and malachite-green was examined. The last reagent had the most definite effect in increasing the yield of carbamide.

S. S. ZILVA.

Preparation of methylguanidine according to Werner and Bell. E. PHILIPPI and K. MORSCH (Ber., 1927, **60**, [*B*], 2120—2122; cf. Werner and Bell, J.C.S., 1922, **121**, 1790; Kapeller, A., 1926, 943).—The action of dicyanodiamide on methylamine hydrochloride gives methylguanidine in 80—90% yield. It

may be isolated through the chloroplatinate or picrate. In the former case, methylamine chloroplatinate must first be removed and the other by-products (methyldiguanide and guanidine) remain in the final mother-liquors, whereas in the latter case methyldiguanide and guanidine are removed as picrates and methylamine is left in the final liquors. Werner and Bell's picrate, decomp. 285°, is derived from methyldiguanide and guanidine; methylguanidine picrate has m. p. 198·5—199·5°.

H. WREN.

Reactions of thiosemicarbazones. III. W. BAIRD, R. BURNS, and F. J. WILSON (J.C.S., 1927, 2527—2534).—Alkyl halides react with the sodium derivative of acetonethiosemicarbazone in alcoholic solution to give *S*-alkyl compounds, which are hydrolysed to *S*-alkylthiosemicarbazides by 0·5*N*-hydrochloric acid. In this way the following compounds are prepared: *acetone*-S-*ethylthiosemicarbazone*, m. p. 55°; S-*ethylthiosemicarbazide dihydrochloride*, m. p. (indef.) 60°; *benzaldehyde*-S-*ethylthiosemicarbazone*, m. p. 66° (*hydrochloride*, m. p. 195°); *acetone*-S-*propylthiosemicarbazone*, b. p. 121°/7 mm., m. p. 26—27°; S-*propylthiosemicarbazide dihydrochloride* (syrup); *benzaldehyde*-S-*propylthiosemicarbazone*, m. p. 54° (*hydrochloride*, m. p. 209°); *acetone*-S-*allylthiosemicarbazone*, m. p. 51°; S-*allylthiosemicarbazide dihydrochloride*, m. p. 75°; *benzaldehyde*-S-*allylthiosemicarbazone*, m. p. 42° (*hydrochloride*, m. p. 190°); *acetone*-S-n-*butylthiosemicarbazone*, b. p. 146°/16 mm.; S-n-*butylthiosemicarbazide dihydrochloride*, m. p. 100—101° (decomp.); *benzaldehyde*-S-n-*butylthiosemicarbazone*, m. p. 50°; *acetone*-S-o-*carbethoxybenzylthiosemicarbazone*, m. p. 66° (from ethyl ω-bromo-*o*-toluate); S-o-*carbethoxybenzylthiosemicarbazide dihydrochloride*, m. p. 125—130° (decomp.); *benzaldehyde*-S-o-*carbethoxybenzylthiosemicarbazone*, m. p. 74° (*hydrochloride* $+H_2O$, m. p. 115°). Acetonethiosemicarbazone reacts with primary amines in boiling toluene solution to give ammonia and the following δ-substituted thiosemicarbazones: with benzylamine, *acetone*-δ-*benzylthiosemicarbazone*, m. p. 147—148°; δ-*benzylthiosemicarbazide*, m. p. 130° [*hydrochloride*, m. p. 189°; *benzylidene* derivative, m. p. 133—134° (also prepared from hydrazine hydrate and benzylthiocarbamide)]; with α-phenylethylamine, *acetone*-δ-α-*phenylethylthiosemicarbazone*, m. p. 89—90°; δ-α-*phenylethylthiosemicarbazide*, m. p. 84° (*hydrochloride*, m. p. 157—158°; *benzylidene* derivative, m. p. 128—129°); with *n*-heptylamine, *acetone*-δ-n-*heptylthiosemicarbazone*, m. p. 75°; δ-n-*heptylthiosemicarbazide*, m. p. 54—55° (*hydrochloride*, m. p. 135—136°; *benzylidene* derivative, m. p. 73°); with aniline, a small amount of an unidentified *substance*, m. p. 245°. With β-naphthylamine, hydrogen sulphide and ammonia were evolved and a *substance*, m. p. 275° (possibly di-β-naphthyliminotetrahydrothiodiazole), and *acetone*-δ-β-*naphthylthiosemicarbazone*, m. p. 150—151° (when crystallised from alcohol; separates from benzene as an amorphous powder, m. p. 137—138°), are produced. The last-named compound, when hydrolysed with dilute hydrochloric acid, gives a *substance*, m. p. 252°, which may be hydrazinedithiocarbo-β-naphthylamide, formed by the decomposition of δ-β-naphthylthiosemicarbazide hydrochloride. *Acetophenone*-δ-*benzylthiosemicarbazide*, m. p. 160—161°, gives acetophenone and δ-benzylthiosemicarbazide hydrochloride, besides hydrazine hydrochloride and benzylthiocarbimide, on hydrolysis.

G. A. C. GOUGH.

Constitution of ordinary hydrocyanic acid. C. J. ENKLAAR (Rec. trav. chim., 1927, **46**, 709—710).—Speculative. E. W. WIGNALL.

Pentenonitriles. A. CASTILLE and J. GUEURDEN (Bull. Soc. chim. Belg., 1927, **36**, 509—516).—See this vol., 961.

Nitrile of thiodipropionic acid. V. NEKRASSOV (J. pr. Chem., 1927, [ii], **117**, 211—213; cf. Bennett and Hock, A., 1926, 146).—β-Chloropropionitrile (Chapman and Stephen, A., 1925, i, 669) and anhydrous sodium sulphide in ether–methyl alcohol afford ββ′-*dicyanodiethyl sulphide*, m. p. 24—25°, which is hydrolysed by boiling concentrated hydrochloric acid to ββ′-thiodipropionic acid (Lovén, A., 1896, i, 412). H. E. F. NOTTON.

Cadet's oil. I. Preparation of cacodylic acid from trimethylarsine. A. VALEUR and P. GAILLIOT (Bull. Soc. chim., 1927, [iv], **41**, 1318—1323).—Trimethylarsine (1 mol.) combines with 1 mol. of arsenious chloride, methylarsenious chloride, or phenylarsenious chloride in benzene solution, yielding crystalline additive *compounds*. The additive compounds from arsenious chloride and methylarsenious chloride decompose when heated at 200° for 10 hrs., yielding, in each case, arsenious chloride, tetramethylarsonium chloride, and arsenic. Trimethylarsine is chlorinated in benzene solution, yielding the *dichloride*, which decomposes when heated at 180°, giving methyl chloride and cacodyl chloride (87%). The latter is oxidised by hydrogen peroxide to cacodylic acid (99%). H. BURTON.

High-boiling products of Cadet's oil. A. VALEUR and P. GAILLIOT (Compt. rend., 1927, **185**, 779—781).—Fractional distillation of crude Cadet's oil (obtained by heating potassium acetate with arsenious acid) yields trimethylarsine, a mixture of cacodyl and cacodyl oxide, and 1—2% of a blue liquid, b. p. 115—120°/5 mm., d^{15} 1·647, which is not spontaneously inflammable in air and does not crystallise at −80°. It consists of a mixture, inseparable by distillation, of two methylated *derivatives*, $AsMe_3<\begin{matrix}AsMe_2\\AsMe\end{matrix}$ and $AsMe_3<\begin{matrix}AsMe\\AsMe\end{matrix}$. The former with 2 mols. of methyl iodide yields a colourless crystalline *product*, $Me_4As{\cdot}AsMeI_2{\cdot}AsMe_4$, the latter with 1 mol. forms a light yellow, viscous *oil*, $Me_4As{\cdot}AsMe{\cdot}AsMeI$. With ethyl iodide two similar *products*, $Me_3EtAs{\cdot}AsMeI_2{\cdot}AsMe_3Et$ and $Me_3EtAs{\cdot}AsMe{\cdot}AsMeI$, are obtained. The blue colour of the liquid mentioned above is readily discharged on exposure to air, and is probably due to the presence of minute particles in suspension. The colour does not fade, however, if the sample is kept in a sealed vessel even when exposed to light. Pure cacodyl has b. p. 163°, m. p. −5°, d^{15} 1·447. W. J. POWELL.

Constitution of Grignard's organo-magnesium derivatives. I. Action of water and hydrogen sulphide on asymmetric organo-magnesium

derivatives. L. KIERZEK (Bull. Soc. chim., 1927, [iv], **41**, 1299—1308; cf. Ivanov, this vol., 961; Grignard, *ibid.*, 962).—Decomposition of magnesium methyl iodide with water or dry hydrogen sulphide (cf. Mingoia, A., 1926, 388; this vol., 147), followed by extraction with ether, and analysis of the ethereal extract, shows that magnesium iodide is dissolved. The results confirm Jolibois' formula, $R_2Mg,MgHal_2$ (A., 1912, i, 753), for the constitution of Grignard reagents. H. BURTON.

Barium phenyl iodide. H. GILMAN and F. SCHULZE (Bull. Soc. chim., 1927, [iv], **41**, 1333—1336).—Iodobenzene reacts slowly with electrolytic barium, in presence of ether and a trace of iodine, yielding *barium phenyl iodide* (not isolated), since the reaction mixture reacts with carbon dioxide giving benzoic acid, with α-naphthylcarbimide affording benz-α-naphthalide, and with ethyl benzoate forming triphenylcarbinol. Ethyl iodide gives practically no metallic derivative. These barium compounds are more difficult to prepare than the corresponding calcium compounds (A., 1926, 1130). H. BURTON.

Differential cleavage of the carbon-to-carbon linking by alkali metals. J. B. CONANT and B. S. GARVEY (J. Amer. Chem. Soc., 1927, **49**, 2599—2603).—Compounds containing a reactive carbon-to-carbon linking can be differentiated by the relative rates of their reactions, in ether or benzene, with the liquid sodium–potassium alloy, 40% sodium amalgam, and 1% sodium amalgam. Thus, when 0·00025 mol. in 5 c.c. of solvent is shaken for 5 min. with 1 c.c. of the liquid metal, hexaphenylethane develops the red colour of the metallic derivative of triphenylmethyl in all cases (cf. Schlenk and Marcus, A., 1914, i, 823; Ziegler and Thielmann, A., 1923, i, 921); dibenzyldixanthyl, di-*n*-butyldixanthyl, diethyldixanthyl, and dimethyldixanthyl are unattacked only by the 1% sodium amalgam; dixanthyl is attacked by the sodium–potassium alloy in either solvent, and by the 40% sodium amalgam in ether only (cf. Conant and Garvey, this vol., 975); tetraphenylethane is attacked only by the sodium–potassium alloy, and dibenzyl is not attacked by either reagent. The rate of cleavage of a number of substituted dixanthyls, and dixanthyl itself, by the sodium–potassium alloy is essentially the same, indicating that this is controlled by a physical process. The following acids, prepared by treating the appropriate metallic derivatives with carbon dioxide (cf. Conant and Garvey, *loc. cit.*), are described: *methylxanthanoic acid*, m. p. 205—206° (*methyl* ester, m. p. 96—97°); *ethylxanthanoic acid*, m. p. 173—174°; *n-butylxanthanoic acid*, m. p. 144—145° (*methyl* ester, m. p. 73—74°); *benzylxanthanoic acid*, m. p. 232° (*methyl* ester, m. p. 103—104°). F. G. WILLSON.

Transformation of phenols into hydrocarbons by hydrogen under pressure in presence of catalysts. A. KLING and D. FLORENTIN (Bull. Soc. chim., 1927, [iv], **41**, 1341—1350).—A more detailed account of work already published (this vol., 452). H. BURTON.

Use of nitrogen tetroxide in place of nitric acid in organic nitrations. L. A. PINCK (J. Amer. Chem. Soc., 1927, **49**, 2536—2539).—Nitrobenzene is obtained in 94·4% yield by adding benzene (1 mol.) to a solution of nitrogen tetroxide (1·05 mols.) in 95% sulphuric acid (1·75 mols.) at 55—60°. Dinitrobenzene is obtained in 93·4% yield by adding nitrobenzene (1 mol.) to a solution of nitrogen tetroxide (1·10 mols.) in fuming sulphuric acid (2·8 mols.; 104·3% H_2SO_4) at 60—75°. Nitrotoluene and α-nitronaphthalene are obtained similarly to nitrobenzene in 87·5% and 88·4% yields, respectively. F. G. WILLSON.

Electropyrogenic decompositions. II. Benzene; turpentine. F. G. MÜLLER and A. BÄNNINGER (Helv. Chim. Acta, 1927, **10**, 763—770).—When an electric arc is maintained below the surface of benzene (cf. A., 1926, 43, 44), the products are amorphous carbon (25%), phenylacetylene (0·1%), diphenyl (0·33%), anthracene, diacetylene (0·03%), traces of higher acetylenes, and a gaseous mixture of acetylene 8·9—9·75%, ethylene 0·0—0·7%, benzene 0·9—1·5%, methane 0·5—3·6%, hydrogen 86·2—88·7%, and carbon monoxide trace. It is suggested that the primary decomposition products are free phenyl and acetylenyl radicals. The polymerisation of diacetylene is hastened by exposure to ultra-violet light. Oil of turpentine is decomposed by the electric arc, yielding carbon (29%), isoprene (3·9%), products condensed at −40° to −80°, from which a mixture (0·03%) containing diacetylene (60%), propinene (25%), and pentinene (15%) is isolated, and a gaseous mixture containing acetylene 8·2—8·9%, ethylene 9·3—11·4%, benzene 0·8—1·1%, methane 17·2—19·8%, and hydrogen 59·7—64·2%. H. E. F. NOTTON.

Condensation of nitrobenzyl chlorides with benzene by the Friedel and Crafts reaction, in relation to the theory of induced alternate polarities. S. C. J. OLIVIER and G. BERGER (Rec. trav. chim., 1927, **46**, 605—608).—The views of van Duin (this vol., 662) are criticised. Although the effect of an *ortho* substituent is unknown *a priori*, it is found experimentally that the $o>p>m$ rule (cf. Shoesmith and Taylor, this vol., 50), and the parallelism between ease of substitution in a certain position in an aromatic nucleus and ease of hydrolysis of halogen in a side-chain attached in that position, hold good. Comparative velocity coefficients are given for the effects of substituents on the hydrolysis of substituted benzyl chlorides, and on the reaction of substituted benzenesulphonyl chlorides with benzene in presence of aluminium chloride. The accelerating effect of the *p*-methyl group is much less in the latter reaction than in the former, and the retarding effect of the *m*-nitro-group also less in the latter than the former. It may be considered that the aluminium chloride attached to the nitro-group renders it more negative, and thus decreases its alternate polar effect. E. W. WIGNALL.

Formation of additive compounds as prelude to chemical changes. F. EBEL (Ber., 1927, **60**, [*B*], 2079—2088).—The action between *p*-toluenesulphonyl chloride and aniline in dry ether has been examined by determination of the amine hydrochloride produced. In the presence of a large excess of aniline, the rate of reaction is directly and the half period inversely proportional to the fourth power of

the concentration of the amine, whilst, if the latter is maintained constant, the half period is independent of the concentration of the sulphonyl chloride. The change appears to consist in the primary formation of an additive compound, $C_7H_7{\cdot}SO_2Cl,3NH_2Ph$, which, under the influence of a fourth molecule of the base, loses hydrogen chloride, the latter reaction determining the velocity of change. The presence of the additive compound cannot be demonstrated at any period of the change. The fourth molecule of aniline may be replaced by a tertiary base such as dimethylaniline and the acceleration produced is proportional to the concentration of the latter substance. The reaction therefore presents an instance of negative autocatalysis in which the catalyst, aniline, is also initial material and disappears during the reaction. It is the converse of the Landolt reaction. The action of the catalyst is not necessarily restricted to the facilitation of a single phase of the reaction, but extends to several such phases.

An explanation is afforded of the favourable action of pyridine in organic acylations, but the use of the cyclic base in the present instance is rendered impossible by the formation of by-products.

Evidence is also adduced in favour of the view that there are no actual processes of substitution but that all reactions occur by the production of additive compounds followed by simple fission. H. WREN.

Preparation of crystalline xylenesulphonic acids and their technical importance. E. ORLOV (Ukraine Chem. J., 1926, 2, 365—369).—Equal volumes of technical xylene (containing the three isomerides with a small amount of ethylbenzene) and sulphuric acid (*d* 1·84) are shaken together until no more heat is evolved, a temperature of 65—70° being reached. On cooling, water equal in volume to half the sulphuric acid is added, and the mixture separates into three layers, the middle one containing the xylenesulphonic acids, which after keeping for 2 days crystallise as a feathery mass, m. p. 70°. On adding water and distilling, almost pure *m*-xylene comes over with the water between 125° and 155°, the yield being 60% of the total xylene originally taken. At 155—200°, a mixture of the *meta* and *para* isomerides distils over. This method for the formation of the sulphonic acids is not suitable for benzene, toluene, or ethylbenzene. E. ROTHSTEIN.

Hydrogenation of naphthalene at high temperature and pressure without catalysts. HUGEL and J. FRIESS (Bull. Soc. chim., 1927, [iv], 41, 1185—1186).—A reply to Kling and Florentin (this vol., 452). Naphthalene is not hydrogenated in the absence of catalysts at 520° and 250 kg./cm.² by hydrogen containing a trace of oxygen. G. A. C. GOUGH.

Hydrogenation of anthracene. II. Transformations of octhracenesulphonic acid [*s*-octahydroanthracene-9-sulphonic acid]. G. SCHROETER [with S. GOTZKY] (Ber., 1927, 60, [*B*], 2035—2045; cf. A., 1925, i, 125, 127, 130).—*s*-Octahydroanthracene is converted by short treatment with concentrated sulphuric acid at a temperature not exceeding 70° into the sparingly soluble *s*-octahydroanthracene-9-sulphonic acid; if the reaction is prolonged or the temperature further raised, the sulphonic acid passes into solution from which *s*-octahydrophenanthrene-9-sulphonic acid can be isolated in yield which is quantitative except for losses caused by oxidation. The transformation is irreversible and takes place only in sulphuric acid solution. If sodium *s*-octahydroanthracene-9-sulphonate is heated under diminished presence, *s*-octahydroanthracene (80—85%), sulphur dioxide, and sodium sulphate are produced. When mixtures of the two sulphonates are heated, the anthracene derivatives alone suffer change. Separation of the sulphonic acids from one another is effected by partial hydrolysis with boiling, fuming hydrochloric acid, the anthracene compound thereby yielding *s*-octahydroanthracene, whereas *s*-octahydrophenanthrene-9-sulphonic acid remains unchanged. The action of bromine water or bromine in glacial acetic acid on *s*-octahydroanthracene-9-sulphonic acid yields 9 : 10-*dibromo*-s-*octahydroanthracene*, m. p. 200—201°, which is also prepared from the hydrocarbon and bromine in chloroform. Nascent bromine and iodine, however, afford 9-*bromo*-s-*octahydroanthracene*, m. p. 74—75°, and 9-*iodo*-s-*octahydroanthracene*, m. p. 72—73°, in which the halogen atom is very firmly retained. Treatment of 9-bromo-*s*-octahydroanthracene with sulphuric acid at 50—60° yields 9 : 10-dibromo-*s*-octahydroanthracene and *s*-octahydroanthracene-9-sulphonic acid, whereas chlorosulphonic acid converts it smoothly into 9-*bromo*-s-*octahydroanthracene*-10-*sulphonyl chloride*, m. p. 146—147°, hydrolysed to *sodium* 9-*bromo*-s-*octahydroanthracene*-10-*sulphonate* ($+5H_2O$). The latter substance is transformed by nitric acid into 9-*bromo*-10-*nitro*-s-*octahydroanthracene*, m. p. 235° (decomp.), also obtained in poorer yield by the action of nitric acid on an emulsion of *s*-octahydroanthracene in chloroform and sulphuric acid; more energetic nitration of the hydrocarbon appears to yield 9 : 10-*dinitro*-s-*octahydroanthracene*. 9-*Bromo*-10-*amino*-s-*octahydroanthracene*, m. p. 157—162°, and its *hydrochloride*, m. p. 138—140°, are obtained from the mononitro-derivative by means of titanium trichloride. The attachment of the sulphur atom to the ring carbon atom is much firmer in *s*-octahydroanthracene-9-sulphonyl chloride than in the corresponding sulphonic acid; the compound reacts with bromine in carbon tetrachloride in sunlight to give a dibromo-derivative, $C_6H_6Br_2<\begin{matrix}CH\text{——}\\ |\\ C(SO_2Cl)\end{matrix}>C_6H_8$, converted by alcoholic sodium hydroxide into *sodium* 1 : 2 : 3 : 4-*tetrahydroanthracene*-9-*sulphonate* ($+2H_2O$) [corresponding *barium* salt ($+8H_2O$)], characterised by conversion into 1 : 2 : 3 : 4-tetrahydroanthracene and 9 : 10-dibromotetrahydroanthracene, m. p. 166—168°.

Godchot's "dibromo-octahydroanthracene," $CHBr<\begin{matrix}C_6H_{10}\\ C_6H\end{matrix}>CHBr$, m. p. 194° (cf. A., 1907, i, 308, 836, 840, 841), is probably 9 : 10-dibromo-*s*-octahydroanthracene, m. p. 200—201°, and his liquid "monobromo-octahydroanthracene," $CH_2<\begin{matrix}C_6H_{10}\\ C_6H_7\end{matrix}>CHBr$, is probably a mixture of *s*-octahydroanthracene and its 9 : 10-dibromo-compound. The "dibromohexahydroanthracene," $CHBr<\begin{matrix}C_6H_8\\ C_6H_4\end{matrix}>CHBr$, m. p. 163°, is regarded as

slightly impure 9 : 10-dibromo-1 : 2 : 3 : 4-tetrahydroanthracene, m. p. 166—168°. Godchot's chloro-derivatives are probably subject to similar interpretation. H. WREN.

Electrometric titration of aniline with bromine. A. V. PAMFILOV and V. E. KISSELEVA (Z. anal. Chem., 1927, 72, 100—112).—The end-point of the potentiometric titration of aniline with bromine in a neutral solution or with bromate in an acid solution is exceedingly sharp, being marked by a potential jump of 0·1—0·2 volt according to the strength of the solution. Bromine is most suitable for weak solutions (0·01*N* or weaker) and bromate for more concentrated solutions of aniline. In solutions as weak as 0·00002*M* the results with bromine are within 2% of the theoretical. A platinum wire is used as indicator electrode and the solution is stirred mechanically during titration. A. R. POWELL.

Nitroaniline styphnates. N. N. EFREMOV (J. Russ. Phys. Chem. Soc., 1927, 59, 391—404).—The systems formed by styphnic acid with aniline and each of the three nitroanilines were investigated. When styphnic acid and aniline are fused together the mixture decomposes violently. When a solution of the components in a mixture of alcohol (75%) and ethyl acetate (25%) is boiled, a 62% yield of a crystalline *compound*, $NH_2Ph,C_6H(OH)_2(NO_2)_3$, is obtained, which decomposes on fusion. Styphnic acid and *o*-nitroaniline give a simple binary system, eutectic at 45·6° with 64·2% of *o*-nitroaniline. With *m*-nitroaniline two *compounds* are formed, $C_6H_4(NH_2)\cdot NO_2,C_6H(OH)_2(NO_2)_3$, bright orange, m. p. 156·6° (calc. 156·2°), and $2C_6H_4(NH_2)\cdot NO_2,C_6H(OH)_2(NO_2)_3$, lemon-yellow, decomp. 110—112° (m. p. calc. 105·0°). The two eutectics are at 140·2° and 98·6°, with 17·7% and 76·4% of *m*-nitroaniline. *p*-Nitroaniline forms a yellow *compound*, $C_6H_4(NH_2)\cdot NO_2,C_6H(OH)_2(NO_2)_3$, m. p. 132·3° (calc. 129·8°). The eutectics are at 124·7° and 112·2° with 28·3% and 62·3% of *p*-nitroaniline, respectively. M. ZVEGINTZOV.

Tenacity of organic radicals. VI. J. VON BRAUN and L. TAUBER (Annalen, 1927, 458, 102—111).—In continuation of previous work (A., 1924, i, 632; 1925, i, 1401) it is shown that the firmness of attachment to nitrogen of the propargyl radical is decreased by introduction of a hydrocarbon residue in the γ-position, and that the relative tenacity of the allyl and propargyl radicals is unchanged by γ-substitution. γ-Amylpropargyl alcohol (Moureu, A., 1901, i, 442) affords with phosphorus tribromide *γ-amylpropargyl bromide* [*α-bromo-Δ$^{\beta}$-octinene*], b. p. 95°/12 mm., together with its *hydrobromide*, b. p. 120—125°/14 mm. *γ-Phenylpropargyl bromide*, b. p. 135°/15 mm., is prepared similarly. By combination of aniline with the requisite alkyl bromide at a low temperature the following secondary bases are obtained: (*a*) *β-bromoallylaniline*, b. p. 147°/15 mm. (*hydrochloride*, m. p. 165°; *benzoyl* derivative, m. p. 79°; oily *picrate* and *nitroso*-derivative), which is converted by boiling aqueous alcoholic alkali into aniline and *propargylaniline*, b. p. 121°/15 mm. (*hydrochloride*, m. p. 141°; *phenylthiourethane*, m. p. 93°; *silver* derivative). The latter gives with cyanogen bromide *propargylaniline hydrobromide*, m. p. 118°, and *phenylpropargylcyanamide*, m. p. 48—49°, and with γ-amylpropargyl bromide, *propargyl-γ-amylpropargylaniline*, b. p. 163°/3 mm., which also yields phenylpropargylcyanamide (60% of theoretical) but no phenyl-γ-amylpropargylcyanamide when treated with cyanogen bromide; (*b*) *γ-phenylpropargylaniline*, m. p. 29°, b. p. 206°/15 mm. (*hydrochloride*, m. p. 166°; *picrate*, decomp. 200°); (*c*) *cinnamylaniline*, m. p. 21°, b. p. 200—202°/12 mm. (*hydrochloride*, m. p. 185°; *hydrobromide*, m. p. 156°; *picrate*, m. p. 137°; *nitroso*-derivative, m. p. 68—69°), from which *phenylcinnamylcyanamide*, m. p. 82—83°, is obtained. With phenylpropargyl bromide it forms the weakly basic *cinnamyl-γ-phenylpropargylaniline*, m. p. 60°, which is converted by cyanogen bromide into a mixture of cyanamide derivatives from which traces only of *phenyl-γ-phenylpropargylcyanamide*, m. p. 94°, can be isolated. H. E. F. NOTTON.

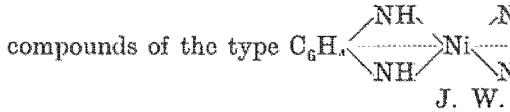
Organic compounds of tin tetrabromide. G. I. COSTEANU (Ber., 1927, 60, [*B*], 2223—2225).—The following compounds are described: *aniline hexabromostannate*, $H_2SnBr_6,2NH_2Ph$; *diphenylamine hexabromostannate*; additive *compounds* of tin tetrabromide with salicylaldehyde, $SnBr_4,2C_7H_6O_2$, and cinnamaldehyde, $SnBr_4,2C_9H_8O$; *hexabromostannates* of pyridine and quinoline. The compounds are very stable and generally crystalline; in aqueous, alcoholic, and ethereal solution they exhibit the properties of their organic components. H. WREN.

Action of trimethylethylene oxide on benzylamine. G. GABEL (Ukraine Chem. J., 1926, 2, 382—386).—One part of trimethylethylene oxide reacts with four parts of benzylamine in a sealed tube at 160—180° in 6—8 hrs., yielding *γ-benzylamino-β-methylisobutyl alcohol*, $OH\cdot CMe_2\cdot CHMe\cdot NH\cdot CH_2Ph$, b. p. 152—154°/20 mm., d_0^{15} 0·9437. The compound is not formed at 100°, but if 1 mol. of water is present in the reaction mixture, the reaction takes place at 90°. The following salts are described: *chloroaurate*, m. p. 140—142°, *picrate*; m. p. 163—164°; *hydrochloride*, m. p. 155—157°. The *chloroplatinate* could be obtained only as a thick syrup. Attempts to prepare dihydroxydi*iso*amylbenzylamine by the action of benzylamine on excess of trimethylethylene oxide were unsuccessful. E. ROTHSTEIN.

Action of chlorosulphonic acid on α- and β-naphthylamines. A. CORBELLINI (Giorn. Chim. Ind. Appl., 1927, 9, 355—357).—Chlorosulphonic acid exerts a sulphonating action on α- and β-naphthylamine sulphates, the principal products formed being those obtained by the use of other sulphonating agents. Thus, with the α-compound the main products are the 4- and 5-sulphonic acids, which result also from the action of oleum, whereas β-naphthylamine gives the 5- and 8-sulphonic acids in proportions similar to those formed by the action of either sulphuric acid or oleum. T. H. POPE.

Compounds of nickel with *o*-phenylenediamine and tolylene-3 : 4-diamine. F. FEIGL and M. FÜRTH (Monatsh., 1927, 48, 445—450).—Addition of an aqueous solution of *o*-phenylenediamine or tolylene-3 : 4-diamine to an ammoniacal solution of nickel chloride yields, on keeping, bluish-violet, amorphous

precipitates of the nickel *compounds* of composition $Ni[C_6H_4(NH)_2]$, and $Ni[C_6H_3Me(NH)_2]_2$, respectively, which are stable, are unattacked by alkalis, and possess oxidising properties. They dissolve in dilute mineral acids to yield brown solutions which no longer liberate iodine from potassium iodide nor oxidise stannous chloride. Attempts to determine the valency of the nickel present by measurements of the iodine liberated from potassium iodide solution, or the oxidation of stannous chloride lead to somewhat inconclusive results, the balance of evidence supporting the view that the nickel is quadrivalent. It is suggested that co-ordination compounds of nickel hydroxide and the diamine are first formed which lose water giving compounds of the type



J. W. BAKER.

Diphenyl and its derivatives. Interpretation of the phenomena of optical isomerism. L. MASCARELLI (Atti R. Accad. Lincei, 1927, [vi], 6, 60—65).—Unsuccessful attempts to resolve 2 : 2′-diaminodiphenyl, 2 : 2′-diamino-4 : 4′-dimethyldiphenyl, and 2 : 2′-diamino-5 : 5′-dimethyldiphenyl into optical isomerides are described. When treated with *d*-tartaric acid, 2 : 2′-diamino-6 : 6′-dimethyldiphenyl yields a less soluble salt, m. p. 159—160°, which, on treatment with ammonia, gives a product, m. p. 151°, which exhibits lævo-rotation in hydrochloric acid solution (cf. Meisenheimer and Höring, this vol., 766).

T. H. POPE.

Manufacture of *ar*-tetrahydronaphthylamines and derivatives thereof. SOC. CHEM. IND. IN BASLE.—See B., 1927, 808.

Manufacture of *cyclo*hexylamines. I. G. FARBENIND. A.-G.—See B., 1927, 809.

New azine dyes and intermediates [1 : 3-di-*p*-anisylaminonaphthalenesulphonic acids]. I. G. FARBENIND. A.-G.—See B., 1927, 808.

Formation of benzeneazoxy-*p*-phenols. D. BIGIAVI (Gazzetta, 1927, 57, 555—556).—The benzoylphenylhydrazone of benzoquinone, when heated with peracetic acid, gives *O*-benzoylbenzeneazophenol, which is immediately oxidised to a mixture of the α- and β-azoxy-compounds, m. p. 156° and 117°, respectively. Since acetic acid has no action on the phenylhydrazone, it is possible that " perhydrolysis " of the benzoyl group is the first stage. E. W. WIGNALL.

The two isomeric benzeneazoxy-*p*-toluenes. D. BIGIAVI and V. SABATELLI (Gazzetta, 1927, 57, 557—567).—When benzeneazo-*p*-toluene is treated with peracetic acid, two *benzeneazoxy*-p-*toluenes* are obtained. The α-isomeride, $NPhO{:}N{\cdot}C_6H_4Me$, (I), has m. p. 46°; the β-isomeride, $NPh{:}NO{\cdot}C_6H_4Me$, (II), obtained in smaller quantity, forms monoclinic crystals, $a : b : c = 0{\cdot}7138 : 1 : 0{\cdot}7145$; β = 70° 55′, m. p. 65°. The former does not react with bromine, but (II) gives a p-*bromo*-derivative, m. p. 112°, reduced by tin and hydrochloric acid to *p*-bromoaniline and *p*-toluidine, and by aluminium amalgam to a product containing the *hydrazo*-compound, which with mercuric oxide yields p-*bromobenzeneazo*-p-*toluene*, m. p. 153°, identical with that obtained from *p*-bromoaniline and *p*-nitrosotoluene. The β-compound gives a p-*nitro*-derivative, m. p. 163°, identical with the product of the action of peracetic acid on *p*-nitrobenzeneazo-*p*-toluene, obtained from *p*-nitroaniline and *p*-nitrosotoluene. The action of light on (I) yields a red *substance*, m. p. 112—114°, probably an *o*-hydroxy-compound; (II) very slowly turns yellow. Chromic acid oxidation converts (I) into *α-azoxybenzene-p-carboxylic acid*, m. p. 230—234°; (II) slowly gives the corresponding *β-acid*, m. p. 241°. Sulphuric acid converts (I) or (II) into a *substance*, $C_{13}H_{12}ON_2$, m. p. 150°, which is not *p*-hydroxy-*p*′-methylazobenzene, and a black substance, m. p. above 250°.

With ethyl nitrite and potassium ethoxide, (II) reacts in a similar manner to *p*-nitrotoluene (which yields the potassium salt of *p*-nitrobenzaldoxime), but no product is isolated. E. W. WIGNALL.

Sulphites of azo-compounds. A. T. KING (J.C.S., 1927, 2639—2647).—The reaction of hydroxyazo-compounds with sodium hydrogen sulphite has been investigated for varying amounts of sulphurous acid and sodium hydroxide. It proceeds at a maximum rate when more than one equivalent of alkali is present. Consequently it is considered that the compounds formed are sulphurous esters of the type $NPh{:}N{\cdot}C_{10}H_6{\cdot}O{\cdot}SO_2H$. The sulphite compounds are stable towards dilute mineral acids and towards acid iodine solution, but the original dye is regenerated with sodium hydroxide. Azo dyes derived from α-naphthol are less reactive towards sodium hydrogen sulphite than those from β-naphthol, whilst aminoazo-compounds do not give sulphite derivatives but may be decomposed completely. The following are described: *sodium* 4-*sulpho-α-naphthaleneazo-β-naphthyl sulphite*, *sodium* p-*sulphobenzeneazo-β-naphthyl sulphite*, *sodium benzeneazo*-6 : 8-*disulpho-β-naphthyl sulphite*, *sodium α-naphthaleneazo*-6 : 8-*disulpho-β-naphthyl sulphite*. M. CLARK.

Metallic complexes [co-ordination compounds] of arylazophenanthrols. G. B. CRIPPA [with G. VENTURINI] (Gazzetta, 1927, 57, 593—597).—The property of arylazo-β-naphthylamines and -β-naphthols of giving co-ordinated copper and other compounds is not shared by the corresponding benzene derivatives; 9-arylazo-10-phenanthrols, however, give such compounds, of the general formulæ M_2Cu, M_2Ni, M_2Co, where M is the organic molecule. The compounds are insoluble in water, insoluble or slightly soluble in alcohol or light petroleum, but more or less soluble in hot chloroform, benzene, or xylene. The majority do not melt below 320°. The cobalt compounds are all obtained with difficulty. 9-Benzeneazo-10-hydroxyphenanthrene in chloroform solution forms with ammoniacal copper sulphate the *copper* compound and, similarly, *nickel* and *cobalt* compounds. 9-*p*-Tolueneazo-10-phenanthrol gives a *copper* compound, m. p. 281—282°, *nickel* and *cobalt* compounds. 9-m-*Tolueneazo*-10-*phenanthrol*, m. p. 149°, obtained by condensing *m*-tolylhydrazine hydrochloride with phenanthraquinone, gives a *copper* compound, m. p. 259°, *nickel* and *cobalt* compounds; the corresponding *o*-tolueneazo-compound is not sufficiently soluble in alcohol or chloroform to give co-ordination compounds.

E. W. WIGNALL.

Diazo-sulphonates. W. L. HALL and H. D. GIBBS (J. Wash. Acad. Sci., 1927, **17**, 433—444).—Success in the preparation of diazo-sulphonates by the action of sodium sulphite on diazo-compounds depends on the proper control of the p_H value of the reaction mixture. The following procedure gave successful results in all the cases investigated. The diazotised solution and an amount of sodium hydroxide solution sufficient to neutralise the excess of acid are added simultaneously to a cooled sodium sulphite solution, the p_H value of the reaction mixture being kept strictly within certain empirical limits (which vary slightly from case to case but are usually 5·6—9·0) so that at no period is sulphur dioxide liberated; the reaction is completed by heating at 70°. High concentration of all solutions is advisable and salting out of the product is sometimes necessary. The compounds obtained are the very stable *anti* type and are all yellow or orange in colour. By this method ten diazo-sulphonates have been prepared from the appropriate amino-compounds of which the following have not previously been described: *sodium toluene*-o-*diazonium*-, *sodium* m-*xylene*-4-*diazonium*-, *sodium* p-*sulphotoluene*-o-*diazonium*-, *sodium* 2 : 6-*dichlorophenol*-4-*diazonium*-, and *sodium* 2 : 6-*dibromophenol*-4-*diazonium-sulphonates*. On reduction with zinc dust and acetic acid the corresponding hydrazinesulphonates are obtained. The following were prepared by reduction of the corresponding inner diazo-anhydride, but are not described: 3 : 5-*dichloro*-4-*hydroxy*-, 3 : 5-*dibromo*-4-*hydroxy*-, and 3 : 5-*dibromo*-4-*methoxy-phenylhydrazine hydrochlorides*. Diazotisation of 2 : 6-dibromo-4-anisidine in the presence of an insufficient excess of acid yields 3 : 5 : 3′ : 5′-*tetrabromo*-4 : 4′-*dimethoxy-diazoaminobenzene*, m. p. 187·7°. J. W. BAKER.

Oxidation of phenol with hydrogen peroxide in presence of iron salts. H. GOLDHAMMER (Biochem. Z., 1927, **189**, 81—87).—A considerable amount of pyrocatechol is always obtained by oxidation of phenol with hydrogen peroxide in presence of ferric sulphate, together with pyrogallol, purpurogallin, and traces of quinol. A method is described for the determination of each of these constituents in the mixture, and it was found that, according to the conditions of the experiment, the yield of pyrocatechol varied from 3 to 45%. The *o*-dihydroxy-derivative obtained by treating tyrosine in a similar way was produced transiently and in such small amount that its determination was impossible. The highest yield of melanin was 7·6%.

P. W. CLUTTERBUCK.

Additive compounds of phenols and ammonia. II. Ammoniation of mononitrophenols; higher ammoniates. E. BRINER and O. AGATHON (Helv. Chim. Acta, 1927, **10**, 770—781).—Vapour-pressure measurements of nitrophenol–ammonia systems (cf. A., 1926, 1241) have been extended to pressures above the atmospheric. Ammonium *o*-nitrophenoxide forms a *diammoniate*, with an energy change of the order of 60 g.-cal. per g.-mol. *Ammonium* m-*nitrophenoxide*, orange-red, m. p. 58°, does not appear to combine with ammonia, but the *p*-nitrophenoxide probably gives a *monoammoniate*. H. E. F. NOTTON.

Hydrolysis of organic compounds: [effect of] hydrogen-ion concentration. S. C. J. OLIVIER and G. BERGER (Rec. trav. chim., 1927, **46**, 609—618).—Hydrogen-ion concentration, which is without influence on the rate of hydrolysis of esters of strong acids (cf. A., 1925, ii, 802), is similarly ineffective in the hydrolysis of picryl acetate, 2 : 4 : 6-trinitrophenetole, acetic anhydride, benzoyl chloride, and benzenesulphonyl chloride, whilst it has a slight influence on that of benzoic anhydride.

Picryl acetate, m. p. 76°, obtained by the method of Hantzsch (A., 1906, i, 353) contains free picric acid; after washing with water and drying very rapidly the m. p. 96·5—97·5° is found. The ester is dissolved in 50% aqueous acetone and is shaken with benzene and a 2% aqueous potassium sulphate solution; the acid passing into solution in the aqueous layer is titrated. The velocity coefficient $k_{20}=0·032$ is unchanged in presence of 0·0215*N*-hydrochloric acid, rising slightly to 0·040(?) in presence of 0·1075*N*-acid. 2 : 4 : 6-Trinitrophenetole (ethyl picrate), which is decomposed by light and is investigated therefore in the dark, has $k_{30}=0·00012$, unchanged by the presence of hydrochloric acid. Acetic anhydride, which is determined by its reaction with aniline to give acetanilide and acetic acid, has $k_0=0·034$, unchanged by hydrochloric acid. Benzoic anhydride has $k_{40}=0·00079$, rising to 0·0015 as hydrochloric acid is added up to a concentration of 0·211*N*. Benzoyl chloride has $k_0=0·027$, unchanged by sulphuric acid; the velocity of hydrolysis of benzenesulphonyl chloride is not increased by adding sulphuric acid.

E. W. WIGNALL.

Trisuccinylpicramine. M. COVELLO and (SIGNA.) R. GABRIELI (Rend. Accad. Sci. fis. mat. Napoli, 1926, [iii], **32**, 147—150).—2 : 4 : 6-Triaminophenol condenses with succinic anhydride to give 2 : 4 : 6-*trisuccinimidophenol*, m. p. 250°, which is hydrolysed by potassium hydroxide solution to *phenol*-2 : 4 : 6-*trisuccinamic acid*, $HO·C_6H_2(NH·CO·CH_2·CH_2·CO_2H)_3$, m. p. 265° (*silver* salt), and is oxidised by nitric acid to 2 : 6-*disuccinimidobenzoquinone*, decomp. 300° (*phenylhydrazide*, m. p. 260° decomp.), which is reduced to the corresponding *quinol*, m. p. 280°.

E. W. WIGNALL.

Relative directive powers of groups of the forms RO and RR′N in aromatic substitution. VII. Nitration of benzphenetidide and of *o*-, *m*-, and *p*-nitrobenzphenetidides. R. C. FAWCETT and R. ROBINSON (J.C.S., 1927, 2414—2422).—The following compounds, obtained by benzoylation of the appropriate phenetoles, are described: 2- and 3-*nitro*-4-*benzamidophenetole* (I) and (II), m. p. 149—150° and 121·5—122°; 2- and 3-*nitro*-4-*o*-*nitrobenzamido-phenetole* (III) and (IV), m. p. 165—166° and 131—131·5°; 2- and 3-*nitro*-4-m-*nitrobenzamidophenetole*, (V) and (VI), m. p. 202—203° and 157·5—158°; 2- and 3-*nitro*-4-p-*nitrobenzamidophenetole*, (VII) and (VIII), m. p. 208·5—209·5° and 183·5—184·5°. Nitration of benz-*p*-phenetidide in acetic acid, using 2·5 mols. of nitric acid, gives a quantitative yield made up of 7·5% of (I) and 92·5% of (II). Nitration with 12 mols. of nitric acid gives 13% of (I) and 87% of (II). Nitration of *o*-, *m*-, and *p*-nitrobenzphenetidides with 12 mols. of nitric acid gives 43·7% of (III) and 56·3%

of (IV), 30·6% of (V) and 69·4% of (VI), and 33·2% of (VII) and 66·8% of (VIII), respectively. The mixtures of nitro-derivative obtained were analysed thermally. The bearing of these results on the electronic theory of benzene substitution is discussed. M. CLARK.

Bromophenols. XXVIII. Dibromo-*o*-anisidine and tribromo-*o*-anisidine. M. KOHN and H. KARLIN (Monatsh., 1927, 48, 599—611).—Nitration of 3 : 5-dibromo-*o*-acetanisidide with a mixture of nitric acid (*d* 1·52) and concentrated sulphuric acid at 0° yields 3 : 5-*dibromo*-4 : 6-*dinitro*-o-*acetanisidide*, decomp. 200°. This on hydrolysis with concentrated sulphuric acid and subsequent treatment with pyridine yields an *N*-methylpyridinium salt which on treatment with dilute sulphuric acid yields 3 : 5-*dibromopicramic acid*, m. p. 150°. Treatment of 3 : 5-dibromoanisidine hydrobromide with either liquid bromine or bromine in acetic acid yields 3 : 5 : 6-*tribromo*-o-*anisidine*, m. p. 102°, which on treatment with nitrous acid yields 3 : 5 : 6-tribromoanisole, m. p. 82°, b. p. 305—312°, and this on demethylation yields 3 : 5 : 6-tribromophenol (Bamberger and Kraus, A., 1907, i, 161) (*benzoate*, m. p. 133°). Nitration of 3 : 5 : 6-tribromoanisole with nitric acid (*d* 1·52) at 0° yields 3 : 5 : 6-*tribromo*-2 : 4-*dinitroanisole*, m. p. 141—142°. Chlorination of 3 : 5 : 6-tribromophenol yields 2 : 4-*dichloro*-3 : 5 : 6-*tribromophenol*, m. p. 208—209°, which on methylation with methyl sulphate yields 2 : 4-dichloro-3 : 5 : 6-tribromoanisole (this vol., 51). Iodination of the tribromophenol yields 3 : 5 : 6-*tribromo*-2 : 4-*di-iodophenol*, m. p. 196—197°, which on methylation yields 3 : 5 : 6-*tribromo*-2 : 4-*di-iodoanisole*, m. p. 176—177°. Nitration of 3 : 5 : 6-tribromo-*o*-acetanisidide with a mixture of nitric acid (*d* 1·52) and concentrated sulphuric acid yields 3 : 5 : 6-*tribromo*-4-*nitro*-o-*acetanisidide*, decomp. 200°. For purposes of comparison the following derivatives of 3 : 4 : 5-tribromophenol were prepared by similar methods: 3 : 4 : 5-*tribromo*-2 : 6-*dinitrophenol*, m. p. 135—136°; 3 : 4 : 5-*tribromo*-2 : 6-*di-iodophenol*, m. p. 207°; 3 : 4 : 5-*tribromo*-2 : 6-*di-iodoanisole*, m. p. 190—190·5°. J. W. BAKER.

Bromophenols. XXIX. Molecular wandering in the preparation of tribromo-*o*-anisidine from *o*-nitroanisole. M. KOHN and H. KARLIN (Monatsh., 1927, 48, 613—618).—Bromination of *o*-nitroanisole yields 4-bromo-*o*-nitroanisole, which on nitration yields 4-bromo-2 : 6-dinitroanisole, m. p. 85—85·5° (Meldola and Streatfeild, J.C.S., 1898, 73, 688, give 81—82°), and on reduction yields 4-bromo-*o*-anisidine. The latter, on bromination, yields 3 : 5 : 6-tribromo-*o*-anisidine (preceding abstract) instead of the expected 3 : 4 : 5-tribromo-compound, a bromine atom wandering from the 4- to the 6-position during bromination. Proof of the constitution of the product is adduced by its conversion consecutively into 3 : 5 : 6-tribromoanisole and 3 : 5 : 6-tribromophenol. Bromination of *p*-nitroanisole yields 2-bromo-*p*-nitroanisole. J. W. BAKER.

Nitration of α-4-methoxy- and α-4-ethoxyphenyl-β-ethylcarbamide. H. F. J. LORANG (Rec. trav. chim., 1927, 46, 635—652).—*p*-Anisidine and ethylcarbimide condense to give α-p-*anisyl*-β-*ethylcarbamide*, m. p. 138°, which is nitrated by absolute nitric acid at −10° to *α-nitro*-β-2 : 3 : 5-*trinitro*-p-*anisyl*-α-*ethylcarbamide*, decomp. 50—60°, which gives nitroamine reactions. With water, the latter yields 2 : 3 : 5-trinitro-*p*-anisidine; with ethyl alcohol, 2 : 3 : 5-trinitro-*p*-anisylurethane (cf. Reverdin, A., 1926, 1243); with methyl alcohol, the corresponding *methylurethane*, m. p. 236—239° (decomp.); with alcoholic ammonia, 2 : 4-dinitro-6-methoxy-*m*-phenylenediamine; with aniline in ether, 2 : 6-*dinitro*-3-*anilino*-4-*methoxycarbanilide*, m. p. 182—183° (decomp.).

p-Phenetidine and ethylcarbimide condense to give α-p-*phenetyl*-β-*ethylcarbamide*, m. p. 152°, which is similarly nitrated to *α-nitro*-β-2 : 3 : 5-*trinitro*-p-*phenetyl*-α-*ethylcarbamide*, m. p. 92—98° (decomp.). This with water yields 2 : 3 : 5-trinitro-*p*-phenetidine, and also 3 : 5-dinitro-2-hydroxy-*p*-phenetidine; with methyl and ethyl alcohols, the 2 : 3 : 5-trinitro-*p*-phenetyl-methyl- and -ethyl-urethanes, m. p. 236—239° (decomp.) and 218—219°, respectively, each hydrolysed to the amine; with alcoholic ammonia, 2 : 4-dmitro-6-ethoxy-*m*-phenylenediamine; with aniline, 2 : 6-*dinitro*-3-*anilino*-4-*ethoxycarbanilide*, m. p. 216—217°.

m-Phenylenediamine reacts with ethylcarbimide to give m-*di*-β-*ethylcarbamidobenzene* (decomp. 120—126° to *s*-diethylcarbamide and *m*-dicarbamidobenzene). The product is nitrated to ββ′ : 2 : 4 : 6′-*pentanitro*-ββ′-*diethyl*-m-*dicarbamidobenzene*, $C_6H(NO_2)_3(NH{\cdot}CO{\cdot}NEt{\cdot}NO_2)_2$, decomp. 80—85°, which with water or alcoholic ammonia yields 2 : 4 : 6-trinitro-*m*-phenylenediamine; with ethyl alcohol, 2 : 4 : 6-*trinitrophenylene*-1 : 3-*diurethane*, m. p. 226°, of which the *methyl* analogue has m. p. 276° (decomp. from 260°); with aniline, 2 : 4 : 6-*trinitro*-1 : 3-*di*-β-*phenylcarbamidobenzene*, m. p. 276°.

E. W. WIGNALL.

Equilibria in binary systems containing trinitro-*m*-cresol. N. N. EFREMOV and M. A. TICHOMIROVA (J. Russ. Phys. Chem. Soc., 1927, 59, 373—389).—The nature of the binary systems formed by the addition of hydrocarbons and nitro-derivatives to trinitro-*m*-cresol was determined, with the view of utilising them on a technical scale in the manufacture of explosives. Trinitro-*m*-cresol and acenaphthene, phenanthrene, fluorene, and retene gave well-defined *compounds*, but no solid solutions. The acenaphthene *compound*, $C_{12}H_{10},C_6HMe(NO_2)_3{\cdot}OH$, has m. p. 117·9°; the eutectics are at 88·2° and 87·8°, with 9·1% and 79·8% of acenaphthene. The phenanthrene *compound*, $C_{14}H_{10},C_6HMe(NO_2)_3{\cdot}OH$, m. p. 113·1°, is deep red; eutectics 85·6° and 84·2° with 13·5% and 77·5% of phenanthrene. The fluorene *compound*, grey when solid, red when liquid, $C_{13}H_{10},C_6HMe(NO_2)_3{\cdot}OH$, grey solid, red liquid, has m. p. 107·2°; eutectics at 85·4° and 90·5° with 13·8% and 67·4% of fluorene. The retene *compound*, $C_{18}H_{18},C_6HMe(NO_2)_3{\cdot}OH$, violet, has m. p. 118·3°; eutectics at 89·5° and 73·5° with 6·7% and 88·6% retene. The system trinitro-*m*-cresol–anthracene was too unstable to be determined. Trinitro-*m*-cresol with tetranitromethylaniline forms a eutectic at 64·4° with 42·3% of the latter; with picric acid the eutectic point is at 52·5° and 35·6%, with *m*-dinitrobenzene, 55·4° and 44·8%, with trinitrotoluene, 41·3° and 42·3%.

There was no trace of compound or solid solution formation. The explosive properties of the systems are being investigated. M. ZVEGINTZOV.

Rule for direct formation of free acid chlorides by action of phosphorus pentachloride on 6-substituted phenol-o-sulphonic acids. R. ANSCHUTZ and T. CURTEN (Annalen, 1927, 457, 256—267; cf. L. Anschutz, this vol., 663).—A hydroxyl group is protected by the presence of two *ortho* substituents from attack by phosphorus pentachloride, so that 6-substituted phenol-2-sulphonyl chlorides may be prepared directly.

o-Nitro-p-cresol-3-sulphonic acid (discovered by Raschig but not hitherto described), m. p. 84° ($+1{\cdot}5H_2O$) or 172° (anhyd.; *ammonium*, *sodium*, *potassium*, *silver*, *magnesium*, *barium*, *nickel*, and *cobalt* salts prepared), is converted by phosphorus pentachloride into *o-nitro-p-cresol-3-sulphonyl chloride*, m. p. 86—87°, from which are obtained the *sulphonamide*, m. p. 210° (decomp.), *sulphonanilide*, m. p. 217°, and *sulphon-p-toluidide*, m. p. 226°. The acid gives the *anhydride*, m. p. 158—159°, when treated with thionyl chloride, and with acetyl chloride or acetic anhydride the *acetate*, which is converted by phosphorus pentachloride into *o-nitro-4-acetoxytoluene-3-sulphonyl chloride*, m. p. 101·5° (*sulphonanilide*, m. p. 141·5°, and *sulphon-p-toluidide*, m. p. 113°, described). 5 : 5′-*Dinitrotolylene*-3 : 4 : 3′ : 4′-*sulphonylide*,

$$(3)\,NO_2>C_6H_2<^{(4)}O\cdot SO_2\cdot O>^{(5')}C_6H_2<NO_2\,(5')\ (4)\ Me \qquad SO_2\cdot O \qquad Me$$

m. p. 84·5°, results from the action of ammonia or diethylaniline on the acetoxy-sulphonyl chloride, or of phosphoryl chloride on the nitrocresolsulphonic acid.

p-Cresol-3 : 5-disulphonic acid, m. p. 115° ($+2H_2O$) or 145° (anhyd.; *silver*, potassium, and barium salts described), reacts with phosphorus pentachloride to form p-*cresol*-3 : 5-*disulphonyl chloride*, from which the *disulphonanilide*, m. p. 231°, *disulphon-p-toluidide*, m. p. 221°, and acetate, m. p. 116°, are prepared. The corresponding tolylene-3 : 4 : 3′ : 4′-sulphonylide-5 : 5′-disulphonyl chloride (Anschutz and Hodenius, A., 1918, i, 425) gives a *disulphonanilide*, m. p. 262—263°, and a *disulphon-p-toluidide*, m. p. 258—259°. C. HOLLINS.

Supposed isomerism of 9-methylfluorenol. H. WIELAND and J. CEREZO (Annalen, 1927, 457, 249—255; cf. Wieland and Krause, A., 1925, i, 902).—The "isomeric 9-methylfluorenol," m. p. 84°, is shown to be 9-methylfluorenyl ethyl ether. It is best obtained by Nakamura's method by the action of alcohol on the *acetate* of the true 9-methylfluorenol (m. p. 175°), and is also formed by treating 9-methylfluorenyl chloride with sodium ethoxide. *9-Methylfluorenyl benzoate*, m. p. 173°, is unchanged by boiling alcohol, but is converted by hot acetic acid into benzoic acid and diphenylene-ethylene [9-methylenefluorane]. C. HOLLINS.

Synthesis of the homologue of urushiol. II. S. KAWAI (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1927, 6, 53—60).—Condensation of sodium phenoxide with geranyl chloride (obtained by Forster's method, J.C.S., 1913, 103, 1338) in toluene by Claisen's method (A., 1925, i, 656) yields *o-geranylphenol*, b. p. 126—130°/0·12—0·09 mm., d_4^{25} 0·97029, n_D^{25} 1·53414, *phenyl geranyl ether*, b. p. 102—106°/0·16 mm. (not quite pure), d_4^{25} 0·9551, n_D^{25} 1·52037, together with an unidentified terpene (cf. Forster, *loc. cit.*). By a similar condensation using pyrocatechol is obtained a mixture of 3-*geranylpyrocatechol*, b. p. 179—180°/0·16 mm., d_4^{20} 1·0566, n_D^{20} 1·55068, and *pyrocatechol monogeranyl ether*, which undergoes isomeric change on distillation in a high vacuum. Separation is effected by conversion into the *lead* salts, that of the former being insoluble in alcoholic lead acetate. Small quantities of a terpene and (?)pyrocatechol digeranyl ether are also obtained. The physiological action of 3-geranylpyrocatechol on the skin closely resembles that of urushiol, whilst *o*-geranylphenol and pyrocatechol monogeranyl ether have no such action. J. W. BAKER.

Relative directive powers of groups of the form RO and RR′N in aromatic substitution. VIII. Nitration of 4-*n*-butoxyanisole. J. CLARKE, R. ROBINSON, and J. C. SMITH (J.C.S., 1927, 2647—2653).—Treatment of 3- and 2-nitro-4-methoxyphenols with *n*-butyl bromide in boiling methyl alcohol gives 2-*nitro*-4-n-*butoxyanisole* (I), m. p. 13·2°, b. p. 143°/1 mm., $n^{14\cdot4}$ 1·5382, and 3-*nitro*-4-n-*butoxyanisole* (II), m. p. −9·7°, b. p. 137°/1 mm., n_D^{14} 1·5358, respectively. Thermal analysis shows that the nitration product of 4-n-*butoxyanisole*, m. p. 24·5—25·5°, obtained by butylation of quinol monomethyl ether, contains 65% of (II). This result is in harmony with the theory advanced previously (A., 1926, 397). A mixture of equal quantities of *n*-propyl gallate, m. p. 147—148°, and *n*-butyl gallate, m. p. 143—144° (lit. 133—134°), melts at 152—154°. Crystallographic data are given for 2-nitro-4-methoxyphenol, 2-nitro-4-ethoxyanisole, and 2-nitro-4-*n*-propoxyanisole. M. CLARK.

Dyes and other compounds from 2 : 6-dihydroxytoluene. F. HENRICH and W. HEROLD (Ber., 1927, 60, [*B*], 2053—2058; cf. A., 1921, i, 886; 1923, i, 145).—The development of fluorescence in alkaline solutions of hydroxybenzoxazole derivatives, $OH\cdot C_6H_3<^{N}_{O}>CR$, is observed only when R is an aryl group directly united to the 2-carbon atom and when the hydroxyl group is in the *para*-position to the nitrogen atom. *5-Nitroso-2 : 6-dihydroxytoluene*, m. p. (from benzene) 147° (from alcohol, m. p. 147° after darkening at 127°), is prepared by the action of amyl nitrite on 2 : 6-dihydroxytoluene in ethylalcoholic potassium hydroxide; the *potassium*, *copper*, *cobalt*, *nickel*, *lead*, *uranium*, and *zinc* salts are described. It is reduced by stannous chloride and hydrochloric acid to 5-amino-2 : 6-dihydroxytoluene, isolated as the *hydrochloride* ($+2H_2O$). The latter substance is converted by boiling benzoyl chloride into a mixture of *o-benzamido-2 : 6-dibenzoyloxytoluene*, m. p. 211°, and 6-*benzoyloxy-2-phenyl-7-methylbenzoxazole*, m. p. 176°, hydrolysed to 6-hydroxy-2-phenyl-7-methylbenzoxazole, m. p. 206°.

Autoxidation of 3-amino-2 : 6-dihydroxytoluene in alkaline solution gives a blue dye which has not been fully investigated. H. WREN.

Action of ammonia on *iso*safrole oxide. K. KRASSOVSKY and T. KUSNER (Ukraine Chem. J., 1926, **6**, 376—381).—Ammonia reacts with *iso*safrole oxide in alcoholic solution at 100° after 10 hrs. to give an *amine* having the structure $CH_2O_2{:}C_6H_3{\cdot}CH(NH_2){\cdot}CHMe{\cdot}OH$ or $CH_2O_2{:}C_6H_3{\cdot}CH(OH){\cdot}CHMe{\cdot}NH_2$. The compound has an alkaline reaction, is soluble in alcohol and ether, and decomposes on distillation. The *chloroplatinate*, m. p. 195—196° (decomp.), and *picrate*, m. p. 204° (decomp.), are described. E. ROTHSTEIN.

Feeble activation of certain extended conjugated systems by doubly-bound oxygen. R. ROBINSON and A. ZAKI (J.C.S., 1927, 2485—2490).—Phenyl 2-chlorostyryl ketone and ethyl 2-chloro-α-cyanocinnamate could not be converted into quinoline derivatives by reaction with carbamide nor would the chlorine atom react with aniline in presence of copper powder. 2-*Chlorobenzylidene*-1 : 3-*diketohydrindone*, m. p. 130—131°, from *o*-chlorobenzaldehyde and diketohydrindene, condenses with carbamide under drastic experimental conditions to give a very small yield of ketoindenoquinoline. 2′-*Chloro*-2 : 4-*dinitrostilbene*, m. p. 174°, and 2′-*methoxy*-2 : 4-*dinitrostilbene*, m. p. 176°, from 2 : 4-dinitrotoluene and *o*-chloro- or *o*-methoxy-benzaldehyde, show no reactivity of the chloro- or methoxyl groups. *Bromodihydrosafrole*, b. p. 160°/16 mm., prepared by the action of hydrobromic acid on safrole, yields *iso*safrole when heated with aniline. *iso*Safrole could not be nitrated directly, but bromodihydrosafrole on nitration in acetic acid solution and subsequent removal of hydrobromic acid yields 6-*nitroisosafrole*, m. p. 88°, the orientation of this compound being established by the preparation of 6-nitropiperonal. No conclusive evidence of reactivity of the methyl group in this compound could be obtained. 6-*Aminoisosafrole*, m. p. 68—69° (*hydrochloride*), may be diazotised and coupled with β-naphthol to give a crimson *azo*-derivative. 6-*Acetamidoisosafrole*, m. p. 206°, yields an oily *dibromide*, converted by alcoholic potassium hydroxide into 5 : 6-methylenedioxy-2-methylindole. It is therefore concluded that extended crotenoid systems may fail to exhibit the reactivity which might be assumed to be their characteristic. *o*-*p*-Substitution in styrene derivatives is probably due to a definite *o*-*p*-orienting influence of the unsaturated group. The views of Baker and Wilson (this vol., 550) regarding the *o*-*p*-orienting influence of ethenoid and benzenoid groups are controverted. M. CLARK.

Tautomerism of phenols. X. Phenylhydrazine and naphthols of the α-series. W. FUCHS and F. NISZEL (Ber., 1927, **60**, [*B*], 2058—2062; cf. this vol., 257).—The action of phenylhydrazine and sulphurous acid on 1 : 4-dihydroxynaphthalene gives an oily base which is conveniently isolated as the *benzoyl* derivative, m. p. 163°. The latter compound is not identical with the benzoyl compound of 4-benzenehydrazo-α-naphthol, m. p. 162° (conveniently prepared by benzoylation of benzeneazo-α-naphthol by the Schotten–Baumann method and reduction of the product by aluminium amalgam in alcohol). Reduction of 4-benzeneazo-α-naphthol by zinc dust and aluminium filings in alkaline solution followed by benzoylation of the product gives the compound, m. p. 163°. Since this compound loses one half of its nitrogen and affords a *compound*, $C_{23}H_{17}O_2N$, m. p. 202°, when treated with nitrous fumes in alcohol, it is considered to be 4-p-*aminoanilino*-2-*naphthyl benzoate*. H. WREN.

Constitution and colour. XIV. F. KEHRMANN (Helv. Chim. Acta, 1927, **10**, 670—676).—The theory of Dilthey (A., 1925, i, 650) is insufficient alone to account for the properties of salt-forming dyes. For instance, the greenish-red diacid salts of azobenzene are represented as derivatives of the feebly-coloured hydrazobenzene, $[Ph{\cdot}NH{\cdot}NH{\cdot}Ph]A_2$. The formulæ ascribed to monoacid salts of *apo*safranine and other quinoneimine dyes contain amino-groups, whereas diazotisation experiments show that these are present only in polyacid salts. Dilthey's formulæ fail to express the close chemical resemblance between quinones and dyes, *e.g.*, between *o*-benzoquinone and *N*-phenylphenazonium salts, neither do they account for the absence of triphenylmethane dyes related to *m*-quinones. If, however, the double linking is regarded as co-ordinatively univalent (cf. Piccard and Dardel, A., 1921, ii, 394) it is possible to introduce the classical chromophores into the co-ordination formulæ. Thus, the above azobenzene derivative is written $[Ph{\cdot}NH{:}NH{\cdot}Ph]A_2$, and dimethylfuchsimonium chloride, $[CPh_2{:}C_6H_4{:}NMe_2]Cl$.
H. E. F. NOTTON.

New derivative of Michler's ketone. E. PACE (Arch. Farm. sperim., 1927, **26**, 225—230).—pp′-*Tetramethyldiaminoethylbenzhydrol*, $OH{\cdot}CEt(C_6H_4{\cdot}NMe_2)_2$, obtained by the action of magnesium ethyl bromide on *pp*′-tetramethyldiaminobenzophenone, has m. p. 127°, and forms a *monohydrochloride*, m. p. 127°, a *monosulphate*, m. p. 144°, an *acetate*, an *oxalate*, and a *tartrate*. Its *benzoyl* derivative, m. p. 166·5°, is without anæsthetic action and passes almost unchanged into the fæces.
T. H. POPE.

Stereoisomerism in trisubstituted α-glycols (phenyldialkylglycols and alkylhydrobenzoins). M. TIFFENEAU and (MLLE.) J. LÉVY (Bull. Soc. chim., 1927, [iv], **41**, 1351—1362).—The action of magnesium alkyl halides on ketols, according to the schemes $OH{\cdot}CHR{\cdot}CO{\cdot}R' \longrightarrow OH{\cdot}CHR{\cdot}CR'R''{\cdot}OH \longrightarrow OH{\cdot}CHR{\cdot}CO{\cdot}R''$, does not produce the same glycol, but results in the formation of stereoisomerides. Thus, propionylphenylcarbinol and magnesium methyl iodide yield a β-isomeride of *α-phenyl-β-methylbutane-αβ-diol*, m. p. 73—74°, whilst acetylphenylcarbinol and magnesium ethyl bromide give the α-isomeride, m. p. 83—84° (Fischer and Taube, A., 1926, 599). Both glycols are dehydrated by concentrated sulphuric acid to α-phenyl-*n*-propyl methyl ketone. Similarly, from acetylphenylcarbinol and magnesium *iso*propyl bromide there is produced an α-isomeride of *α-phenyl-βγ-dimethylbutane-αβ-diol*, m. p. 98—99°, whilst the β-*isomeride*, m. p. 124—125°, results from magnesium methyl iodide and *iso*butyrylphenylcarbinol. Pairs of isomeric (α- and β-) glycols have been prepared from the requisite ketols and magnesium alkyl

halides as follows: *α-phenyl-β-ethylpentane-αβ-diols*, m. p. 94—95° and 99—100°; *α-phenyl-β-isopropylbutane-αβ-diols*, m. p. 75° and 113°; *α-phenyl-β-ethylhexane-αβ-diols*, m. p. 88—89° and 81—81·5° (α- and β-*acetonyl* derivatives, b. p. 155—158°/25 mm., d^0 0·999, and b. p. 170—173°/30 mm., d^0 0·992, respectively); *α-phenyl-δ-methyl-β-ethylpentane-αβ-diols*, m. p. 85—86° and 90—91°; *α-phenyl-β-n-propylhexane-αβ-diols*, m. p. 115° and 91—92°; *α-phenyl-β-isopropylhexane-αβ-diols*, m. p. 90° and 75—76°; and *α-phenyl-β-benzylpentane-αβ-diols*, m. p. 115—116°, and viscous oil. Dehydration of this last pair of glycols yields αβ-diphenylethyl propyl ketone.

Acetylphenylcarbinol and magnesium phenyl bromide yield α-methylhydrobenzoin, m. p. 94—95°, also formed by hydrating methylstilbene oxide. The β-isomeride is obtained from benzoin and magnesium methyl iodide, and has m. p. 104—105° (cf. Fischer and Taube, *loc. cit.*). Similarly, α-ethylhydrobenzoin, m. p. 105—106° (*acetonyl* derivative, m. p. 62—63°), is obtained from magnesium phenyl bromide and propionylphenylcarbinol, whilst the β-isomeride from benzoin and magnesium ethyl bromide has m. p. 116—117° (*acetonyl* derivative, m. p. 42°). Diacetyl and magnesium phenyl bromide yield α-dimethylhydrobenzoin, m. p. 121—122°, whereas benzil and magnesium methyl iodide give β-dimethylhydrobenzoin, m. p. 87°. Dehydration of the α- and β-isomerides gives αα-diphenylethyl methyl ketone.

H. Burton.

Constitution of *iso*campholic acid. P. Lipp and F. Reinartz (Helv. Chim. Acta, 1927, **10**, 611—614).—Evidence is adduced in favour of the view that campholic and *iso*campholic acids are stereoisomeric 1 : 2 : 2 : 3-tetramethyl*cyclo*pentane-1-carboxylic acids, the carboxyl group and the 3-hydrogen atom being relatively *cis* and *trans*, respectively. The bromination of *iso*campholic acid by the method of Hell, Volhard, and Zelinsky (Rupe and Briellmann, A., 1922, i, 1017) is not conclusive evidence of the presence of an α-hydrogen atom, since campholic acid is also brominated under these conditions, giving a mixture of products, b. p. 65—75°/2 mm., containing less than 1 atom of bromine per mol. It is assumed that a 3-bromo-derivative is formed in each case, that of campholic acid being partly converted into the lactone, whilst that of *iso*campholic acid is stable. The optically active unsaturated acid obtained (*loc. cit.*) by treating the latter with alkali would, accordingly, be 1 : 2 : 2 : 3-tetramethyl-Δ^3-*cyclo*pentene-1-carboxylic acid. Attempts to isomerise campholic acid by heating at 170—180° with acetic and hydrochloric acids, or by means of ultra-violet light, were unsuccessful.

H. E. F. Notton.

Benzoylformhydroxamic acid oximes. XIV. C. Gastaldi (Gazzetta, 1927, **57**, 620—621).—A final contribution to the controversy with Ponzio (cf. this vol., 462). Hydroxylamine is considered unlikely to cause an isomerisation of benzoylformhydroxamic acid to a nitronic acid; the α-oxime is still held to be stereoisomeric with the β-oxime.

E. W. Wignall.

Mechanism of the thermal decomposition of benzoyl peroxide. H. Erlenmeyer (Helv. Chim. Acta, 1927, **10**, 620—627).—The formation of benzoic acid in the thermal decomposition of benzoyl peroxide (cf. Gelissen and Hermans, A., 1925, i, 379) may be due (*a*) to the formation of diphenyl which then reacts as follows (*R·H* scheme): $Ph{\cdot}Ph+(Ph{\cdot}CO{\cdot}O)_2 \longrightarrow C_6H_4Ph_2+Ph{\cdot}CO_2H$; or (*b*) to initial decomposition thus $(Ph{\cdot}CO{\cdot}O)_2 \longrightarrow (Ph{\cdot}CO)_2O+O$, followed by hydrolysis. According to (*a*) the amount of benzoic acid formed should decrease in proportion as the peroxide is diluted with an inert material such as finely-divided carborundum; actually it is found to increase. Further evidence in favour of (*b*) is obtained by exploding the peroxide in air in a closed vessel when the atmospheric oxygen is converted into carbon monoxide, whilst in an atmosphere of carbon dioxide unsaturated gaseous hydrocarbons are formed. In air the reaction (*b*) is probably followed by complete oxidation: $(Ph{\cdot}CO{\cdot}O)_2+O+O_2 \longrightarrow CO_2+CO+H_2O$. This reaction provides the water necessary for the hydrolysis of the benzoic anhydride and the heat required for secondary decompositions, *e.g.*, $(Ph{\cdot}CO{\cdot}O)_2 \longrightarrow Ph{\cdot}Ph+CO_2$. The formation of benzoic acid from iodine and benzoyl peroxide (A., 1926, 1138) is explained along similar lines, the *R·H* mechanism suggested by Reynhart (this vol., 356) being disproved by analysis of the reaction product, which contains no iododiphenyl. A further exception to the *R·H* scheme is the decomposition of perbenzoic acid which yields only benzoic acid and oxygen.

H. E. F. Notton.

Method of hydrolysing amides and nitriles. G. Berger and S. C. J. Olivier (Rec. trav. chim., 1927, **46**, 600—604).—2 : 6-Dimethylbenzonitrile, which is not hydrolysed by 90% sulphuric acid, nor by a methyl- or amyl-alcoholic solution of potassium hydroxide, is hydrolysed by concentrated sulphuric acid merely to 2 : 6-*dimethylbenzamide*, m. p. 138·5—139° (corr.). This amide can be hydrolysed by 100% phosphoric acid at 145—150°, which is employed also for the hydrolysis of benzamide, benzonitrile, α-naphthonitrile, acetonitrile, and propionitrile, and gives good yields of the acids. Phosphoric acid forms a crystalline *compound* with acetonitrile, m. p. 51—53°.

E. W. Wignall.

Rearrangement of acid azides and hydroxamic acids of geometrical isomerides. L. W. Jones and J. P. Mason (J. Amer. Chem. Soc., 1927, **49**, 2528—2536; cf. A., 1926, 279).—When allo*cinnamyl chloride*, obtained by the action of thionyl chloride on ethereal *allo*cinnamic acid at 0°, is treated with sodium azide in ethereal suspension, nitrogen is continuously evolved, indicating the decomposition and rearrangement of the allo*cinnamyl azide*. Treatment of the product with ammonia affords a *styrylcarbamide*, m. p. 143°, identical with that obtained similarly from *styrylcarbimide*, b. p. 107°/12 mm., which is the product of the rearrangement of cinnamyl azide (cf. Forster, J.C.S., 1909, **95**, 437) in benzene at 75—80°. It is therefore concluded that the stable configuration is assumed during the rearrangement of *allo*cinnamyl azide. Treatment of styrylcarbimide with water at 50°, or of cinnamyl azide with boiling water, affords s-*distyrylcarbamide*, m. p. 214°. Treatment of ethereal crotonyl chloride with sodium azide affords *crotonyl azide*, a pungent liquid, which loses

nitrogen at 75—85° with formation of *propenylcarbimide*, a liquid. Treatment of the latter with ethereal ammonia affords *propenylcarbamide*, m. p. 122°. iso*Crotonyl azide*, obtained similarly, undergoes slow rearrangement at 25—28°, and treatment of the product with ammonia affords propenylcarbamide, identical with the above, indicating that in this case also the stable configuration had been assumed during rearrangement. Cinnamhydroxamic acid is best prepared by the method of Jones and Hurd (A., 1922, i, 248). It has m. p. 119·5° (benzoyl derivative, m. p. 156·5°). When cinnamhydroxamic acid is treated with an equivalent of aqueous sodium carbonate, or when the potassium salt of the benzoyl derivative is warmed with water, a *product*, m. p. 152°, is obtained, which is not the expected disubstituted carbamide. F. G. Willson.

Derivatives of diphenylamine-2-carboxylic acid. III. H. Goldstein and M. de Simo (Helv. Chim. Acta, 1927, 10, 603—606; cf. this vol., 558).—2-Chloro-5-nitrobenzoic acid and *m*-phenylenediamine afford, in presence of potassium carbonate and catalytic copper ("Naturkupfer C"), *4-nitro-3′-aminodiphenylamine-2-carboxylic acid*, decomp. about 250°. This is reduced by stannous chloride to *4 : 3′-diaminodiphenylamine-2-carboxylic acid*, m. p. 221° (decomp.) (double *tin* salt; *dihydrochloride*; *methyl* ester, m. p. 120°; *diacetyl* derivative, decomp. 252°). Attempts to condense 2-chloro-4-nitrobenzoic acid with *p*-phenylenediamine yielded only *p*-nitrobenzoic acid. 4′-Diethylaminodiphenylamine-2-carboxylic acid, m. p. 215° (*methyl* ester, m. p. 61°), has been obtained crystalline (cf. Tuttle, A., 1923, i, 1011). 4-Nitro-4′-diethylaminodiphenylamine-2-carboxylic acid is reduced by stannous chloride to *4-amino-4′-diethylaminodiphenylamine-2-carboxylic acid*, m. p. 194° (decomp.) (double *tin* salt; *dihydrochloride*; *methyl* ester, m. p. 86°). H. E. F. Notton.

3-Hydroxy*cyclo*hexylacetolactone. R. Robinson and A. Zaki (J.C.S., 1927, 2411—2413).—Reduction of *m*-hydroxyphenylacetic acid with hydrogen in the presence of platinum-black gives, as main product, hexahydrophenylacetic acid together with a small quantity of *3-hydroxycyclohexylacetolactone*, b. p. 240—243°. The lactone contains a ring system similar (O instead of N) to that which occurs in the molecules of alkaloids of the morphine group (Gulland and Robinson, J.C.S., 1923, **123**, 980). Treatment of ethyl acetonedicarboxylate with ethyl bromoacetate and an alcoholic solution of sodium ethoxide gives *ethyl βδ-dicarbethoxy-γ-ketopimelate*, b. p. 168—170°/1 mm., hydrolysed by dilute sulphuric acid to acetonediacetic acid. Further treatment with the same reagents gives *ethyl -tricarbethoxyisobutyrylsuccinate*, b. p. 189—191°/1 mm. M. Clark.

Beckmann rearrangement of salicylhydroxamic acid derivatives. A. W. Scott and J. H. Mote (J. Amer. Chem. Soc., 1927, 49, 2545—2549).—The *potassium* salt of the *acetyl* derivative, m. p. 142°, of salicylhydroxamic acid (cf. Jeanrenaud, A., 1889, 870) explodes at 85° without evolving any odour of phenylcarbimide. When boiled in aqueous solution, it yields oxycarbanil and acetic acid, whilst *o*-aminophenol could not be detected. The *sodium* and *potassium* salts of the *benzoyl* derivative, m. p. 153°, of salicylhydroxamic acid explode similarly when heated, without evolving odours of phenylcarbimide, and yield oxycarbanil and benzoic acid when boiled in aqueous solution. The results indicate that a carbimide is not formed during the Beckmann rearrangement of these derivatives. F. G. Willson.

Chlorination and bromination of hydroxybenzoic acids with a mixture of halogen acid and hydrogen peroxide. A. Leulier and L. Pinet (Bull. Soc. chim., 1927, [iv], **41**, 1362—1370).—Treatment of *o*- and *p*-hydroxybenzoic acids with a mixture of hydrochloric or hydrobromic acid and hydrogen peroxide gives mono- or dihalogenated products according to the conditions employed. *m*-Hydroxybenzoic acid yields the tribromo-derivative. H. Burton.

Velocity measurements on the opening of the lactone ring in derivatives of phthalide. A. Tasman (Rec. trav. chim., 1927, **46**, 653—698).—The solubilities, and velocities of ring-opening under the influence of 0·1*N*-potassium hydroxide solution have been determined at 25° for phthalide and its derivatives. For phthalide, $k_{25}\times10^4=49$; for derivatives containing the following substituents the respective values for the solubilities in g. per 100 c.c. of water at 25° and for the velocity coefficient $k_{25}\times10^4$ are: 5-nitro- (new m. p. 147°), 0·0420, 520; 5-amino- (new m. p. 182°), 0·1356, 15; 5-acetamido-, 0·0480, 37; 5-chloro-, 0·0556, 65; 5-bromo-, 0·0480, 75; 5-iodo-, 0·0160, 98; 5-*cyano*- (m. p. 194°, obtained from phthalidediazonium chloride), 0·0316, 280; 5 : 6-dimethoxy- (meconine), 0·2548, 32; 3-nitro-5 : 6-dimethoxy-, 0·0148, 440; 3-amino-5 : 6-dimethoxy-, 0·1752, 29; 3-bromo-5 : 6-dimethoxy-, 0·0032, insufficiently soluble; 3-*cyano*-5 : 6-*dimethoxy*- (m. p. 233·5°, decomp.), 0·0072, insufficiently soluble; 2-methyl- (b. p. 284—285·5°), 0·1012, 34; 5-nitro-2-methyl-, 0·0468, 210; 5-amino-2-methyl-, 0·2652, 22; 5-*cyano*-2-*methyl*- (m. p. 117°), 0·0540 (at 17·5°), 360; 2-ethyl- (b. p. 294·5—295·5°, 151—152°/17 mm.), 0·2904, 30; 5-nitro-2-ethyl-, 0·0584, 160; 5-amino-2-ethyl-, 0·0568, 7·9; 5-*cyano*-2-*ethyl*- (m. p. 90°), 0·0912, 230; 2-*propyl*- (m. p. 20°, b. p. 150°/14 mm., d_{15}^{15} 1·1073, $n_D^{17·5}$ 1·5327; prepared by reducing *propylidenephthalide*, obtained from phthalic and butyric anhydrides and sodium butyrate), 0·0030, 12; 2-iso*propyl*- (m. p. 36°, b. p. 166·5°/24 mm.; obtained from 2-iso*propylidenephthalide*, m. p. 95°), 0·0976, 18; 2-*butyl*- (b. p. 178—180°/16 mm., volatile in steam; prepared from phthalaldehydic acid and butyl iodide), 0·0480, 9·3; 2-phenyl-, 0·0040, ring-opening not detected; 2 : 2-dimethyl-, 0·2196, 11; 5-nitro-2 : 2-dimethyl-, 0·0184, 83; 5-amino-2 : 2-dimethyl- (m. p. 117°), 0·2164, 8·7; 5-*cyano*-2 : 2-*dimethyl*- (m. p. 159°), 0·0232, 67; 2 : 2-diethyl-, 0·0260, and 5-nitro-2 : 2-diethyl-, 0·052, ring-opening not detected; 2 : 2-diphenyl- (m. p. 116°), 0·0040, insufficiently soluble.

The results are compared with those of Teppema (A., 1923, i, 256) on ring-opening under the action of hydrazine. It is observed that the stability of the ring increases as the size and number of substituents in the α-position increase. In the case of nuclear substitution, results obtained using hydrazine are not

directly comparable with those obtained using potassium hydroxide; thus the ring of 5-nitrophthalide, opened by potassium hydroxide and giving a velocity coefficient three times as great as that for phthalide itself, is not opened by hydrazine. Attempts are made to explain the effects of nuclear substitution on the basis of (the discarded form of) Lapworth, Kermack, and Robinson's theory of induced alternate polarities, but with little success; it is, however, concluded that the general effect is more powerful than the alternating effect. In the case of phthalide substituted in the 5-position by halogen, it is found that ring-opening is accelerated most by iodine, less by bromine, and least by chlorine.

The great stability of a phthalide ring containing two substituents in the 2-position leads the author to question the view that the red colour produced by the action of alkali on phenolphthalein is due to opening of the ring and formation of a quinonoid structure (cf. the failure on the part of Bassett and Bagnall, A., 1924, i, 856, to isolate coloured salts of phenolphthalein). It is suggested that a keto–enol change at the *p*-hydroxyl group may be concerned in the colour change. E. W. Wignall.

Chlorohydrin formation in glycerol and glycol and esterification of hydroxy- and 2 : 5- and 2 : 6-dihydroxy-benzoic acids and of phenylacetic acid in glycerol. A. Kailan and E. Goitein (Monatsh., 1927, 48, 405—443; cf. A., 1925, ii, 49).—The velocity of chlorohydrin formation and of esterification of benzoic, *o*-, *m*-, and *p*-hydroxybenzoic, and phenylacetic acids in absolute glycerol and in glycerol containing varying amounts of water in the presence of hydrogen chloride as a catalyst at 25° is investigated, and the results are compared with those of the corresponding reactions in glycol and alcohol. Esterification in the absence of a catalyst is also studied. At 25°, in glycerol containing 0·01 mol. of water per litre, the unimolecular coefficient for chlorohydrin formation is more than twice as great as that for glycolchlorohydrin in glycol, the ratio being reversed in the presence of 1·35 mols. of water per litre. The influence of water on the velocity in glycerol is large, the presence of 0·66 mol. of water per litre lowering the velocity coefficient to one tenth of its value in absolute glycerol. In the presence of salicylic, anthranilic, and *o*-hydroxybenzoic acids the velocity is increased in both media, and in the presence of 0·03 mol. of water per litre with an acid concentration of 0·1 mol., approximately the same values of the coefficient are obtained with each acid. A comparison of the velocity of chlorohydrin formation in glycol and glycerol with the formation of ethyl chloride in alcohol shows that the effect of water is much smaller in glycol than in alcohol, but is three times as great in glycerol as in alcohol. Esterification in both absolute and moist glycerol is almost quantitative. The unimolecular velocity coefficients for the esterification of *o*-, *m*-, and *p*-hydroxybenzoic and phenylacetic acids in absolute and moist glycerol in the presence of hydrogen chloride as a catalyst are, in all cases, proportional to the concentration of the hydrogen chloride; interpolation formulæ showing the relationship between the values of the velocity coefficients and varying concentration of water are given. In the presence of *N*/6-hydrogen chloride the velocity of esterification of salicylic acid with a water concentration of 0·03 and 0·065 mol. per litre is greater in glycerol than in alcohol, whilst with the other organic acids the velocity is respectively 72—221% and 49—186% greater in alcohol than in glycerol for the same concentrations of water. With water concentrations of 0·73 and 1·35 mols. per litre, the velocity in alcohol is only 55—71% and 37—49%, respectively, of that in glycerol, except with phenylacetic acid, in which case, with a water concentration of 0·73 mol. per litre, it is 40% greater in alcohol than in glycerol. As in the case of butyric and benzoic acids, the velocity of esterification of *o*-, *m*-, and *p*-hydroxybenzoic acids is less in glycerol than in glycol, the ratios of the values of the velocity coefficients for benzoic acid and its *o*-, *m*-, and *p*-hydroxy-derivatives (*N*/6-hydrogen chloride) being, in ethyl alcohol 1·0 : 0·37 : 1·17 : 0·43; in glycol 1·0 : 0·073 : 1·15 : 0·39; and in glycerol 1·0 : 0·081 : 1·23 : 0·38, the relative values for the *o*-, *m*-, and *p*-hydroxybenzoic acids in the three solvents being, respectively, 1·0 : 31·5 : 11·7; 1·0 : 15·8 : 5·4; and 1·0 : 15·3 : 4·8. The velocity of esterification of 2 : 6-dihydroxybenzoic acid in glycerol is less than one half that of the isomeric 2 : 5-acid, whilst the latter is esterified at one fourteenth the rate of salicylic acid. The velocity coefficients for esterification of *o*-, *m*-, and *p*-hydroxybenzoic and phenylacetic acids in the absence of a catalyst at 83° indicate that the reaction is "sesquimolecular" in type, the values of the coefficients for benzoic acid and *o*-, *m*-, and *p*-hydroxybenzoic acids in glycerol containing 0·03—0·05 mol. of water per litre being in the ratios 1·0 : 0·267 : 0·095 : 0·097. In glycerol containing 2 mols. of water per litre the value of the velocity coefficient is 20% smaller than in absolute glycerol, whilst in the case of the fatty acids such water addition has very little effect on the value. J. W. Baker.

Isomerism of halogenohydroxybenzoyltoluic acids. M. Hayashi (J.C.S., 1927, 2516—2527).—β-*5′-Chloro-2′-hydroxy-2-benzoyl*-m-*toluic acid*, m. p. 238—239° [*sodium* salt ($+6H_2O$); *barium* salt ($+8H_2O$)], is obtained by condensation of 3-methylphthalic anhydride and *p*-chloroanisole (or *p*-chlorophenol) in presence of aluminium chloride. It isomerises in presence of concentrated sulphuric acid at the ordinary temperature to α-*5′-chloro-2′-hydroxy-2-benzoyl*-m-*toluic acid*, m. p. 169—171° [*sodium* salt ($+4H_2O$); *barium* salt ($+2H_2O$)]. Treatment of either isomeride with concentrated sulphuric acid at 100° gives an equilibrium mixture of the two forms (containing only about 1% of the β-isomeride) together with partial conversion into *5-chloro-8-hydroxy-1-methylanthraquinone*, m. p. 223—224°. The last-named compound is converted by heating with a solution of boric acid in concentrated sulphuric acid into 5 : 8-dihydroxy-1-methylanthraquinone (A., 1922, i, 946). β-*5′-Bromo-2′-hydroxy-2-benzoyl*-m-*toluic acid*, m. p. 246—246·5° [*sodium* salt ($+6H_2O$); *potassium* salt ($+3H_2O$)], is similarly isomerised to α-*5′-bromo-2′-hydroxy-2-benzoyl*-m-*toluic acid*, m. p. 163·5—164° [*sodium* salt ($+4H_2O$); *potassium* salt ($+H_2O$)]. *5-Bromo-8-hydroxy-1-methylanthraquinone* has m. p.

198—198·5°. When 5′-chloro-2′-hydroxy-*o*-benzoylbenzoic acid is heated with concentrated sulphuric acid at 100°, 4-chloro-1-hydroxyanthraquinone is obtained in 90% yield; at the ordinary temperature reaction is incomplete (5% yield), and an isomeric form of the acid was not produced. Two theories, one postulating stereoisomerism, the other structural isomerism of the halogenohydroxybenzoyltoluic acids, are advanced. The absence of isomerism in the corresponding benzoic series lends support to the latter explanation. M. CLARK.

Catalytic hydrogenations with platinum oxide. I. Salicylic acid and phthalic anhydride. F. DÍAZ AGUIRRECHE (Anal. Fís. Quím., 1927, **25**, 313—331).—By the hydrogenation of salicylic acid using platinum oxide as catalyst, hexahydrosalicylic acid is obtained, together with a small quantity of pimelic acid. Phthalic acid, similarly, yields hexahydrophthalic acid. G. W. ROBINSON.

Ether of a ketone hydrate. α-Benzylidene-β-(β-phenylethyl)succinic and benzyl-β-phenylethylmaleic acids. J. BOUGAULT (Compt. rend., 1927, **185**, 717—718).—When benzyl-β-phenylethylmaleic acid (I) (this vol., 665) is boiled for 10 hrs. with sodium hydroxide solution, some *benzyl-β-phenylethylfumaric acid* (?) (II), m. p. 194°, is formed, which is separated from (I) by the greater solubility of its calcium salt. The action of acetic anhydride at 100° for 30 min. on the acid (II) produces the anhydride of (I), showing (II) to be the *trans*-isomeride of (I). The acid (II), on prolonged boiling with acetic anhydride, reverts to the parent anhydride. B. W. ANDERSON.

Keto- and lactone forms of benzil-*o*-carboxylic acid. A. HANTZSCH (J. pr. Chem., 1927, [ii], **117**, 151—153).—Polemical against Meerwein (this vol., 875). J. W. BAKER.

Synthesis of *dl*-2 : 5-dihydroxyphenylalanine. K. HIRAI (Biochem. Z., 1927, **189**, 88—91).—Gentisaldehyde (2 : 5-dihydroxybenzaldehyde) is prepared by the method of Neubauer and Flatov (A., 1907, i, 771), converted into the dimethyl ether, b. p. 50—51°, and condensed with glycine anhydride by Sasaki's method. 2 : 5-*Dimethoxybenzylidineglycine anhydride* crystallises from hot acetic acid, m. p. 278—279°, and on treatment with red phosphorus and hydrogen iodide gives *dl*-2 : 5-dihydroxyphenylalanine, m. p. 203—204° (decomp.) (cf. this vol., 56). P. W. CLUTTERBUCK.

Products of conversion of *peri*-cyanonaphthalenesulphonic acids [1 : 8-hydroxy- and amino-naphthoic acids]. I. G. FARBENIND. A.-G.—See B., 1927, 808.

Manufacture of salts of *o*-aminophenylpropionic acids, its homologues, substitution products, and analogues. I. G. FARBENIND. A.-G.—See B., 1927, 810.

Sulphur derivatives of substituted benzaldehydes. H. H. HODGSON and H. G. BEARD (J.C.S., 1927, 2423—2428).—Sodium disulphide reacts with 4- and 6-chloro-3-nitrobenzaldehyde in alcoholic solution giving respectively 3 : 3′-*dinitrodibenzaldehyde* 4 : 4′-*disulphide* (I), m. p. 237—238° [*dioxime* (II), m. p. 260—261°; *di*-p-*nitrophenylhydrazone*, m. p. 305—310° (decomp.)], and 3 : 3′-*dinitrodibenzaldehyde* 6 : 6′-*disulphide* (III), m. p. 257° [*dioxime* (IV), explodes 140—160°; *di*-p-*nitrophenylhydrazone*, m. p. 283—284° (decomp.)]. The stable yellow dioxime (II) is converted by cold aqueous sodium hydroxide into an isomeride of deeper colour, m. p. 230—232° (decomp.), which explodes like the dioxime (IV) if suddenly heated at 170°. Compounds (I) and (II) are converted by reduction with alkaline sodium sulphide and subsequent treatment with methyl sulphate into 3-*nitro*-4-*methylthiolbenzaldehyde* (V), m. p. 141—142° [*oxime*, m. p. 210° (*sodium* salt); p-*nitrophenylhydrazone*, m. p. 294—296° (decomp.)], and 3-*nitro*-6-*methylthiolbenzaldehyde* (VI), m. p. 159—160° [*oxime*, m. p. 187° (*sodium* salt); p-*nitrophenylhydrazone*, m. p. 250—252°]. 3-*Nitroso*-4-*methylthiolbenzyl alcohol* (?), m. p. 127°, is obtained as a by-product in the preparation of (V). Reduction of (V) and (VI) with sodium hyposulphite gives unstable amino-derivatives, which diazotise normally in acid solution giving, on treatment with cuprous chloride, 3-*chloro*-4-*methylthiolbenzaldehyde*, m. p. 58—59° [*oxime*, m. p. 134°; p-*nitrophenylhydrazone* (VII), m. p. 222—223°], and 3-*chloro*-6-*methylthiolbenzaldehyde*, m. p. 65° [*oxime*, m. p. 114°; p-*nitrophenylhydrazone* (VIII), m. p. 246°]. The phenylhydrazones (VII) and (VIII) are scarlet and orange respectively and give bluish-purple and reddish-purple colorations with alkali hydroxides, showing the much more pronounced bathochromic effect of the methylthiol group when *para* than when *ortho* to the hydrazine group (cf. A., 1926, 515). Reduction of the oximes of (V) and (VI) with alkaline ferrous sulphate gives 3-*amino*-4-*methylthiolbenzaldoxime* (IX), m. p. 100°, and 3-*amino*-6-*methylthiolbenzaldoxime* (X), m. p. 140°. Treatment with bromine displaces the methylthiol group from (IX), giving 2 : 4 : 5 : 6-*tetrabromo*-3-*aminobenzaldoxime*, m. p. 202—203°, whereas (X) is decomposed. M. CLARK.

Preparation of protocatechualdehyde and vanillin. N. FROSCHL and P. BOMBERG (Monatsh., 1927, **48**, 571—575).—The method of Dimroth and Zoeppritz (A., 1902, i, 293) has been applied to the synthesis of protocatechualdehyde and vanillin from pyrocatechol and veratrole, respectively. By the method of Wallach and Wuster (Ber., 1883, **16**, 145) the authors obtained no formanilide but only diphenylformamidine, it being assumed that at the high temperature employed (>220°) the formanilide is partly decomposed with the liberation of aniline which reacts with unchanged formanilide thus: $NHPh{\cdot}CHO+NH_2Ph=NHPh{\cdot}CH{:}NPh+H_2O$. At 190°, however, formanilide is obtained. When equimolecular quantities of dry pyrocatechol and formanilide are fused together in the absence of solvents and with rigid exclusion of moisture, the product treated with phosphorus oxychloride, hydrolysed with alkali, distilled with steam to remove the aniline produced, and the residue acidified and extracted with ether, a mixture of *protocatechualdehyde* in 5% yield (*phenylhydrazone*, m. p. 174—175°) and unchanged pyrocatechol is obtained, the latter being removed by extraction with cold benzene. Vanillin is

similarly prepared. An explanation of the mechanism of the reaction is given. J. W. Baker.

Hadromal. C. Hoffmeister (Ber., 1927, **60**, [*B*], 2062—2068).—The treatment of wood powder with boiling stannous chloride solution according to Czapek's method ("Lotosberichte," 1898, No. 7) gives hadromal if interrupted at a suitable time, but if prolonged gives vanillin and pyrocatechol and is thus difficult to control on a considerable scale. Better results are achieved in an apparatus which permits the mixture to be heated by benzene vapour and the product to be extracted simultaneously by benzene. Hadromal is most readily obtained by allowing wood meal, previously extracted with alcohol and benzene, to remain in contact with lead acetate solution and subsequently treating an alcoholic suspension of the insoluble compound of hadromal and lead thus formed with hydrogen sulphide (cf. Combes, A., 1907, i, 839). Gentle treatment of hadromal with potassium permanganate gives vanillin and (?) pyrocatechol, whereas cautious oxidation with very dilute potassium ferricyanide affords 4-hydroxy-3-methoxycinnamic acid. Its identity with 4-hydroxy-3-methoxycinnamaldehyde is confirmed by synthesis of the latter from vanillin and acetaldehyde in the presence of sodium hydroxide. It appears to be present in wood to the extent of about 3% in the form of a cellulose ester. H. Wren.

Derivatives of orcinol. I. E. L. Hirst (J.C.S., 1927, 2490—2495).—The constitutions of the two isomeric orcylaldehyde monomethyl ethers are established by condensation with acetophenone and acetylanisole. Everninaldehyde (Hoesch, A., 1913, i, 474) readily forms pyrylium salts and must therefore be orcylaldehyde 5-methyl ether, in which the hydroxyl group is *ortho* to the aldehyde group. The isomeric ether (Gattermann, A., 1908, i, 31) fails to yield pyrylium salts and is accordingly the 3-methyl ether. The 4′ : 7-dimethoxy-2-phenyl-5-methylbenzopyrylium salts show greatly enhanced fluorescence ascribed to the simultaneous presence of the two methoxy-groups. Orcylaldehyde condenses with acetophenone in presence of hydrogen chloride, giving *7-hydroxy-2-phenyl-5-methylbenzopyrylium chloride*, m. p. 206° (decomp.) [*perchlorate*, m. p. indefinite, below 245°; *iodide*, m. p. 225° (decomp.); *mercurichloride*, m. p. 229—230° (decomp.); *ferrichloride*, m. p. 147—148° (decomp.)]. Precipitation with sodium acetate gives the *anhydro-base*, m. p. 156—165° (decomp.), which, after methylation and treatment with ferric chloride, yields *7-methoxy-2-phenyl-o-methylbenzopyrylium ferrichloride*, m. p. 181° (decomp.). Orcylaldehyde undergoes similar condensation with acetylanisole, giving *7-hydroxy-4′-methoxy-2-phenyl-o-methylbenzopyrylium chloride* ($+1\frac{1}{2}H_2O$), m. p. 242—243° (decomp.) [*iodide*, m. p. 235—236° (decomp.); *ferrichloride*, m. p. 149—150° (decomp.)]. Everninaldehyde condenses with acetophenone, giving *7-methoxy-2-phenyl-5-methylbenzopyrylium chloride* ($+1\frac{1}{2}H_2O$), m. p. 173—174° (decomp.) [*iodide*, m. p. 191—192° (decomp.)], and with acetylanisole giving 4′ : 7-*dimethoxy-2-phenyl-o-methylbenzopyrylium chloride*, m. p. 214—215° (decomp.) [*ferrichloride*, m. p. 177° (decomp.)]. Orcylaldehyde 3-methyl ether condenses with acetylanisole in presence of potassium hydroxide solution giving p-*anisyl* 4-*hydroxy*-2-*methoxy*-6-*methylstyryl ketone*, m. p. 194—195°. An acetone solution of orcylaldehyde 3-methyl ether reacts with methyl chloroformate giving 5-*methylcarbonato-orcylaldehyde* 3-*methyl ether*, m. p. 80—81° (phototropic). This compound is oxidised in neutral solution by potassium permanganate to 5-methylcarbonato-orsellinic acid 3-methyl ether, converted by alkali into orsellinic acid 3-methyl ether.

M. Clark.

Cyclic thioketones. E. Fromm (Ber., 1927, **60**, [*B*], 2090—2094).—Successive treatment of *cyclo*pentanone dissolved in alcohol with hydrogen chloride and hydrogen sulphide yields *trithio*cyclo*pentanone*, $(C_5H_8S)_3$, m. p. 99°, oxidised by potassium permanganate to the corresponding *trisulphone*, m. p. 172°. *Trithio*cyclo*hexanone*, m. p. 101—102°, is oxidised to the *sulphidedisulphone*, $C_{18}H_{30}O_4S_3$, m. p. 175·5—176·5°, and converted when heated at 160° into hydrogen sulphide and the *compound*, $C_{18}H_{28}S_2$, m. p. 182°. *cyclo*Hexanone and ethyl mercaptan afford 1 : 1-diethylthiol*cyclo*hexane (cf. Rècsei, this vol., 750) oxidised to 1 : 1-diethylsulphonyl*cyclo*hexane, m. p. 118—119°. *p*-Methyl*cyclo*hexanone is converted successively into *trithio*-p-*methyl*cyclo*hexanone*, m. p. 94·5—95·5°, and the corresponding *sulphidedisulphone*, m. p. 253—254°; *diethylthiol*-p-*methyl*cyclo*hexane* and *diethylsulphonyl*-p-*methyl*cyclo*hexane*, m. p. 112—113°, are described. Pulegone is converted by hydrogen sulphide and hydrogen chloride into *trithio*-m-*methyl*cyclo*hexanone*, m. p. 182—183°, and trithioacetone; the corresponding *sulphidedisulphone*, m. p. 266—267°, *diethylthiol*-m-*methyl*cyclo*hexane*, and *diethylsulphonyl*-m-*methyl*-cyclo*hexane*, m. p. 107—108°, have been isolated.

H. Wren.

Carbon rings. IX. Degradation of civetone, civetol, and civetane. L. Ruzicka, H. Schinz, and C. F. Seidel (Helv. Chim. Acta, 1927, **10**, 695—706).—Civetone is reduced, (*a*) by sodium and alcohol to *civetol* (Δ^9-cyclo*heptadecenol*), b. p. 157—158°/1 mm., m. p. 65°; (*b*) by hydrogenation in presence of platinum-black in glacial acetic acid to *dihydrocivetol* (cyclo*heptadecanol*), m. p. 80°, b. p. 155°/0·5 mm.; (*c*) by Wolff's method through the semicarbazone to a mixture of civetol, removed as the hydrogen phthalate, and *civetane* (*cyclo*heptadecene), b. p. 120—125°/1 mm., m. p. 47°; (*d*) by Clemmensen's method to a mixture (I) of civetane and *cyclo*heptadecane (A., 1926, 727), from which the former is removed by oxidation with permanganate. Dihydrocivetol is oxidised by aqueous chromic acid to dihydrocivetone (A., 1926, 615) and dehydrated by potassium hydrogen sulphate to civetane. With phosphorus tribromide it yields *bromo*cyclo*heptadecane*, b. p. 150—160°/0·5 mm., which gives civetane with alcoholic potassium hydroxide. Oxidation of any of the above samples of civetane or of the mixture (I) with permanganate yields mainly tetradecane-$\alpha\xi$-dicarboxylic acid together with suberic and sebacic acids; whilst ozonisation affords pentadecane-$\alpha\omega$-dicarboxylic acid and other products. Civet contains about 3% of civetol, which may be isolated as the hydrogen phthalate from the fraction of b. p. 160—170°/1 mm. after removing

the civetone as semicarbazone. In order to establish the identity of natural and synthetic civetol, the former was oxidised with chromic acid to civetone and with permanganate to *9-ketopentadecane-αo-dicarboxylic acid* (*methyl* ester, m. p. 60°), identical with the keto-acid previously obtained (*loc. cit.*) from civetone and erroneously described as *n*-ketotetradecane-αζ-dicarboxylic acid. The synthesis of both acids will be described later. The constitutions of civetol and civetone are thus completely established.

H. E. F. NOTTON.

Mechanism of molecular rearrangements. (MME.) RAMART-LUCAS (Compt. rend., 1927, **185**, 718—721).—Theoretical. An explanation of the mechanism of the Beckmann and pinacolin rearrangements and of the dehydration of alcohols in terms of the migration of valency electrons between neighbouring atoms (cf. this vol., 1051; Perrin, *ibid.*, 1009).

B. W. ANDERSON.

Reduction of benzophenone by magnesium amalgam. Correction. M. GOMBERG and W. E. BACHMANN (J. Amer. Chem. Soc., 1927, **49**, 2666; cf. following abstract).—Benzophenone is reduced by a mixture of magnesium and mercury, but not by magnesium amalgam previously prepared by heating the metals together (cf. Schlenk and Thal, A., 1913, i, 1205).

F. G. WILLSON.

Reduction of benzil by the binary system, magnesium–magnesium iodide (or bromide). M. GOMBERG and W. E. BACHMANN (J. Amer. Chem. Soc., 1927, **49**, 2584—2592; cf. this vol., 245).—When metallic magnesium is added to a solution of benzil in ether–benzene containing magnesium iodide or bromide, an amount of magnesium is dissolved, corresponding with 1 atom per mol. of benzil, and the solution contains the colourless *halomagnesium glycoloxide*, $[Hal{\cdot}Mg{\cdot}O{\cdot}CPh{\cdot}]_2$, in quantitative yield. The reaction proceeds more slowly, but completely, in presence of only traces of the magnesium halide, with production of the *magnesium glycoloxide*, $Mg<^{O\cdot CPh}_{O\cdot CPh}$. Whilst the reaction mixture is finally only pale yellow, deep green and brown colorations are produced as the reaction proceeds, and these are ascribed to the formation of derivatives of the quinhydrone type, or alternatively, to the presence of free radicals. The glycoloxides react vigorously with oxygen, with production, on subsequent hydrolysis, of benzil (40%), a polymeride of benzilic acid anhydride (40%), and benzoic acid (13%) (cf. Staudinger and Binkert, A., 1922, i, 1016), apparently through the intermediate formation of the *oxide*, $O<^{CPh\cdot OMgI}_{CPh\cdot OMgI}$. The production of both benzil and benzilic acid probably indicates the existence of this oxide in two stereoisomeric forms. Treatment of the magnesium glycoloxide with water affords benzoin, whilst acetyl chloride and benzoyl chloride yield, respectively, diacetoxy- and dibenzoyloxy-stilbene. Benzyl chloride and methyl iodide are without action on the glycoloxide, but triphenylmethyl chloride affords a small proportion of a yellow *product*, m. p. 180—190°, probably the corresponding triphenylmethyl ether, together with oxidation and reduction products of triphenylmethyl. Bromine and iodine oxidise the glycoloxide, with production of benzil. A solution of benzil and magnesium bromide in ether–benzene deposits the *compound* $(CPhO)_2,MgBr_2,Et_2O$, which dissociates in presence of water. The addition of benzil to a solution of magnesium iodide in ether–benzene causes liberation of iodine. Subsequent treatment with oxygen affords the above oxide, indicating the formation, from the benzil and magnesium iodide, of the iodomagnesium glycoloxide. The latter can also be demonstrated by treating the magnesium iodide–benzil mixture with molecular silver, mercury, or zinc, which displace the equilibrium by removal of the iodine. A similar result is obtained with magnesium bromide, although bromine is not liberated from the latter and benzil alone. Similar results can be obtained with benzil and beryllium and beryllium iodide, and with magnesium amalgam. These reactions probably proceed through an intermediately-formed magnesium subhalide.

F. G. WILLSON.

Nitrogen trichloride and unsaturated ketones. G. H. COLEMAN and D. CRAIG (J. Amer. Chem. Soc., 1927, **49**, 2593—2596).—Treatment of phenyl styryl ketone with nitrogen trichloride in carbon tetrachloride affords the *hydrochloride*, m. p. 206—208°, of *phenyl α-chloro-β-amino-β-phenylethyl ketone* (*benzoyl* derivative, m. p. 186—187°). On reduction with sodium amalgam, this yields *α-amino-γ-hydroxy-αγ-diphenylpropane*, m. p. 122—124°, which is also obtained similarly from the monoxime of dibenzoylmethane.

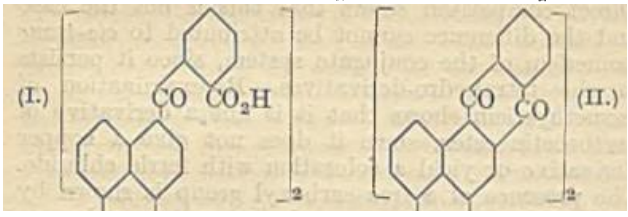
F. G. WILLSON.

Perylene and its derivatives. XIII. A. PONGRATZ (Monatsh., 1927, **48**, 585—591).—3 : 9-Dibromo- and 3 : 9-dichloro-perylene (Zinke, Linner, and Wolfbauer, A., 1925, i, 383) when heated with cuprous cyanide (in the former case with quinoline as a solvent) are converted into 3 : 9-*dicyanoperylene*, not melting at 360°, which when heated with alcoholic potassium hydroxide at 200° yields *perylene*-3 : 9-*dicarboxylic acid*, sintering and decomp. about 360° (*diethyl* ester, m. p. 264—265°). Perylene when treated with acetyl, *p*-chlorobenzoyl, and *o*-toluoyl chlorides in carbon disulphide with aluminium chloride as a catalyst yields, respectively, 3 : 9-*diacetyl*-, m. p. 300—301°, 3 : 9-*di*-p-*chlorobenzoyl*-, m. p. 284—285°, and 3 : 9-*di*-o-*toluoylperylene*, m. p. 280—282°. Similar treatment of 3 : 9-dichloroperylene with acetyl and propionyl chlorides yields, respectively, 3 : 9-*dichloro*-4 : 10-*diacetyl*-, decomp. above 320°, and 3 : 9-*dichloro*-4 : 10-*dipropionyl-perylene*.

J. W. BAKER.

Perylene and its derivatives. XIV. A. ZINKE, G. GORBACH, and O. SCHIMKA (Monatsh., 1927, **48**, 593—598).—The action of phthalic anhydride on perylene in the presence of anhydrous aluminium chloride in solvents under varying conditions yields a mixture of mono- and di-carboxybenzoylperylenes (I). Retreatment of the product with aluminium chloride at 170° for 2 hrs., or heating perylene, phthalic anhydride, and aluminium chloride together at 170° for 3 hrs. yields 3 : 9-*diphthaloylperylene* (II). The action of 4-chlorophthalic anhydride on perylene in carbon disulphide in the presence of aluminium chloride yields a mixture of 4-*chloro*-2-*carboxybenzoyl*-

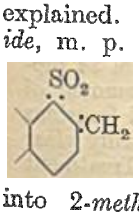
perylene, m. p. 263°, and *di*-(4-*chloro*-2-*carboxybenzoyl*)-*perylene*, m. p. 350° (decomp.), which are separated



by extraction with boiling benzene, the mono-compound being soluble. When the dibenzoyl compound is heated with aluminium chloride at 170° for 2 hrs. it yields *dichlorodiphthaloylperylene*. J. W. Baker.

Formation of anthraquinone by vapour-phase oxidation of toluene and petroleum distillates containing toluene. A. R. Bowen and A. W. Nash (Nature, 1927, 120, 621).—Small amounts of anthraquinone, together with benzoic acid and benzaldehyde, have been obtained by passing air mixed with the vapour of toluene or a petroleum distillate containing toluene (12 litres per hr.) over a catalyst, consisting of aluminium grains coated with vanadium pentoxide, at 400°. A. A. Eldridge.

1-Nitro-2-methylanthraquinone. A. Locher and H. E. Fierz (Helv. Chim. Acta, 1927, 10, 642—670).—Nitration of 2-methylanthraquinone (cf. Eder, A., 1924, i, 528) with sulphuric acid and potassium nitrate at 0° yields a mixture from which pure 1-nitro-2-methylanthraquinone (82% of theoretical) is obtained by boiling with 10% sodium sulphite, the other isomerides being converted into sulphonic acids. Bromination of 1-amino-2-methylanthraquinone at the ordinary temperature affords 4-*bromo*-1-*amino*-2-*methylanthraquinone*, m. p. 346—347° (decomp.). This is converted by diazotisation and heating into 4-*bromo*-1-*hydroxy*-2-*methylanthraquinone*, m. p. 176—177°, and by boiling with *p*-toluenesulphonamide in presence of sodium and copper acetates into 1-*amino*-4-*toluenesulphonamido*-2-*methylanthraquinone*, m. p. 271—272°, hydrolysed by sulphuric acid to 1 : 4-*diamino*-2-*methylanthraquinone*, m. p. 247—248°. 1-Amino-4-hydroxy-2-methylanthraquinone is obtained by heating the bromo-derivative at 150° with sulphuric and boric acids. 2-Methylanthraquinone-1-sulphonic acid ($+2H_2O$) [*potassium*, *sodium* ($+2H_2O$), and *barium* salts] is obtained (60% yield) together with 2-methylanthraquinone by heating 1-nitro-2-methylanthraquinone with 15% sodium sulphite at 135—140° (cf. Ullmann and Bincer, A., 1916, i, 483). Unlike other anthraquinonesulphonic acids, this loses the sulphonic group when heated at 120—130° with sulphuric acid or oleum. The formation in the direct sulphonation of 2-methylanthraquinone of a mixture of sulphonic acids from which none of the 2-derivative can be isolated is thus explained. 2-*Methylanthraquinone*-1-*sulphonyl chloride*, m. p. 165° (decomp.), loses hydrogen chloride when heated in indifferent solvents, giving yellow 2-*methyleneanthraquinone*-1-*sulphene* (annexed formula), m. p. 221—222°. This is converted by water into the sulphonic acid and by aniline into 2-*methylanthraquinone*-1-*sulphonanilide*, m. p. 132—133°.



1 : 5-Dinitro-2-methylanthraquinone, m. p. 346—347° (cf. Eder, *loc. cit.*), is not attacked by boiling sodium sulphite solution, but 1 : 8-dinitro-2-methylanthraquinone gives 2-*methylanthraquinone*-1 : 8-*disulphonic acid* ($+5H_2O$) (*sodium* and *lead* salts). 1 : 5-Diamino-2-methylanthraquinone (*dibenzoyl* derivative, m. p. 286—287°) has m. p. 213—214° (cf. Schaarschmidt, A., 1913, i, 95).

Careful bromination of 1-nitro-2-methylanthraquinone in nitrobenzene at about 160° affords 80% of 1-*nitro*-2-*bromomethylanthraquinone* (I), m. p. 210—211° (decomp.), which is oxidised by nitric and chromic acids to 1-nitroanthraquinone-2-carboxylic acid, and gives on further treatment with bromine (?) 1-*nitro*-2-*dibromomethylanthraquinone*, m. p. 245—246°. The compound (I) undergoes a remarkable intramolecular oxidation–reduction when heated in dichlorobenzene, giving 1-aminoanthraquinone-2-carboxylic acid, and when heated with aqueous sulphuric acid at 155° it gives 3-*bromo*-1-*aminoanthraquinone*-2-*carboxylic acid* (II), m. p. 326—327°. The mechanism of these reactions is discussed (cf. Scholl, Monatsh., 1913, 34, 1011). (II) is quantitatively converted by sulphuric and boric acids into 1-*amino*-3-*hydroxyanthraquinone*-2-*carboxylic acid*, m. p. 322—323° (*silver* salt, which gives phthalic anhydride on heating). 1 : 3-*Diaminoanthraquinone*-2-*carboxylic acid*, m. p. 320—325°, with sublimation (*sulphate*), is prepared from (II) through the insoluble 3-p-*toluenesulphonamido*-derivative. 4-Bromo-1-aminoanthraquinone-2-carboxylic acid has m. p. 324—325° (cf. Scholl, *loc. cit.*). The bromo-derivative (I) is converted by 15% sodium sulphite at 120° into 2-*sulphomethylanthraquinone*-1-*sulphonic acid*, the *potassium* salt of which is converted by water at 200° into *potassium* 1-*hydroxy*-2-*methylanthraquinone*-ω-*sulphonate*. H. E. F. Notton.

New class of vat dyes of the anthraquinone series. H. T. Bucherer and T. Maki (Ber., 1927, 60, [*B*], 2068—2078).—The action of concentrated sulphuric acid on aminoanthraquinones and nitro-compounds leads to the production, *inter alia*, of vat dyes. For the reaction, 2-aminoanthraquinone is the most important component, followed by 2 : 6-diamino- and 1-amino-anthraquinone, whilst *m*-nitroaniline, nitrobenzene, and *p*-nitroaniline are most serviceable as nitro-compounds. With concentrated sulphuric acid the reaction is frequently violent and is then accompanied by production of ammonia as well as of sulphur dioxide. The change may be moderated by employing a large excess of acid; with 80—90% acid the reaction is less violent but condensation is incomplete. Inorganic addenda appear to offer no advantages. 2-Aminoanthraquinone and nitrobenzene yield unchanged amino-compound, products soluble in alkali hydroxide (mainly 2-amino-1-hydroxyanthraquinone), a *substance* (?)

$$C_6H_4\langle\begin{matrix}CO\\CO\end{matrix}\rangle C_6H_2(NH_2)\cdot NH\cdot C_6H_4\cdot NH\cdot C_6H_2(OH)\langle\begin{matrix}CO\\CO\end{matrix}\rangle C_6H_4$$

soluble in quinoline but not in dimethylaniline, the actual *dye*, $C_{60}H_{39}O_{11}N_5$, insoluble in quinoline, and traces of anthraquinone. The *dye*, $C_{68}H_{33}O_{10}N_5$, obtained from 2-aminoanthraquinone, nitrobenzene, and 84% sulphuric acid is more violet in colour and less sensitive to acids than that obtained with the

concentrated acid. The brownish-black *dye* derived from 2-aminoanthraquinone, *p*-nitroaniline, and concentrated sulphuric acid resembles that obtained with nitrobenzene and appears to be a mixture of di- and tri-hydroxy-compounds. From 2-aminoanthraquinone, *p*-nitrosophenol, and 80% sulphuric acid the *substance* $C_{60}H_{32}(CO)_8(NH)_5(NH_2)\cdot OH$ is derived in poor yield. With *m*-nitroaniline and 1-nitronaphthalene, 2-aminoanthraquinone and concentrated sulphuric acid yield respectively the *dyes* $C_{58}H_{40}O_9N_4$ and $C_{76}H_{43}O_{11}N_5$, the latter being produced in small yield. If nitrobenzene is replaced by *o*-nitrotoluene, the *compound* $C_{70}H_{41}O_{10}N_5$ is produced, the methyl group of the *o*-nitrotoluene suffering oxidation. Anthraquinone, nitrobenzene, and concentrated sulphuric acid give the *dye* $C_{46}H_{23}O_7N_3$ in good yield. Nitrobenzene, 1-aminoanthraquinone, and concentrated sulphuric acid yield unchanged aminoanthraquinone, products soluble in alkali hydroxide (? aminohydroxyanthraquinones), a *substance*, $C_{40}H_{23}O_5N_3$, soluble in quinoline but insoluble in dimethylaniline, and a *dye*, $C_{68}H_{39}O_{10}N_5$, in much poorer yield than is the case when 2-aminoanthraquinone is used. Substitution of *p*-nitroaniline for nitrobenzene makes little difference in the character of the dye produced, whereas a bluish-grey vat dye with much better affinity for cotton is prepared by using *m*-nitroaniline. From aniline, nitrobenzene, and concentrated sulphuric acid a black dye, insoluble in alkali hydroxide, is produced which, in paste form, dissolves in alkaline hyposulphite but loses this property after being dried. H. WREN.

New products of the anthraquinone series [hexahydroarylaminoanthraquinones, acid wool dyes]. I. G. FARBENIND. A.-G.—See B., 1927, 809.

Constituents of kawa root. V. Synthesis of yanganol. W. BORSCHE and C. WALTER (Ber., 1927, **60**, [*B*], 2112—2113; cf. this vol., 664).—*p*-Methoxycinnamic acid, prepared in 80—90% yield by heating a mixture of anisaldehyde, malonic acid, pyridine, and piperidine, is converted by thionyl chloride into the corresponding chloride, m. p. 50°, which with methyl sodioacetoacetate affords *methyl p-methoxycinnamoylacetoacetate*, m. p. 80—81° (*copper* derivative, m. p. 196—197°). The latter substance is converted by water at 130° into βδ-diketo-ζ-*p*-methoxyphenyl-Δ$^{\epsilon}$-hexene, m. p. 93°, identical with yanganol (cf. Borsche and Gerhardt, A., 1915, i, 438). *Methyl* p-*methoxycinnamoylacetate*, m. p. 84—85°, is prepared by the action of aqueous ammonia (*d* 0·91) on the corresponding acetoacetate. H. WREN.

Constituents of kawa root. VI. Constitution of methysticin. W. BORSCHE, C. H. MEYER, and W. PEITZSCH (Ber., 1927, **60**, [*B*], 2113—2120; cf. this vol., 563, 664).—The observation of optical activity in methysticin has led Murayama and Shinozaki (Chem. Zentr., 1925, ii, 2062) to assign to it the constitution

$CH_2O_2{:}C_6H_3\cdot CH{:}CH\cdot CH{<}\begin{matrix}CH_2 & CO\\ O\cdot C & OMe)\end{matrix}{>}CH$ in place of the Pomeranz structure, $CH_2O_2{:}C_6H_3\cdot[CH{:}CH]_2\cdot CO\cdot CH_2\cdot CO_2Me$, which they attribute to *iso*methysticin. The latter substance might therefore be identical with the *allo*methysticin prepared by Borsche, Rosenthal, and Meyer (*loc. cit.*) by deacetylation of methyl piperonoylacetoacetate. Direct comparison shows that this is not the case and the difference cannot be attributed to *cis–trans* isomerism of the conjugate system, since it persists in the tetrahydro-derivatives. Re-examination of *iso*methysticin shows that it is not a derivative of acetoacetic ester, since it does not give a copper derivative or yield a coloration with ferric chloride. The presence of a free carboxyl group is shown by its solubility in dilute ammonia and sodium carbonate and the evolution of 1 mol. of carbon dioxide without loss of methoxyl when heated above its m. p. The identity of methystic acid of Pomeranz and Winzheimer (A., 1908, i, 805), which has the composition $C_{15}H_{14}O_5$, and not $C_{14}H_{12}O_5$ as previously supposed, with the *iso*methysticin of Murayama and Shinozaki (*loc. cit.*) is established and the substance is therefore β-methoxy-ζ-methylenedioxyphenyl-Δ$^{\alpha\gamma\epsilon}$-heptatrienoic acid, which accords with its hydrolysis by dilute acids into methyl alcohol, carbon dioxide, and methysticol and accounts for the impossibility of converting methystic acid into methysticin by methyl-alcoholic hydrogen chloride. The conversion of *iso*methysticin into *allo*methysticin is accomplished by methylation with diazomethane followed by cautious treatment of the product with alcoholic hydrogen chloride, whereby only the enolic methoxyl group is affected. The transformation of methysticin into methystic acid (=*iso*methysticin) is not a case of hydrolysis, but of the isomerisation of a dihydro-α-pyrone to a trebly unsaturated acid, and as there is no analogy for the simultaneous displacement of the methyl group from the α- to the γ-oxygen atom the constitution

$CH_2O_2{:}C_6H_3\cdot CH{:}CH\cdot CH{<}\begin{matrix}O & H_2\cdot C(OMe)\\ & CO\end{matrix}{>}CH$ must be assigned to methysticin. Similarly, kawaic acid is probably to be regarded as β-methoxy-ζ-phenyl-Δ$^{\alpha\gamma\epsilon}$-heptatrienoic acid.

The following new compounds are incidentally described: *ammonium methystate*; *tetrahydro*iso*methysticin*, m. p. 137—138°, identical with tetrahydromethystic acid of Goebel (A., 1922, i, 657); *copper* compound of *allo*methysticin, $(C_{15}H_{13}O_5)_2Cu$, decomp. about 220° after darkening; *tetrahydro*allo*methysticin*, isolated as the *copper* compound, $(C_{15}H_{17}O_5)_2Cu$, m. p. 130°. H. WREN.

Caoutchouc. III. Preparation of homogeneous caoutchouc hydrocarbons. R. PUMMERER and H. MIEDEL (Ber., 1927, **60**, [*B*], 2148—2152).—Extraction of caoutchouc with acetone combined with repeated intermediate precipitation of the material from benzene by alcohol or acetone removes oxygenated impurities soluble in acetone, but does not eliminate albumins and sugars. Systematic extension of the fractional precipitation method of Pummerer and Koch (A., 1924, i, 1214), in which benzene, hexahydrotoluene, light petroleum, and ether are used as solvents and acetone or alcohol as precipitants, does not lead to the certain removal of nitrogenous impurities, although individual fractions are free from nitrogen and soluble to initially clear solution in hexahydrotoluene or ether. Treatment of caoutchouc with methyl-alcoholic potassium hydr-

oxide removes nitrogenous and acidic substances completely, but the loss of material and the difficulty of removing the last traces of alkali render the method suitable only on a small scale. The portion of caoutchouc soluble in ether can be obtained by fractional dissolution (cf. Feuchter, B., 1926, 100), but "smoked sheet" and "crêpe caoutchouc" are unsuitable for this purpose. Crude, preserved latex is subjected to dialysis to remove salts, carbohydrates, etc. soluble in water, coagulated, and extracted with acetone to remove water and resinous material. The finely-divided material gives a solution of nitrogen-free "diffusion caoutchouc" in ether which is readily freed from oxidation products by precipitation with acetone. The portion insoluble in ether contains the impurities present originally in the caoutchouc which may amount to 33% of its weight. H. WREN.

Caoutchouc. IV. Preparation of pure caoutchouc from latex by means of alkali and its division into sol and gel caoutchouc. R. PUMMERER and H. PAHL (Ber., 1927, **60**, [*B*], 2152—2163; cf. preceding abstract).—Rubber latex, preserved with ammonia, is agitated with aqueous sodium hydroxide (2%) during 2 days at 50°, the cream is separated, and the operation repeated until the biuret and ninhydrin reactions are negative and the aqueous solution reacts only slowly with permanganate. The cream is washed with water, dialysed, and coagulated by acetone or acetic acid. Extraction of the product with acetone serves essentially to remove the water, thus giving "total caoutchouc" which retains the double linkings of the original material and contains 0·077% of ash. All the actual hydrocarbons of the latex, including the sparingly soluble portions, are present. Systematic treatment of "total caoutchouc" with ether in an atmosphere of carbon dioxide leads to its division into "sol caoutchouc" and "gel caoutchouc," the latter of which contains the integument components of the latex droplet. "Sol," "gel," and "total" caoutchouc soften at 115—130°, 145—160°, and 130—145°, respectively. "Gel caoutchouc" behaves normally towards iodine monochloride, requiring 1 mol. of iodine for each C_5H_8 group. Prolonged rolling renders "gel caoutchouc" soluble in ether. Similar solubility is conferred by treatment with benzene, toluene, xylene, chlorobenzene, or, particularly, cumene, but the regenerated "gel caoutchouc" is not identical with "sol caoutchouc." A well-defined end-point to the solubility of "total caoutchouc" in ether as assumed by Feuchter does not exist. "Sol" and "total" caoutchouc give closely similar hydrochlorides. When treated in hexahydrotoluene with tetranitromethane at 0° the caoutchoucs give additive products stable at 60° in a high vacuum. With the technical varieties such as crêpe or smoked sheet or the authors' pure caoutchouc the ratio of tetranitromethane to isoprene groups is 1 : 5. This ratio is also observed with "gel caoutchouc" whether suspended or rendered soluble, but with "sol caoutchouc" the ratio is 1 : 6. It is uncertain whether the reaction affords a definite chemical method of distinguishing between "sol" and "gel" caoutchouc. The additive compounds are not crystalline; when heated they become yellow at 150°, brown at 175°, and ultimately carbonise. Vulcanisation with 10% of sulphur under 3½ atm. of steam converts pure caoutchouc into a product very similar to that derived from the best technical varieties, whereas with 7½% of sulphur vulcanisation of the pure material occurs more slowly owing to the absence of albumins. "Sol" and "gel" caoutchouc appear to be vulcanised much more slowly than "total" caoutchouc with 7·5% of sulphur. Vulcanisation of pure caoutchouc with 30% of sulphur gives a product with better insulating properties than that obtained from crepe rubber. H. WREN.

Caoutchouc. V. Absorption of caoutchouc and guttapercha in the ultra-violet region of the spectrum. G. SCHEIBE and R. PUMMERER (Ber., 1927, **60**, [*B*], 2163—2167).—Comparison of the absorption curves of caoutchouc at various stages of purification dissolved in hexahydrotoluene in an atmosphere of carbon dioxide allows the elucidation of the true curve for caoutchouc. This, when considered in conjunction with the curves of trimethylethylene and diallyl, leads to the conclusion that not more than one conjugated double linking can be present in the caoutchouc molecule for every thousand ordinary double linkings. Optical observations are in harmony with Harries' formulation of caoutchouc, but scarcely reconcilable with Staudinger's assumption of the presence of tervalent carbon atoms in considerable number. The varying behaviour of solutions of caoutchouc in hexahydrotoluene towards hydrogenation (cf. Pummerer and Burkard, A., 1923, i, 49) does not appear to be due to difference in the number of double linkings in the molecule. The absorption curve of purified guttapercha in hexahydrotoluene is completely identical with that of caoutchouc; the number and type of double linkings in the two compounds must therefore be very similar. "Sol," "gel," and "total" caoutchouc have been examined in hexane solution after addition of piperidine. In the lower portion of the curve "gel" caoutchouc exhibits a rather more pronounced absorption; otherwise the curves are identical. H. WREN.

Caoutchouc. VI. Cryoscopic determinations of the mol. wt. of caoutchouc. R. PUMMERER, H. NIELSEN, and W. GÜNDEL (Ber., 1927, **60**, [*B*], 2167—2175; cf. A., 1924, i, 1214).—When precautions are taken to secure a true solution of the caoutchouc in camphor (by spreading the material in a film over the inside of the tube by evaporation of a solution and subsequently adding the camphor) every purified sample has approximately the same mol. wt., varying from 1100 to 1600. Variation of the concentration of the solutions between 1 in 4 and 1 in 10 is without effect. In spite of the high m. p. of camphor, the caoutchouc does not appear to be changed chemically. In benzylidenecamphor, m. p. 98°, the observed mol. wts. are generally higher than in camphor (1400—2500), but the depression constant is much smaller and the results are less accurate. In menthol (using Beckmann's apparatus) the mol. wt. of caoutchouc is 1200—1600 at concentrations of 1 in 50, whereas in 1% solution the mol. wt. sinks to 520—620 and

remains constant at greater dilutions as far as the method permits of accurate measurement. This corresponds with the presence of eight isoprene components in the molecule. It is remarkable that "sol" and "gel" caoutchouc which differ most widely in their solubilities have exactly the same mean mol. wt. in camphor and menthol. The decisive factor in the different caoutchouc fractions cannot therefore be the mean mol. wt.

Abnormalities in the hydrogenation of caoutchouc have been observed by Pummerer and Koch (A., 1924, i, 1214) whereby double linkings disappear without absorption of hydrogen, presumably owing to ring formation. Almost quantitative ring formation is recorded in the case of a sample of "sol" caoutchouc exposed to hydrogen at 60 atm. pressure in the presence of spongy platinum. In the presence of purified caoutchouc spongy platinum frequently acquires the ability to absorb very large quantities of hydrogen whilst the caoutchouc is not invariably actually hydrogenated; the platinum passes partly into colloidal solution. Hydrocaoutchouc, containing 14% of hydrogen and traces of colloidal platinum, is autoxidisable, containing more than 20% of oxygen after exposure to the air during 5—8 weeks. Dehydrogenation is not caused thereby. The older experiments of Pummerer and Burkard (A., 1923, i, 49) were not performed with isolated material.

H. WREN.

Oxidation of santonin. I. S. S. MEDVEDEV (Trans. Karpov Inst. Chem., 1924, No. 3, 41—53).—Oxidation of santonin (10 g.) with ammonium persulphate in acetic acid yields a *compound*, $C_{10}H_{12}O_3$, m. p. 80—90° (2·6 g.); chromic acid and acetic acid give santeninic acid, m. p. 130—131° (*bromo*-derivative $C_{15}H_{16}O_4Br_2$, m. p. 120° [decomp.]; *oxime*, decomp. 190°). At 125—130° in a vacuum, santeninic acid loses 2 mols. of water, affording santenin, m. p. 135—136°, yellow (*acetyl* derivative, m. p. 112·5°; *oxime*, decomp. 190—200°). Santeninic acid is regarded as 1 : 4-dimethyl-3 : 7-diketohexahydronaphthylpropionic acid, and santenin the lactone.

CHEMICAL ABSTRACTS.

Two sterol-like substances from *Asclepias syriaca*. II. L. SCHMID and E. LUDWIG (Monatsh., 1927, 48, 577—583).—The mixture of two sterol-like substances, m. p. 176°, isolated by Schmid and Stohr from *Asclepias syriaca* (this vol., 248) has now been separated and shown by comparison of a series of derivatives to be identical with α- and β-amyrin isolated by Rollett (cf. this vol., 248) from *Manila elemi* resin. The mixture is benzoylated and from the product the pure β-benzoate, m. p. 231° (corr.), is obtained, from which are prepared the *alcohol*, m. p. 199·5—200°, *acetate*, m. p. 238—239°, and *formate*, m. p. 238—239°, identical with the corresponding derivatives obtained from β-amyrin benzoate. Treatment of the mother-liquor from the β-benzoate with bromine in acetic acid yields the bromo-α-benzoate, m. p. 239°, identical with bromoamyrin α-benzoate (Zinke, Friedrich, and Rollett, A., 1921, i, 39, give m. p. 229°) obtained by the same method from the mixture of amyrin α- and β-benzoates. From the bromo-α-benzoate are obtained the *bromo-α-alcohol*, m. p. 180°, and the *bromo-α-acetate*, m. p. 263°, identical with the preparations from bromoamyrin α-benzoate. All m. p. are corrected.

J. W. BAKER.

Strophanthin. XI. Hydroxyl groups of strophanthin. XII. Oxidation of trianhydrostrophanthidin. XIII. *iso*Strophanthidin and its derivatives. XIV. Isomerisation in the *iso*strophanthidin series. W. A. JACOBS and E. L. GUSTUS (J. Biol. Chem., 1927, 74, 795—804, 805—810, 811—827, 829—837).—XI. Methyl strophanthidinate (cf. A., 1926, 73) was oxidised by chromic acid to a monoketo-ester, *methyl strophanthidonate*, $C_{24}H_{32}O_7$, m. p. 161—162°, $[\alpha]_D$ +26° in pyridine, which no longer gave a benzoate; the acylatable carbinol group of strophanthidin is therefore secondary. On warming with methyl-alcoholic hydrochloric acid, the above ester lost $1H_2O$ to give *methyl monoanhydrostrophanthidonate*, m. p. 210°, $[\alpha]_D$ +123° in pyridine (*oxime*, m. p. 290—291°); this, on hydrogenation, yielded a *dihydro*-derivative, m. p. 209°, which gave a nitroprusside reaction, indicating the persistence of the βγ-unsaturated linking. On similar, but more drastic, treatment with methyl-alcoholic hydrochloric acid, methyl strophanthidinate yielded an *anhydro*-derivative, m. p. 205—206°, $[\alpha]_D$ +25° in pyridine, which, with chromic acid, gave *methyl dianhydrostrophanthidonate*, $C_{24}H_{28}O_5$, m. p. 202—203°, $[\alpha]_D$ +131° in pyridine. Dihydrostrophanthidinic lactone gave a *benzoate*, m. p. 271—272°; strophanthidinic lactone, a *benzoate*, m. p. 263—264°. The enhanced lability of one hydroxyl group in methyl strophanthidonate indicates that the latter is an αβ-unsaturated ketone; in the dehydration of methyl strophanthidinate the third hydroxyl group must be involved. The results further indicate that the action of concentrated hydrochloric acid in forming ψ-strophanthidin from strophanthidin (A., 1925, i, 566), and the neutral dilactone, now designated strophanthidinic lactone, from strophanthidinic acid (A., 1926, 73), involves one of the tertiary carbinol groups, and must cause a rearrangement of the aldehyde (or carboxyl) group into the *cis*-position with respect to this carbinol group.

XII. Trianhydrostrophanthidin gave, with potassium permanganate in acetone, an *acid*, $C_{20}H_{24}O_3$, m. p. 206—208°, which did not contain a lactone group, failed to give the nitroprusside reaction, and did not absorb bromine; the substance was therefore formed by oxidation of the βγ-unsaturated lactone linking, which is probably the lactone of an aldehydo-acid, of which the β- or γ-carbon atom is linked to the benzene ring of trianhydrostrophanthidin. Oxidation of the latter with chromic acid gave an *acid*, $C_{23}H_{24}O_6$, m. p. 236—237° (*methyl* ester, m. p. 144—146°), which retained the unsaturated lactone group and the benzene ring of trianhydrostrophanthidin, and contained, in addition, a new lactone group; this result is explained by oxidative cleavage of the second ring between the carbon atom carrying the acylatable carbinol group of strophanthidin (which now becomes a lactone carbon atom) and the adjoining CH_2 group, which is oxidised to carboxyl.

XIII. Methyl α-*iso*strophanthate gave, with chromic acid, *methyl* α-iso*strophanthonate*, $C_{25}H_{34}O_8$, m. p. 254—255°, $[\alpha]_D$ −6·2° in pyridine, which gave no

benzoate, but yielded an *oxime*, m. p. 228°, and, with alcoholic hydrochloric acid, readily gave an *anhydro*-derivative, $C_{25}H_{32}O_7$, m. p. 210°, $[\alpha]_D^{25}$ +74° in pyridine; the latter, with sodium hydroxide, gave the *methyl hydrogen* ester, m. p. 260°, and, on hydrogenation, *methyl deoxy*-α-iso*strophanthonate*, m. p. 206°, $[\alpha]_D$ −4° in pyridine. Methyl strophanthidinate, with methyl-alcoholic potassium hydroxide, gave *methyl* α-iso*strophanthidinate*, m. p. 270—271°, $[\alpha]^{25}$ +84° in pyridine, from which was obtained α-iso*strophanthidindiacid methyl hydrogen* ester, m. p. 204—206°; this gave the *methyl* ester, m. p. 226—228° (*semicarbazone*, m. p. 144—146°). On prolonged contact with cold methyl-alcoholic potassium hydroxide, methyl strophanthidinate gave the *methyl half-acetal* of *methyl oxido*-α-iso*strophanthidinate*, m. p. 219—220°. After hydrolysis of the lactone group, α-*iso*strophanthidindiacid methyl hydrogen ester gave, with hypobromite, α-*iso*strophanthic methyl hydrogen ester; the methyl ester, with chromic acid, yielded methyl α-*iso*strophanthonate (see above). The results indicate that on hydrolysis of the lactone group of α-*iso*strophanthidin a second aldehyde group is liberated, which, on oxidation, is converted into carboxyl and forms a lactone with the same (tertiary) carbinol group as was involved in the original lactone grouping; this original lactone grouping of α-*iso*strophanthidin is a βγ-unsaturated lactone of a β-aldehydo-acid.

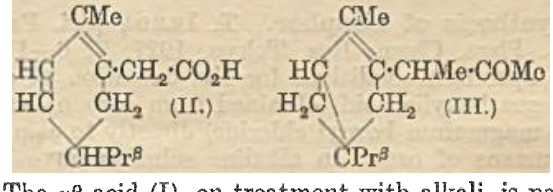
XIV. From the mixture of substances produced by boiling α-*iso*strophanthidic acid in dilute sodium hydroxide, there was isolated, by means of its insoluble ammonium salt, β-iso*strophanthidic acid*, m. p. 175—180°, $[\alpha]_D$ −14° in alcohol, which on oxidation with permanganate gave β-iso*strophanthic acid*, m. p. 280°, $[\alpha]_D^{25}$ −24° in methyl alcohol, and, with hypobromite, the previously described acid, $C_{23}H_{30}O_7$ (A., 1924, i, 1331), which is now shown to be β-iso*strophanthic lactone acid*; α-*iso*strophanthidic acid could not be oxidised in the above manner and therefore does not exist in the oxidic form; the aldehyde and secondary carbinol groups must therefore be in the *cis*-position in the β-acid and *trans*- in the α-acid. On treatment with concentrated hydrochloric acid, α-*iso*strophanthic acid gave γ-iso*strophanthic acid*, m. p. 231—232°, $[\alpha]_D$ +90° in alcohol (*methyl* ester, m. p. 227°, $[\alpha]_D$ +120° in pyridine, giving, on oxidation, *methyl* γ-iso*strophanthonate*, m. p. 235°, $[\alpha]_D$ +106° in pyridine, *anhydro*-derivative, m. p. 168—171°, $[\alpha]_D$ +160° in pyridine). β-*iso*Strophanthic acid gave similarly δ-iso*strophanthic lactone acid*, m. p. 230—231°, $[\alpha]_D$ +29° in pyridine, which, on hydrolysis, yielded δ-iso*strophanthic acid*, m. p. 209—210°, $[\alpha]_D^{17}$ +72° in methyl alcohol. C. R. Harington.

Crossed dismutation between aldehydes and ketones. I. Benzaldehyde and menthone in relation to the menthone-menthol reactions in *Mentha piperita*, L. S. M. Gordon (J. Biol. Chem., 1927, 75, 163—168).—*l*-Menthone condenses with benzaldehyde in presence of aluminium ethoxide, giving *l*-*neomenthyl benzoate*, b. p. 165—170°/10 mm., $[\alpha]_D$ −20·24°; *l*-neomenthol gives an α-*naphthylcarbamate*, m. p. 32°, and a 3 : 5-*dinitrobenzoate*, m. p. 94°. C. R. Harington.

Existence of menthone in the enol form. S. M. Gordon (Amer. J. Pharm., 1927, 99, 599—603).—Mixtures of menthone with acetic anhydride, prepared in 1910, have been analysed for the amount of ester present. This was greatest for the mixture containing equimolecular proportions. S. I. Levy.

Chemistry of the three-carbon system. XV. Pulegone and *iso*pulegone. W. E. Hugh, G. A. R. Kon, and R. P. Linstead (J.C.S., 1927, 2585—2594).—The conditions are defined for the oxidation of *iso*pulegol to *iso*pulegone. The pure ketone is regarded as having b. p. 101—102°/17 mm., $d_4^{20\cdot4}$ 0·92177, $n_D^{17\cdot8}$ 1·46787, α_D +24·7° in methyl alcohol. A small quantity of the inactive ketone is also obtained by this method. No *iso*pulegone could be found in oil of pennyroyal as stated by Grignard (A., 1926, 408); the fraction of the oil corresponding with Grignard's *iso*pulegone consists principally of menthone. The equilibrium between pulegone and *iso*pulegone was studied in the presence of sodium ethoxide, barium hydroxide, sodium carbonate, piperidine, and sulphuric acid. In the first two cases, equilibration is rapid and the final product is indistinguishable from pure pulegone within the limits of experimental error. The iodometric method of Linstead and May (this vol., 1167) serves for accurate determination of the proportion of pulegone and *iso*pulegone in mixtures of the two ketones. M. Clark.

Chemistry of the three-carbon system. XVI. Effect of bridged and unsaturated rings on tautomerism. W. E. Hugh and G. A. R. Kon (J.C.S., 1927, 2594—2600).—Dehydration of β-thujolacetic acid with acetic anhydride gives β-*thujylideneacetic acid* (I), m. p. 103—104° (*acid chloride*, b. p. 136—138°/14 mm.; *ethyl* ester, b. p. 136—137°/10 mm., $d_4^{17\cdot8}$ 0·95995, $n_D^{17\cdot8}$ 1·47800; *anilide*, m. p. 118·5°), oxidised by potassium permanganate in a current of steam to oxalic acid and β-thujone. Dehydration of ethyl β-thujolacetate gives, instead of the βγ-isomeride of (I), an *acid* (II), m. p. 169° (*sodium* and *silver* salts).



The αβ-acid (I), on treatment with alkali, is partly converted into the liquid βγ-isomeride, but the extent of conversion (75% of βγ-isomeride) is much less than in *cyclo*hexylideneacetic acid (cf. this vol., 356). β-*Thujylideneacetone*, b. p. 120°/10 mm., $d_4^{17\cdot4}$ 0·93111, $n_D^{17\cdot4}$ 1·48464 (*semicarbazone*, m. p. 191°), obtained by the action of zinc methyl iodide on the chloride of β-thujylideneacetic acid, has the αβ-structure, although the corresponding *cyclo*hexane compound has the double linking in the ring. Methylation yields a *ketone* (III), b. p. 122°/14 mm., $d_4^{17\cdot8}$ 0·91690, $n_D^{17\cdot8}$ 1·47339 (*semicarbazone*, m. p. 194°), with the βγ-structure. β-Thujone condenses with acetone, giving 2-iso*propylidene*-β-*thujone*, m. p. 78·5° (*semicarbazone*, m. p. 208°). It is concluded that bridged rings in which the strain of the *cyclo*hexane ring is

already relieved have a much diminished tendency to acquire a double linking. When one double linking is already present in the ring, the tendency to produce a conjugated system with two double linkings in the ring is so great that, as in the case of dihydro-*m*-tolylacetic acid, the $\beta\gamma$-form alone is stable.

M. CLARK.

Catalytic action of reduced copper on *iso*borneol. T. IKEDA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1927, 7, 1—5).—The action of reduced copper on the vapour of *iso*borneol has been investigated at various temperatures and pressures. At 135—140°/1 atm. the main product is camphene together with 10—15% of camphor. At 170° only a trace of camphor is obtained, whilst at 210—220° camphene is the sole product. At 350—360° terpenes and high-boiling substances are also produced by the action of the copper on the camphene. At 190—200° or 270—280°/3—4 mm., *iso*borneol gives a little camphor, but is otherwise unaffected.

J. W. BAKER.

Oxidation of *iso*bornyl acetate with ozone. T. IKEDA and Y. FUJITA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1927, 7, 12—20).—No appreciable amount of oxidation occurs when *iso*bornyl acetate is treated in glacial acetic acid with twice the theoretical quantity of ozone at temperatures between 1° and 100°, and under similar conditions in acetone solution a substance chemically identical with *iso*bornyl acetate but with a much higher b. p., 153—154°/10 mm., is obtained. A large excess of ozone in acetic acid solution gives rise to *keto*iso*bornyl acetate*, b. p. 150—155°/10 mm., d_4^{20} 1·0657, 1·47131 (*semicarbazone*, m. p. 187°), which is not identical with acetoxycamphor. Hydrolysis of the semicarbazone with aqueous sodium carbonate yields the *semicarbazone*, m. p. 224°, of keto*iso*borneol. A second *semicarbazone*, m. p. 197—198°, was obtained from the residues of the original oxidation product. Ozonolysis of *iso*bornyl acetate in cold acidified acetone gave a small quantity of a viscous *substance*, b. p. 135—140°/8 mm.

J. W. BAKER.

Synthesis of camphor. T. IKEDA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1927, 7, 6—11).—The optimum conditions for the oxidation of camphanecarboxylic acid (obtained from carbon dioxide and magnesium bornyl chloride) directly to camphor by means of ozone in alkaline solution have been investigated. No oxidation occurs at the ordinary temperature (or in glacial acetic acid) and the velocity of formation of camphor is greater the more concentrated the alkali. The best catalysts found for the oxidation were manganese borate and ferrous sulphate; with a 10% solution of the potassium salt in *N*-potassium hydroxide with the addition of 2% of the former catalyst at 90—95°, a 15% yield of camphor was obtained in 9 hrs.

J. W. BAKER.

Action of potassium cyanide on pernitroso-derivatives. M. PASSERINI and (SIGNA.) G. BRUSCOLI (Gazzetta, 1927, 57, 598—605).—See this vol., 670: a more detailed account is now given.

E. W. WIGNALL.

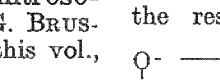
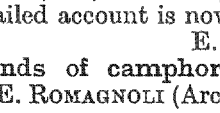
New compounds of camphor with amines. P. SACCARDI and E. ROMAGNOLI (Arch. Farm. sperim., 1927, 26, 197—204).—*Camphanylidene*-p-*aminophenol*, $C_{10}H_{16}{:}N{\cdot}C_6H_4{\cdot}OH$, prepared by the interaction of pernitrosocamphor and *p*-aminophenol, has m. p. 144°, and forms unstable, soluble *sodium* and *potassium* compounds, also a *hydrochloride*, m. p. 212° (decomp.); an *oxalate*, m. p. 190° (decomp.); an *acetate*, and an insoluble *ferrocyanide*, which turns brown at 105° and chars at above 200°.

Camphanylidene-p-*phenetidine*, m. p. 207°, similarly obtained, forms an unstable *hydrochloride*, an *oxalate*, m. p. 175° (decomp.), and a *ferrocyanide* which turns brown at 150° and chars at above 200°.

T. H. POPE.

Influence of the sulphur atom on optical rotatory power. P. P. SHUKLA (J. Indian Inst. Sci., 1927, **10A**, 33—41; cf. Hilditch, J.C.S., 1908, 93, 1618).—The depression in rotatory power due to the introduction of a bivalent sulphur atom was found to vary considerably in some thio-derivatives of arylbisiminocamphors. The following compounds were prepared by boiling alcoholic solutions of camphorquinone and the appropriate thio-base (modifications of the published methods for the preparation of these thio-bases had to be adopted to obtain good yields) in presence of anhydrous sodium sulphate: *thiodiphenylenebisiminocamphor*, $(C_{10}H_{14}O{:}N{\cdot}C_6H_4{\cdot})_2S$, m. p. 215° $[\alpha]_D$ 947°; *methylbenzthiazolebenzenyliminocamphor*, $C_{10}H_{14}O{:}N{\cdot}C_6H_4{\cdot}C{<}\overset{N}{\underset{S}{>}}C_6H_3Me$, m. p. 182°, $[\alpha]_D$ 564·8°; pp′-*dithiodiphenylenebisiminocamphor*, $(C_{10}H_{14}O{:}N{\cdot}C_6H_4{\cdot}S{\cdot})_2$, m. p. 201—202° (colour changes at 160° and 195°), $[\alpha]_D$ +820°; pp′-*thioditolylenebisiminocamphor*, m. p. 216°, $[\alpha]_D$ +407·6°; and a brown *compound*, m. p. 216°, formed in the attempt to condense dithio-*p*-toluidine with camphorquinone. Dinitrodiphenyl disulphide has m. p. 182°.

B. W. ANDERSON.

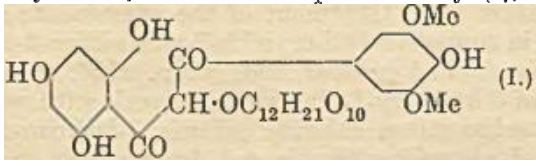
Synthesis of phenylcoumalin and of a quinoline derivative. J. KALFF (Rec. trav. chim., 1927, 46, 594—599).—Attempts to synthesise phenylcoumalin (6-phenyl-α-pyrone) by condensing benzoylacetaldehyde with malonic acid or by condensing phenylglyoxal with succinic anhydride and sodium succinate were unsuccessful. The mixed anhydride of crotonic and benzoic acids cannot be obtained from crotonyl chloride and sodium benzoate, and the product of the action of sodamide on acetophenone when treated with ethyl phenylpropiolate gives only 2 : 6-diphenyl-γ-pyrone. Phenylpropargylaldehyde, obtained by the action of alcoholic potassium hydroxide solution on the acetal of bromocinnamaldehyde, followed by hydrolysis by dilute sulphuric acid (Weigand, Diss., Kiel, 1902), condenses, however, with malonic acid to give *propargylidenemalonic acid*. This is obtained in two forms: at the ordinary temperature (I), soluble in sodium hydrogen carbonate solution, m. p. 208—218° (corr., decomp.), and at 100° (II), insoluble, m. p. 218° (corr., decomp.), are obtained. For these the respective formulæ  and  are suggested. On heating in dilute sulphuric acid, (I) is largely converted into

(II), stable to sulphuric acid, but also loses carbon dioxide to give phenylcoumalin, m. p. 68°, identical with that obtained from Coto bark.

When phenylpropargylaldehyde is warmed with β-naphthylamine in acetic acid, 1-phenyl-β-naphthaquinoline is obtained. E. W. WIGNALL.

2 : 3 : 4′-[6 : 7 : 4′-]Trihydroxyflavone. G. BARGELLINI and A. GRIPPA (Gazzetta, 1927, **57**, 605—609).—When 2 : 4 : 5-trimethoxyacetophenone is condensed with methyl anisate in presence of sodium, 2 : 4 : 5 : 4′-*tetramethoxybenzoylacetophenone*, m. p. 138—140°, is obtained, which when heated with hydrobromic acid gives 6 : 7 : 4′-*trihydroxyflavone*, ($+H_2O$), decomp. 300° (*triacetyl* derivative, m. p. 234—236°). Heating with hydriodic acid gives, however, a mixture containing also mono-, di-, and tri-methoxy-compounds. A *dimethyl ether* of 6 : 7 : 4′-trihydroxyflavone ($+H_2O$), m. p. 158—162° (decomp.) (*acetyl* derivative, m. p. 164—166°), can thus be isolated. 6 : 7 : 4′-*Trimethoxyflavone*, m. p. 184—186°, is obtained by methylation of the latter or of the trihydroxyflavone. E. W. WIGNALL.

Vegetable colouring matters. IV. Anthocyanins and anthocyanidins. P. KARRER, R. WIDMER, A. HELFENSTEIN, W. HURLIMAN, O. NIEVERGELT, and P. MONSARRAT-THOMS (Helv. Chim. Acta, 1927, **10**, 729—757; cf. this vol., 252, 571).—Malvin chloride is oxidised by 15% hydrogen peroxide to *malvone*, $C_{29}H_{36}O_{19},H_2O$ (65% of theoretical), m. p. 220—230°, sintering from 100°, and traces of syringic and phloroglucinolcarboxylic acids. Malvone reduces Fehling's solution and yields 2 mols. of dextrose on acid hydrolysis. It is very readily hydrolysed by boiling alkali to syringic acid (70% of theoretical). At the same time the disaccharide residue is detached entire and converted into a product which has no further reducing properties, but gives 1 mol. of dextrose when boiled with acid. Since the glucosides of phloroglucinol and of syringic acid are not hydrolysed by alkali, malvone is represented by (I), the



(I.)

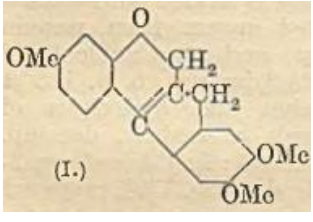
extra H_2O (above) being probably attached to one of the keto-groups. With phenylhydrazine and sodium acetate, malvone gives a *phenylhydrazone*, $C_{23}H_{20}O_7N_2(OC_6H_{11}O_5),H_2O$, m. p. indef., losing 1 mol. of dextrose as phenylglucosazone. After prolonged treatment with diazomethane the ketone gives a crystalline *product* which contains 7 methoxyl groups and is hydrolysed to 3 : 4 : 5-trimethoxybenzoic acid. When other anthocyanins and anthocyanidins are oxidised with 15% hydrogen peroxide, the latter yield secondary oxidation products much more readily than the former. Ketones resembling malvone have not been isolated. Thus, syringidin gives syringic acid, pæonidin vanillic acid, and pelargonidin, *p*-hydroxybenzoic acid in fair yield, whilst malvin and pæonin give only traces and pelargonin none of the corresponding acids. This is due to the disaccharide residue in the 3-position (cf. Atree and Perkin, this vol., 231) which prevents the pyrylium nucleus from assuming tautomeric forms in which it is more readily oxidised. Proof of this explanation is furnished by comparing the behaviour of 3 : 5 : 7-trimethoxy-2-phenylbenzopyrylium chloride (Pratt and Robinson, A., 1924, i, 306) towards hydrogen peroxide with that of 3-*hydroxy*-5 : 7-*dimethoxy*-2-*phenylbenzopyrylium chloride*, prepared by Robinson's method from 2-hydroxy-4 : 6-dimethoxybenzaldehyde and ω-hydroxyacetophenone. Under similar conditions the former gave a trace, the latter a considerable amount of benzoic acid. The hydrogen peroxide method is not suitable for the degradation of anthocyanins with adjacent hydroxyl groups, which usually yield black, insoluble products.

In order further to determine the position and nature of the disaccharide residue, pæonin and cyanin have been methylated with methyl sulphate and alkali, then thrice with methyl iodide and silver oxide. When the amorphous product is hydrolysed with methyl-alcoholic hydrochloric acid, the same methylated dye is formed in both cases. It is identified as 3-*hydroxy*-5 : 7 : 3′ : 4′-*tetramethoxy*-2-*phenylbenzopyrylium chloride*, m. p. 138°, sintering from 113°, by the formation of an insoluble *carbinol base* when its concentrated aqueous solution is treated with sodium hydroxide. The methylated sugars from pæonin contain tetramethylglucose and an unidentified syrupy *trimethylglucose* (*methylglucoside*, b. p. 118°/1 mm.). Similarly methylation and hydrolysis of monardin (pelargonin) affords a product, decomp. 120°, identified with 3-*hydroxy*-5 : 7 : 4′-*trimethoxy*-2-*phenylbenzopyrylium chloride*, decomp. 130°, prepared from ω-hydroxy-4-methoxyacetophenone and 2-hydroxy-4 : 6-dimethoxybenzaldehyde. 5-*Hydroxy*-3 : 7 : 4′-*trimethoxy*-2-*phenylbenzopyrylium chloride* and 7-hydroxy-3 : 5 : 4′-trimethoxy-2-phenylbenzopyrylium chloride (Pratt and Robinson, *loc. cit.*) were synthesised for comparison. Methylation and hydrolysis of malvin give 3-*hydroxy*-5 : 7 : 3′ : 4′ : 5′-*pentamethoxy*-2-*phenylbenzopyrylium chloride*. In all four anthocyanins, therefore, the disaccharide residue is in the 3-position. In spite of their apparent homogeneity and crystalline nature, most of the methylated dyes described in this and the following abstract have methoxyl contents 1—3% below the theoretical and probably contain traces of impurities. Attempts to hydrogenate anthocyanins in presence of platinum-black or platinum oxide were unsuccessful. Since all anthocyanins known at present have a 4′-hydroxyl group their colour in the plant will depend on the p_H of the cell-sap. This is confirmed by analyses of 3 species of blue and 4 of red flowers, the former having a higher ash content than the latter, on account of the presence of more alkali. The presence of the sugar residue in the 3-position renders the molecule more stable towards alkali. H. E. F. NOTTON.

Vegetable colouring matters. V. Primula colouring matters. P. KARRER and R. WIDMER (Helv. Chim. Acta, 1927, **10**, 758—763 cf. preceding abstract).—The colouring matter of *Primula viscosa* is identical with malvin, which is also present with compounds of lower methoxyl content in *P. integrifolia*. *P. hirsuta* contains an anthocyanin, *hirsutin*,

the *chloride*, $C_{30}H_{37}O_{17}Cl$, of which is hydrolysed by acids to *hirsutidin* (a delphinidin trimethyl ether) and 2 mols. of dextrose, and oxidised by hydrogen peroxide to *hirsutone*, $C_{30}H_{38}O_{19},H_2O$, which gives syringic acid on hydrolysis. The new products differ only slightly in colour and chemical properties from malvin, syringidin, and malvone, respectively. Hirsutin is, therefore, the 3-*diglucoside* of 5(?7) : 4′-*dihydroxy*-7(?5) : 3′ : 5′-*trimethoxy*-2-*phenylbenzopyrylium chloride*. H. E. F. Notton.

Brazilin and hæmatoxylin question. V. Synthesis of a trimethylanhydrobrazilin. P. Pfeiffer and H. Oberlin (Ber., 1927, **60**, [*B*], 2142—2148; cf. A., 1925, i, 1303).—The reduction of 7 : 3′ : 4′-trimethoxy-3-benzylidene-2 : 3-dihydro-γ-benzopyrone by hydrogen in the presence of platinum-black to 7 : 3′ : 4′-trimethoxy-3-benzyl-2 : 3-dihydro-γ-benzopyrone is confirmed (cf. Pfeiffer and Emmer, A., 1920, i, 562); the ketone has m. p. 90—90·5° after purification through the *oxime*, m. p. 143·5—144·5°, and is not identical with the 7 : 3′ : 4′-trimethoxy-3-benzylchroman described by Perkin, Ray, and Robinson (A., 1926, 732). 7 : 3′ : 4′-Trimethoxy-3-benzylidene-2 : 3-dihydro-γ-benzopyrone is converted by phosphoric oxide in the presence of boiling benzene into trimethylanhydrobrazilin (I), m. p. 167—170°, identical with trimethyldeoxybrazilone (cf. Gilbody and Perkin, J.C.S., 1902, **81**, 1046; Herzig and Pollak, A., 1905, i, 605). The constitution of the compound is confirmed by its oxidation by ferric chloride to *iso*brazilein ferrichloride trimethyl ether (cf. Crabtree and Robinson, J.C.S., 1918, **113**, 872). H. Wren.



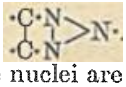
(I.)

Fission of the heterocyclic compounds of coal tar. R. Weissgerber and C. Seidler (Ber., 1927, **60**, [*B*], 2088—2090).—The use of sulphuric acid for the removal of heterocyclic compounds from coal-tar distillates involves considerable losses of material and usually transforms the heterocyclic substances into worthless resins. The application of potassium hydroxide promises better results. Thus thionaphthen is transformed by solid potassium hydroxide at 300—310° into *o*-thiocresol in 83% yield and formic acid, which suffers oxidation to carbon dioxide. Similarly, coumarone affords *o*-cresol without appearance of by-products. Indene gives a black, amorphous mass together with hydrindene, a little *o*-xylene, and (?)chrysene and truxene. Indole at 200° yields unchanged material and pure *o*-toluidine. Diphenylene oxide, diphenylene sulphide, and thiophen are stable towards potassium hydroxide at 300°. H. Wren.

Diphenylthiophens. E. Fromm, P. Fantl, and E. Leibsohn (Annalen, 1927, **457**, 267—277; cf. Baumann and Fromm, Ber., 1897, **30**, 117; Steinkopf, A., 1921, i, 630).—The non-identity of the two isomeric diphenylthiophens obtained by heating cinnamic acid with sulphur (Baumann and Fromm, *loc. cit.*) is shown by the preparation of derivatives. The identical mercurichlorides described by Steinkopf are accounted for by the presence of 2 : 4-diphenylthiophen in the 2 : ɔ-isomeride used; the latter gives no mercurichloride.

The mixture of products obtained by Baumann and Fromm's method gives by repeated purification pure 2 : 5-diphenylthiophen, m. p. 153°, and the pure 2 : 4-isomeride, m. p. 124°. Bromination of these in chloroform yields *tetrabromo*-derivatives, m. p. 203° and 150°, respectively. In the absence of solvent the 2 : 5-compound gives the tetrabromo-derivative, m. p. 203°, whilst the 2 : 4-compound is converted into a *substance*, m. p. 245°, with much higher sulphur content. The 2 : 4-compound is also degraded by concentrated nitric acid, with formation of a nitrogenous *substance*, m. p. 271°, with high sulphur content, whereas the 2 : 5-isomeride gives *trinitro*-2 : 5-*diphenylthiophen*, m. p. 243°, in 80% yield, together with a *dinitro*-compound, m. p. 189°. 2 : 4-Diphenylthiophen yields a *picrate*, m. p. 133—134°; the 2 : 5-compound gives no picrate. By condensation with acetyl chloride the isomerides form, respectively, 2 : 5-*diphenyl*-3-*thienyl methyl ketone*, m. p. 214°, and a 2 : 4-*diphenylthienyl methyl ketone*, m. p. 94°. 2 : 4-Diphenylthiophen gives with mercuric chloride Steinkopf's mercurichloride, m. p. 222°, and with mercuric acetate a mixture, m. p. 207—208°, of *mercuriacetate* and *mercury tetraphenyldithienyl*. The pure 2 : 5-isomeride does not react with mercuric chloride or acetate. C. Hollins.

Comparison of heterocyclic systems with benzene. II. Reduction potentials of quinones containing the pyridine, glyoxaline, triazole, and thiophen rings. L. F. Fieser and L. A. Ames (J. Amer. Chem. Soc., 1927, **49**, 2604—2617; cf. A., 1926, 625).—Treatment of 4-nitroso-5-hydroxy-2-phenylbenztriazole (cf. Fries and Roth, A., 1912, i, 656) with aqueous sodium hydrogen sulphite affords the *sodium* 4-*amino*-5-*hydroxy*-2-*phenylbenztriazole*-7-*sulphonate* ($1\frac{1}{2}H_2O$), which is oxidised by 25% nitric acid to 2-*phenylbenztriazole*-4 : ɔ-*quinone*-7-*sulphonic acid* (*potassium* salt), treatment of the ammonium salt of which in aqueous solution yields 7-p-*toluidino*-2-*phenylbenztriazole*-4 : 5-*quinone*, red, m. p. 215°. Condensation of 5-hydroxy-1-phenylbenztriazole with aqueous benzenediazonium chloride affords 5-*hydroxy*-4-*benzeneazo*-1-*phenylbenztriazole*, red, from which an amine could not be obtained by reduction. αβ-Naphthatriazolequinone (cf. Zincke and Noack, A., 1897, i, 355) is obtained by the oxidation of αβ-naphthatriazole with chromium trioxide in glacial acetic acid. αβ-*Naphthiminazole*-4 : 5-*quinone*, orange, darkening at 210°, m. p. not below 250°, is obtained by heating 1 : 2-diamino-3 : 4-dihydroxynaphthalene dihydrochloride with sodium acetate and formic acid, with subsequent oxidation of the resulting quinol with nitric acid. The reduction potentials of the above quinones, as well as of 2-phenyl-αβ-naphthatriazole-4 : 5-quinone, 3-phenyl-αβ-naphthatriazole-4 : 5-quinone, α-naphthaquinolinequinone, phenanthraquinone, 1-phenyl-ββ-naphthatriazole-4 : 9-quinone, 1-*p*-tolyl-ββ-naphthatriazole-4 : 9-quinone, 3-phenyl-2-methyl-ββ-naphthiminazole-4 : 9-quinone, thionaphthenquinone, and thiophenanthrenquinone, were measured by electrometric titration with titanous chloride in

aqueous 50% alcohol in presence of 0·1*M*-hydrogen chloride and 0·2*M*-lithium chloride. The results obtained indicate a marked similarity between the 2-phenyltriazole ring and benzene. The 3-phenyltriazole grouping exhibits greater reactivity than the 2-phenyl- or unsubstituted triazole groupings, and it is therefore concluded that both these have the structure  . The effects of the pyridine and glyoxaline nuclei are not comparable with that of the phenylene group, but the observed results are probably modified by the basicities of these groups. Heterocyclic analogues of anthraquinone do not bear the same relationship to the latter as is observed between phenanthraquinone and the corresponding heterocyclic isomerides. It is suggested that this observation is connected with the abnormally low reduction potential of anthraquinone, which may possibly be ascribed to an *o*-quinonoid structure of anthraquinol, which would increase the tendency of the latter to revert to the quinone. If the *o*-quinonoid phenylene group be now replaced by a more stable system, such as dihydroglyoxaline (cf. Fries, this vol., 778) the tendency of the whole molecule to assume the *p*-quinonoid structure by oxidation will be greatly reduced. The results obtained with thionaphthenquinone indicate that the thiophen ring has a much greater tendency than benzene to assume the quinonoid structure. F. G. Willson.

Configuration of the ammonium ion. II. Geometrically isomeric quaternary ammonium salts derived from 4-phenyl- and 4-hydroxypiperidine. W. H. Mills, J. D. Parkin, and W. J. V. Ward (J.C.S., 1927, 2613—2626; cf. Mills and Warren, A., 1926, 178).—The tetrahedral configuration of the quaternary ammonium ion is demonstrated by the existence of pairs of stereoisomerides in piperidinium salts, $CHR<^{CH_2\cdot CH_2}_{CH\cdot CH}>NR'R''X$, only when R′ and R″ are different, and the absence of isomerism when R′=R″, whereas a pyrimidal configuration requires pairs of stereoisomerides whether R′ and R″ are different or identical, and the isomerides would in the former case be racemic compounds.

By the action of alkyl iodide and sodium hydroxide 4-phenylpiperidine is converted into its 1-*methyl* [m. p. 9°, b. p. 122—123°/11 mm.; *hydrochloride*, m. p. 196—198°; *perchlorate*, m. p. 106—107°; *picrate*, m. p. 244° (decomp.)], 1-*ethyl* (m. p. 11°, b. p. 137°/11 mm.; *hydrochloride*, m. p. 203—205°; *perchlorate*, m. p. 112°), and 1-n-*propyl* [m. p. 13°, b. p. 150°/11 mm.; *hydrochloride*, m. p. 250° (decomp.); *perchlorate*, m. p. 160—162·5°] derivatives. α-4-*Phenyl*-1-*methyl*-1-*ethylpiperidinium iodide*, m. p. 180—181° (*perchlorate*, m. p. 135°), is isolated from the mixture formed by the action of ethyl iodide on 4-phenyl-1-methylpiperidine. The dimorphous β-*isomeride*, m. p. 140° and 146° (*perchlorate*, m. p. 159°), is best obtained from the mixed methiodides of 4-phenyl-1-ethylpiperidine (from which the α-compound may also be isolated). Addition of benzyl chloride to 4-phenyl-1-ethylpiperidine yields a mixture of α- and β-4-phenyl-1-benzyl-1-ethylpiperidinium salts, separable as *perchlorates*, m. p. 208° (α) and 189° (β). The β-*iodide*, m. p. 210—215°, is converted, when kept above its m. p., into the α-*iodide*, m. p. 240° (decomp.); both are obtainable from the perchlorates. On the other hand, 4-*phenyl*-1 : 1-*diethylpiperidinium iodide*, m. p. 177°, and 4-*phenyl*-1 : 1-*di*-n-*propylpiperidinium iodide*, m. p. 190°, show no separation into isomerides when fractionated.

4-Hydroxy-1-methylpiperidine, m. p. 28°, b. p. 105°/18 mm. (*hydrochloride*, m. p. 157—158°; *hydrobromide*, m. p. 139—140°), reacts with ethyl bromoacetate to give a mixture, m. p. 204°, of *ethyl* 4-*hydroxypiperidylacetate methobromides*. The α-isomeride, m. p. 221° (decomp.; *picrate*, m. p. 152—153°), is converted by silver oxide into the α-*methylbetaine*, m. p. 271—272°, from which by treatment with hydrobromic acid α-4-*hydroxypiperidylacetic acid methobromide*, m. p. 170—172°, is obtained. With less hydrobromic acid the betaine gives a basic *salt*, $C_{16}H_{31}O_6N_2Br$, m. p. 215—218° (decomp.). The β-*methylbetaine*, m. p. 266—267° (anhyd. and $+H_2O$), similarly yields β-4-*hydroxypiperidylacetic acid methobromide*, m. p. 210° [decomp.; *picrate*, m. p. 126°; *ethyl* ester, m. p. 206°; *ethyl* ester *methochloride*, m. p. 206° (decomp.)], and a basic *salt*, m. p. 220—221° (decomp.). Neither the α- nor the β-methobromide of 4-hydroxypiperidylacetic acid shows any tendency to lactone formation, and an attempt to convert 4-*bromoacetoxy*-1-*methylpiperidine* (*hydrobromide*, m. p. 172°) into a lactone was unsuccessful. C. Hollins.

Condensation products of isatin. I. M. Kotake (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1927, **6**, 61—65).—Condensation of isatin with hydantoin in the presence of acetic anhydride and fused sodium acetate at 100° yields the *diacetyl* derivative, decomp. 245°, of *oxindolidenehydantoin*, not decomp. below 310°; the latter is obtained crystalline on hydrolysis with cold dilute ammonia. Reduction of the diacetyl derivative with excess of sodium amalgam in potassium hydroxide yields *oxindolylhydantoin*, m. p. 283—284° (*diacetyl* derivative, m. p. 220—224°), whilst reduction with acetic acid and zinc at 100° yields a supposed intermediate *substance*, $C_{11}H_{13}O_2N_3$, which yields oxindolylhydantoin on reprecipitation from its solution in alkali by means of acid. On prolonged hydrolysis with barium hydroxide at 100° oxindolylhydantoin yields 3-*hydroxy*-2-*keto*-1 : 2 : 3 : 4-*tetrahydroquinoline*-4-*carboxylic acid*, m. p. above 310° (*copper* and *silver* salts) and not oxindolylglycine. On heating the silver salt of the latter, 2-keto-1 : 2-dihydroquinoline is obtained. J. W. Baker.

Facile ring-closure to a derivative of dihydro-*iso*quinoline contrasted with the difficulty of analogous formation of a derivative of *iso*indole. J. Malan and R. Robinson (J.C.S., 1927, 2653—2657).—When the compound $CHO\cdot N(CH_2\cdot C_6H_3\cdot O_2CH_2)_2$ (I), which might by cyclisation yield an *iso*indole or a dihydro*iso*quinoline, is treated with phosphoryl chloride only the six-membered ring is formed. This result is attributed to the field associated with the positive charge of the nitrogen atom (become quinquevalent), which is more effective on the nearer nucleus in preventing condensation with the aldehydic group.

(Piperonylmethyl)amine [*chloroplatinate*; *picrate*,

m. p. 198°; *piperonylmethyltrimethylammonium iodide*, m. p. 219° (decomp.); *benzylidene* derivative, m. p. 51—52° (*picrate*, m. p. 206°)], condenses with methyl opianate at 150° to form a 2-*carbomethoxyveratrylidene* derivative, m. p. 181°, which by the action of sodium methoxide in hot methyl alcohol loses the elements of methyl alcohol, yielding a *compound*, $C_{18}H_{15}O\text{-}N$, m. p. 159°. This is probably not the expected 4-hydroxy-5 : 6-dimethoxy-3-piperonyl*iso*quinoline, since with methyl iodide it gives an *iodide*, m. p. 72°, having nearly the composition of (piperonylmethyl)-methylamine hydriodide. In the preparation of the primary amine by reduction of piperonaldoxime a by-product is *di*(*piperonylmethyl*)*amine*, m. p. 114°, b. p. 230°/50 mm. *Acetopiperonylmethylamide*, m. p. 103°, and the corresponding benzamide (Mannich and Kuphal, A., 1912, i, 850) are not cyclised by phosphoryl chloride, phosphorus pentoxide, sulphuric acid, zinc chloride, or stannic chloride. Phenacyl veratrate, $C_6H_3(OMe)_2\cdot CO_2\cdot CH_2Bz$, m. p. 122°, prepared from phenacyl bromide and silver veratrate, could not be converted into an *iso*coumarin derivative.

Piperonylmethyl-β-*piperonylethylamine* (as I), m. p. 53° (*hydrochloride*; *nitroso*-derivative, m. p. 127—128°; *dinitro*-derivative, m. p. 134—135°), is obtained by reduction of piperonylidene-β-piperonylethylamine with sodium and alcohol. The formyl derivative (I), m. p. 89—90°, is converted by phosphoryl chloride into 6 : 7-*methylenedioxy*-2-*piperonylmethyl*-3 : 4-*dihydro*iso*quinoline* salts (*picrate*, m. p. 184—185°). The *bromide*, m. p. 230°, which gives the same picrate, is synthesised from 6 : 7-methylenedioxy-3 : 4-dihydro*iso*quinoline and piperonylmethyl bromide. The bromide and the picrate both combine with nitromethane to form 6 : 7-*methylenedioxy*-1-*nitromethyl*-2-*piperonylmethyl*-1 : 2 : 3 : 4-*tetrahydro*iso*quinoline*, m. p. 124—125°, and the bromide or *chloride* with potassium cyanide gives the corresponding 1-*cyano*-compound, m. p. 151°.

C. Hollins.

Preparation of 2 : 3-diaminopyridine by amination of 3-aminopyridine. A. Konopnicki and E. Plazek (Ber., 1927, **60**, [*B*], 2045—2047).—2 : 3-Diaminopyridine, m. p. 113°, is prepared in poor yield by the action of an excess of sodamide in boiling *p*-cymene on 3-aminopyridine, the bulk of which suffers resinification; the *picrate*, m. p. 262—264°, is described. The diamine is more conveniently prepared by the method of Tschitschibabin and Kirsanov (this vol., 466).

H. Wren.

***p*-Hydroxy- and *p*-amino-phenyl-lutidine.** B. Emmert, E. Diefenbach, and R. Eck (Ber., 1927, **60**, [*B*], 2216—2222).—Ethyl 4-phenyl-2 : 6-dimethylpyridine-3 : 5-dicarboxylate is converted by nitric acid (*d* 1·51) and concentrated sulphuric acid at 60—70° into a mixture of *ethyl* 4-p-*nitrophenyl*-2 : 6-*dimethylpyridine*-3 : 5-*dicarboxylate*, m. p. 117°, and ethyl 4-*m*-nitrophenyl-2 : 6-dimethylpyridine-3 : 5-dicarboxylate, m. p. 63°. The former compound is reduced by tin and hydrochloric acid to *ethyl* 4-p-*aminophenyl*-2 : 6-*dimethylpyridine*-3 : 5-*dicarboxylate*, m. p. 146° (*dihydrochloride*; *chlorostannate*), transformed by nitrous acid into *ethyl* 4-p-*hydroxyphenyl*-2 : 6-*dimethylpyridine*-3 : 5-*dicarboxylate*, m. p. 171°. The constitution of the latter compound is established by its production (together with ethyl 2 : 6-dimethylpyridine-3 : 5-dicarboxylate) by the action of nitrous fumes on *ethyl* 4-p-*hydroxyphenyl*-2 : 6-*dimethyldihydropyridine*-3 : 5-*dicarboxylate*, m. p. 226—227°, obtained from *p*-hydroxybenzaldehyde, ethyl acetoacetate, and ammonia. *Ethyl* 1-*phenyl*-4-p-*hydroxyphenyl*-2 : 6-*dimethyldihydropyridine*-3 : 5-*dicarboxylate*, m. p. 155—156°, is prepared from *p*-hydroxybenzylideneaniline and ethyl acetoacetate in cold alcohol. Anisaldehyde, ethyl acetoacetate, and ammonia afford *ethyl* 4-p-*methoxyphenyl*-2 : 6-*dimethyldihydropyridine*-3 : 5-*dicarboxylate*, m. p. 159°, oxidised by nitrous acid to *ethyl* 4-p-*methoxyphenyl*-2 : 6-*dimethylpyridine*-3 : 5-*dicarboxylate*, m. p. 51—53°. 4-Phenyl-2 : 6-dimethylpyridine is converted by concentrated nitric and sulphuric acids at 65—70° into a mixture of 4-p-*nitrophenyl*-2 : 6-*dimethylpyridine*, m. p. 165—166° (*hydrochloride*), and a 4-*nitrophenyl*-2 : 6-*dimethylpyridine*, m. p. 122—123°. 4-p-*Aminophenyl*-2 : 6-*dimethylpyridine*, m. p. 132—133° (*dihydrochloride*, m. p. 85°; *methiodide*), and a *compound*, m. p. 223°, are obtained by reduction of the nitro-compound with tin and hydrochloric acid. The colourless solutions of ethyl 4-*p*-aminophenyl-2 : 6-dimethylpyridine-3 : 5-dicarboxylate and 4-*p*-aminophenyl-2 : 6-dimethylpyridine become intensely yellow when a small proportion of hydrochloric acid is added, whereas the bases and their dihydrochlorides are colourless. The cause of the halochromy is not established.

H. Wren.

Quinoline derivatives. IV. Substituted 2-styrylquinoline-4-carboxylic acids. H. John (J. pr. Chem., 1927, [ii], **117**, 214—224).—These have been prepared by an extension of Friedlander's quinoline synthesis, substitution products of isatin and of styryl methyl ketone being condensed together in presence of concentrated aqueous potassium hydroxide at 100°. 2-Styrylquinoline-4-carboxylic acid (cf. Doebner and Peters, A., 1890, 176) (*ethyl* ester, m. p. 76°) is reduced by hydriodic acid to 2-β-*phenylethylquinoline*-4-*carboxylic acid*, m. p. 219—220°. The following derivatives of 2-styrylquinoline-4-carboxylic acid are described: 6-*methyl*-, m. p. 271°; 6-*chloro*-, m. p. 242—243°; 6-*bromo*-, m. p. 287°; 6-*iodo*-, m. p. 295—296° (decomp.); 6 : 8-*dibromo*-, m. p. 238—240°; 5-*chloro*-6-*bromo*-, m. p. 279°; p-*methyl*-, m. p. 271—272°; p-*chloro*-, m. p. above 300°; p-*dimethylamino*-, m. p. 260—261°; o-*hydroxy*-, m. p. above 300°; p-*methoxy*-, m. p. 285°; mp-*dihydroxy*-, m. p. above 300°; p-*hydroxy*-m-*methoxy*-, m. p. 282—283°; mp-*dimethoxy*-, m. p. 253—254°; mp-*methylenedioxy*-, m. p. 270—271°; p-*dimethylamino*-6-*bromo*-, m. p. 264—265°; mp-*methylenedioxy*-6-*bromo*-, m. p. above 305°. The solubility and appearance of a large number of metallic salts of each of the new acids are listed.

H. E. F. Notton.

Syntheses of quinoline and quinazoline derivatives; attempts to synthesise eight-membered rings containing nitrogen. J. Troger and J. Bohnekamp (J. pr. Chem., 1927, [ii], **117**, 161—184).—When 2-amino-3-methoxybenzaldehyde (I) (cf. A., 1926, 68) and ethyl benzoylacetate are heated together at 160°, 2-*hydroxy*-8-*methoxy*-3-*benzoylquinoline*, m. p. 206° (*phenylhydrazone*, m. p. 159°),

is formed, but in presence of sodium hydroxide at 100° they give *ethyl* 8-*methoxy*-2-*phenylquinoline*-3-*carboxylate*, m. p. 129°, which is hydrolysed by acid to 8-*methoxy*-2-*phenylquinoline*-3-*carboxylic acid*, m. p. 210° (*chloroplatinate*), whilst under other conditions 2-amino-3-methoxybenzoic acid (?) and anhydrobis-2-amino-3-methoxybenzaldehyde are obtained. In alkaline solution the aminoaldehyde gives, (*a*) with ω-cyanoacetophenone, 8-*methoxy*-3-*cyano*-2-*phenylquinoline*, m. p. 192° (*hydrochloride*, *chloroplatinate*), which is hydrolysed by alkali to the corresponding acid; (*b*) with malononitrile, 2-*amino*-3-*cyano*-8-*methoxyquinoline*, m. p. 225°, which is easily hydrolysed to 2-*amino*-8-*methoxyquinoline*-3-*carboxylic acid*, m. p. 268° (decomp.) (*chloroplatinate*). The aldehyde (I) and ethoxalyl chloride yield *ethyl* 2-*aldehydo*-6-*methoxyanilinoglyoxylate*, m. p. 138°, which is hydrolysed to the corresponding *glyoxylic acid*, m. p. 161° [*potassium*, *silver*, and *barium* (+3H_2O) salts], and converted by alcoholic ammonia into *di*-(8-*methoxyquinazoline*-2-*carboxyl*)*imide*, $(OMe{\cdot}C_8H_4N_2{\cdot}CO)_2NH$, m. p. 230° (*picrate*, *perchlorate*, and *silver nitrate* derivative, $C_{20}H_{15}O_4N_5,AgNO_3$), which, when hydrolysed, gives 8-methoxyquinazoline. Similarly, ethyl 2-aldehydoanilinoglyoxylate (m. p. 196°, not 106° as given by Bischler and Lang, A., 1895, i, 250) affords *di*(*quinazoline*-2-*carboxyl*)*imide*, m. p. 198° (*picrate*, *perchlorate*, and *silver nitrate* derivative). When the aldehyde (I) is fused with carbamide at 120—125°, amorphous 8-*methoxy*-2-*quinazolone*, m. p. 205° (*chloroplatinate*), is formed, and at 150°, a *substance*, m. p. 196°, probably a biuret derivative, $NH_2{\cdot}C_6H_3(OH){\cdot}CH(OH){\cdot}NH{\cdot}CO{\cdot}NH{\cdot}CO{\cdot}NH_2$. Treatment of the methylcarbonato-derivative of (I) with alcoholic ammonia gave condensation products of (I) and an amorphous *substance*, m. p. 238—240°. Attempts to prepare eight-membered rings of the type probably present in anhydrobis-2-amino-3-methoxybenzaldehyde, $C_{16}H_{16}O_3N_2$ (Troger and Sabewa; cf. Bamberger, this vol., 361), by condensing 2-amino-3-methoxybenzaldehyde with isatoic acid, anthranilic acid, or 2-amino-8-methoxyquinoline-3-carboxylic acid, were unsuccessful.

H. E. F. Notton.

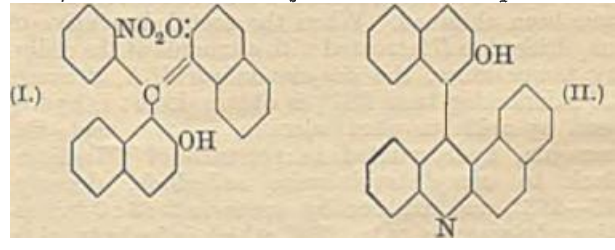
Unsymmetrical phenanthridones. II. Preparation of 7-nitrophenanthridone by Beckmann rearrangement of 2-nitrofluorenoneoxime. F. J. Moore and E. H. Huntress (J. Amer. Chem. Soc., 1927, 49, 2618—2624; cf. this vol., 665).—2-Nitrofluorenone and hydroxylamine hydrochloride in aqueous alcohol afford, in 75% yield, an *oxime*, m. p. 269—270° (decomp.), which appears to undergo partial rearrangement when heated with solvents. When boiled with a mixture of phosphorus pentachloride and phosphoryl chloride (which converts fluorenoneoxime into phenanthridone), it yields what is apparently a mixture of 2-*nitrofluorenone*-9-*iminochloride* with 9-*chloro*-7-*nitrophenanthridine*. When boiled with aqueous 50% sulphuric acid, this mixture affords a 90% yield of 7-nitrophenanthridone.

F. G. Willson.

Carbazine syntheses. III. H. Goldstein and M. de Simo (Helv. Chim. Acta, 1927, **10**, 607—610).—Methyl 4 : 3′-diaminodiphenylamine-2-carboxylate and magnesium phenyl bromide (cf. A., 1926, 1151; this vol., 575) give 2 : 7-*diamino*-5 : 5-*diphenyldihydroacridine* (*diacetyl* derivative, decomp. 295°). The *dihydrochloride* of this is oxidised by ferric chloride to 2-*amino*-5 : 5-*diphenyldihydroacridine*-7-*immonium chloride*, from which the bluish-violet *imide base*, decomp. above 300°, is liberated by ammonia. Similarly, methyl 4-diethylaminodiphenylamine-2-carboxylate yields 3-*diethylamino*-5 : 5-*diphenyldihydroacridine* [*hydrochloride*, m. p. 245° (decomp.)], which is oxidised to 5 : 5-*diphenyldihydroacridine*-3-*diethylimmonium chloride* (orange *perchlorate*, decomp. 114°). 3-*Amino*-7-*diethylamino*-5 : 5-*diphenyldihydroacridine* (*dihydrochloride*, *monoacetyl* derivative, m. p. 209°), from methyl 4-amino-4′-diethylaminodiphenylamine-2-carboxylate (this vol., 1186), is oxidised by ferric chloride to green 3-*diethylamino*-5 : 5-*diphenyldihydroacridine*-7-*immonium chloride*, from which the violet *imide base*, m. p. 325°, blackening at 81°, is prepared.

H. E. F. Notton.

***o*-Nitrobenzylidene-di-β-naphthol [*o*-nitrophenyldi-(2-hydroxy-α-naphthyl)methane].** O. Dischendorfer (Monatsh., 1927, **48**, 543—557). The yield of *o*-nitrophenyldi-(2-hydroxy-α-naphthyl)-methane [*diacetate*, m. p. 196—197°; *dibenzoate*, m. p. 213—214°; *dimethyl ether*, m. p. 191° (decomp.)] prepared by Zenoni's method (A., 1894, i, 136) is increased to 85% by the use of a larger amount of sulphuric acid and by avoiding rise in temperature during condensation, ring closure during crystallisation being prevented by using as a solvent boiling acetic acid containing a little sodium acetate. On oxidation in alcoholic solution with bromine and alkali at the ordinary temperature it yields *dehydro-o-nitrophenyldi*-(2-*hydroxy*-α-*naphthyl*)*methane* (I), m. p. 206° [*oxime*, m. p. 197° (decomp.): *dinitro*-derivative, m. p. 295° (decomp.)]. On reduction with zinc and acetic acid in benzene solution it yields a hydroacridine derivative which during purification is converted into 12-(2-*hydroxy*-α-*naphthyl*)-β-*phennaphthacridine* (II), m. p. 352° (decomp.) (*acetate*, m. p. 194°). The action of hydrochloric or sulphuric acid



on a boiling acetic acid solution of *o*-nitrophenyldi-(2-hydroxy-α-naphthyl)methane yields *ms-o*-nitrophenyldinaphthaxanthen (Zenoni, *loc. cit.*), which is best prepared by the direct action of concentrated sulphuric acid on a solution of *o*-nitrobenzaldehyde and β-naphthol in acetic acid at 100°. This compound when heated with concentrated sulphuric acid at 100° for 0·5 hr. is converted into ms-*o*-*nitrophenyldinaphthaxanthhydrol*, m. p. 235° (decomp.) [*pyrylium chloride hydrochloride*, m. p. 310°; *mercurichloride*, m. p. 268° (decomp.); *perbromide*; *perchlorate*, m. p. 308° (decomp.); *ethyl ether*, m. p. 255—256° (decomp.); *methyl ether*, m. p. 260°], which is better prepared by the decomposition of the pyran *ferrichloride*, m. p.

chloride, m. p. 51° (cf. Erdmann and Huth, A., 1898, i, 35); *NN'*-diphenyl-*N*-benzylcarbamide, m. p. 85° (cf. Mailhe, A., 1919, i, 395); *phenylbenzylcarbamyl azide*; 1-benzylbenzpyrazolone (Milrath, A., 1908, i, 1014); *phenyl-α-naphthylcarbamyl chloride*, m. p. 102°, b. p. 245—250°/18 mm., and *azide*, m. p. 79°; 1-*phenyl*-6 : 7-*benzobenzpyrazolone* [1-*phenyl*-αβ-*naphthpyrazolone*], m. p. 267°; *phenyl*-β-*naphthylcarbamyl azide*; 1-*phenyl*-4 : 5(?5 : 6)-*benzobenzpyrazolone* [1-*phenylnaphthpyrazolone*], m. p. 234°; *di*-β-*naphthylcarbamyl azide*, m. p. 124° (decomp.); 1-β-*naphthyl*-4 : 5(?5 : 6)-*benzobenzpyrazolone* [1-β-*naphthylnaphthpyrazolone*], m. p. 254°. From di-*p*-tolylcarbamyl chloride are prepared as-*di*-p-*tolylcarbamide*, m. p. 163°, and *di*-p-*tolylcarbamyl azide*, which is converted in boiling xylene into 1-p-*tolyl*-5-*methylbenzpyrazolone*, m. p. 202°, together with *bis*-as-*carbonyldi*-p-*tolylhydrazine*, $[(C_6H_4Me)_2N{\cdot}N{:}CO]_2$, m. p. 202°. α-*Naphthylethylcarbamyl azide*, m. p. 100°, from α-*naphthylethylcarbamyl chloride*, m. p. 73°, gives in boiling xylene a mixture of 1-*ethyl*-6 : 7-*benzobenzpyrazolone* [1-*ethyl*-αβ-*naphthpyrazolone*], m. p. 195°, and s-*di*-α-*naphthyldiethylcarbazide*, $(C_{10}H_7{\cdot}NEt{\cdot}NH)_2CO$, m. p. 212°. *Dimethylcarbamyl azide*, b. p. 59°/15 mm., is similarly decomposed into a product which yields ammonia, dimethylamine, and *as*-dimethylhydrazine on hydrolysis. *Diisobutylcarbamyl chloride*, b. p. 115°/15 mm., gives with aniline carbanilide, instead of the expected *N*-*phenyl*-*N'N'*-*diisobutylcarbamide*, m. p. 110°, and with sodium azide, *diisobutylcarbamyl azide*, b. p. 113—115°/15 mm., which is transformed in tetrahydronaphthalene at 180—190° into a *substance*, m. p. 81°. Similarly, *diisoamylcarbamyl azide*, b. p. 146—149°/15 mm., from the corresponding *chloride*, b. p. 136—140°/15 mm., gives a *substance*, (?)$C_{22}H_{47}O_2N_5$, m. p. 138°. Benzaldehydephenylhydrazone-*N*-carboxyl chloride (Busch and Walter, A., 1903, i, 522) and sodium azide in acetone yield the corresponding *azide*, m. p. 133° (decomp.), which decomposes in boiling xylene into cyanuric acid, an impure *substance*, m. p. 365°, a *substance*, (?)$C_{21}H_{16}ON_4$, m. p. 182°, and a *substance*, $C_{14}H_{11}ON_3$, m. p. 229°, which may be 1-benzylideneaminobenzpyrazolone or 4-hydroxy-2 : 5-diphenyl-1 : 2 : 5-triazole; whilst the *azide*, m. p. 160°, of *o*-chlorobenzaldehydephenylhydrazone-*N*-carboxylic acid [*methyl* ester, m. p. 159°; *acid chloride*, m. p. 86°; *anilide* (*o-chlorobenzaldehyde*-2 : 4-*diphenylsemicarbazone*), m. p. 209°] is similarly decomposed into cyanuric acid, a *substance*, m. p. 240°, and 1-*o*-*chlorobenzylideneaminobenzpyrazolone* (?4-*hydroxy*-2-*phenyl*-5-*o*-*chlorophenyl*-1 : 2 : 5-*triazole*), m. p. 193°.

H. E. F. Notton.

Manufacture of *cyclo*trimethylenearylpyrazolones. C. Mannich.—See B., 1927, 869.

4-Hydroxypyrazoles and their tautomerism. A. Bertho and H. Nussel (Annalen, 1927, 457, 278—307).—A series of 4-hydroxypyrazoles has been synthesised by the condensation of ethyl diazoacetate with malonic esters, and the amount of enol form in each product determined. The results show that the 4-hydroxypyrazoles exist in solution as an equilibrium of keto- and enol tautomerides, the amount of each depending on the substituents present.

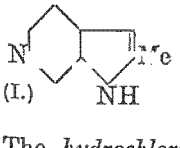
Ethyl diazoacetate and ethyl malonate condense below 0° in presence of sodium ethoxide to give *ethyl* 4-*hydroxypyrazole*-3 : 5-*dicarboxylate*, m. p. 151°, which with silver nitrate yields the *silver* salt of the dicarboxylic acid. The ester is converted by hot hydrochloric acid into 4-hydroxypyrazole-5-carboxylic acid, m. p. 204°, which when heated gives 4-hydroxypyrazole. By using sodium methoxide in the condensation, or by heating the ethyl ester with sodium methoxide, the *methyl* ester, m. p. 232°, is obtained. *Ethyl* 4-*hydroxy*-3-*benzylpyrazole*-5-*carboxylate*, m. p. 169°, results directly from the condensation of ethyl diazoacetate with ethyl benzylmalonate, and is converted into 4-*hydroxy*-3-*benzylpyrazole*-5-*carboxylic acid*, m. p. 183·5° (decomp.), and 4-*hydroxy*-3-*benzylpyrazole*. From ethyl *iso*amylmalonate are similarly prepared *ethyl* 4-*hydroxy*-3-iso*amylpyrazole*-5-*carboxylate*, m. p. 115° [free *acid*, m. p. 186° (decomp.)], and 4-*hydroxy*-3-iso*amylpyrazole*, m. p. 85°. *Ethyl* 4-*hydroxy*-3-*phenylpyrazole*-5-*carboxylate*, m. p. 162°, is obtained in only minute quantities from ethyl phenylmalonate, the main product being phenylacetic acid. Ethyl diazoacetate condenses with ethyl cyanoacetate in presence of sodium ethoxide to form *ethyl* 4-*aminopyrazole*-3 : 5-*dicarboxylate*, m. p. 144°, which by diazotisation and coupling with α-naphthol gives a red *dye*, decomp. 210°. 4-*Aminopyrazole*-5-*carboxylic acid*, m. p. 212·5° (decomp.), may also be diazotised and coupled with α-naphthol; it is converted at 220° into 4-aminopyrazole (picrate, m. p. 195—196°).

All the 4-hydroxypyrazoles above mentioned give an enol colour reaction with ferric chloride, and silver salts with silver nitrate. The ferric chloride coloration is deeper with the acids than with the esters, and least intense with the pyrazoles themselves. The enol reaction depends also on the solvent, being most intense in water and decreasing in the order: ethyl alcohol, methyl alcohol, acetone, ether, chloroform, benzene. Ethyl 4-hydroxypyrazole-3 : 5-dicarboxylate is 91·7% enolised in water, but only 3·5% in ethyl alcohol (indirect bromine titrations by K. Meyer's method). A variety of methods of determining the extent of enolisation is examined. C. Hollins.

Internally complex salts of 2 : 2'-pyridylpyrrole and picolinamide. B. Emmert and F. Brandl (Ber., 1927, 60, [*B*], 2211—2216).—1 : 2'-Pyridylpyrrole is prepared by the action of potassium pyrrole on 2-chloropyridine in benzene at 160° and becomes isomerised when its vapour is superheated into 2 : 2'-pyridylpyrrole (cf. Tschitschibabin and Bylinkin, A., 1923, i, 954; Wibaut and Dingemanse, *ibid.*, 1232). The latter compound is converted by tetramminecopper sulphate or copper acetate in aqueous alcohol or by copper powder at 145° into the complex *copper* salt, $C_{18}H_{14}N_4Cu$, m. p. 149—150°. The corresponding *zinc* compound, $C_{18}H_{14}N_4Zn$, m. p. about 260° (decomp.), is prepared from 2 : 2'-pyridylpyrrole and zinc powder or zinc oxide in boiling naphthalene. The *iron* salt, $C_{27}H_{21}N_6Fe$, is obtained by the use of iron powder and boiling naphthalene or ferric chloride in alcoholic solution. The *cobalt* derivative, $C_{27}H_{12}N_6Co$, is prepared from pyridylpyrrole and cobaltic oxide in boiling naphthalene. Like the chlorophyll derivatives, the metallic com-

pounds of pyridylpyrrole are very stable towards alcoholic alkali. Alcoholic solutions of the zinc and copper compounds are rapidly decomposed by acids which affect the iron compound more slowly. The zinc salt is unstable towards water. In the salts the pyrrole hydrogen atom is replaced by metal as shown by the evolution of hydrogen during the preparation, the formation when the metallic oxide is used, and the non-production when the hydrogen atom of the NH group is replaced by methyl. Similar complex salts might be expected from picolinamide, which contains a similar arrangement of the nitrogen atoms. The properties of the *copper* compound, $C_{12}H_{10}O_2N_4Cu$, differ so widely from those of the pyridylpyrrole complexes as to render its place in the series improbable. Internally complex salts of pyrrole-2-carboxylamide could not be prepared. H. WREN.

2-Methyl-3γ-pyrindole. E. KOENIGS and A. FULDE (Ber., 1927, **60**, [*B*], 2106—2111).—3-Nitro-4-hydroxypyridine, m. p. 280—281°, free from the corresponding dinitro-derivative, is prepared by a modification of the method of Koenigs and Freter (A., 1924, i, 990) and converted by phosphorus pentachloride into 4-chloro-3-nitropyridine (unstable *hydrochloride*, m. p. 156°). The 4-chloro-atom is so labile that the base cannot be obtained from the hydrochloride by treatment with sodium ethoxide, which affords unchanged material and 3-nitro-4-ethoxypyridine, m. p. 49—50°. Condensation of 4-chloro-3-nitropyridine hydrochloride with ethyl disodiomalonate in the presence of alcohol yields *ethyl* 3-*nitro*-4-*pyridylmalonate* (*sodium* salt, decomp. about 250° after darkening at 80°), which is transformed by boiling 20% hydrochloric acid into the very hygroscopic 3-*nitro*-4-*methylpyridine* (*hydrochloride*, m. p. 178°; *chloroplatinate*, m. p. 267°; *picrate*, m. p. 118°). Reduction of the nitro-compound with stannous chloride and hydrochloric acid or with ammonium sulphide gives 3-*amino*-4-*methylpyridine*, m. p. 106°, b. p. 254°/735 mm., in 80% yield; the hygroscopic *hydrochloride*, m. p. 180°, *chloroplatinate*, m. p. 227°, and *picrate*, m. p. 179—180°, are described. 4-*Acetamido*-4-*methylpyridine*, m. p. 84° (*picrate*, m. p. 194°), and 3-*benzamido*-4-*methylpyridine*, m. p. 81° (*chloroplatinate*, m. p. 240°; *picrate*, m. p. 164°), have been prepared. The acetyl compound is converted when heated with sodium ethoxide into 2-*methylpyrindole* (I), m. p. 183°, which is not alkaline or volatile with steam. It does not give the pine-shaving reaction or red coloration with nitrite in nitric acid solution. The *hydrochloride*, m. p. 225—226°, *chloroplatinate*, m. p. 221°, and *picrate*, m. p. 193°, are described.


(I.)

H. WREN.

Quinazolines. XXXVIII. Synthesis of some new analogues of cinchophen and intermediate products. M. T. BOGERT and E. M. MCCOLM (J. Amer. Chem. Soc., 1927, **49**, 2650—2654; cf. A., 1924, i, 1238).—2-o-*Nitrobenzamidoacetophenone* (I), m. p. 156°, and 2-m-*nitrobenzamidoacetophenone*, m. p. 170°, are obtained by the Schotten–Baumann reaction from o-aminoacetophenone. o-*Salicyloylamidoacetophenone*, m. p. 135°, is obtainable only by boiling *o*-aminoacetophenone with salicoyl chloride. Treatment of *o*-aminoacetophenone with *p*-acetoxybenzoyl chloride and alkali affords 2-p-*acetoxybenzamidoacetophenone*, m. p. 97·5°, which, when treated with cold aqueous 5% sodium hydroxide, or with ethyl alcohol and a trace of concentrated sulphuric acid, yields 2-p-*hydroxybenzamidoacetophenone*, m. p. 219°. Oxidation of (I) with alkaline permanganate affords o-*nitrobenzoylisatoic acid*, and this, when heated with alcoholic ammonia for 10 hrs. at 140°, yields 2-o-*nitrophenylquinazoline*-4-*carboxylic acid*, m. p. 235° (impure). *Salicyloylisatoic acid*, yellow, m. p. about 209—210° (decomp.), depending on the rate of heating, p-*hydroxybenzoylisatoic acid*, m. p. similar, 2-o-*hydroxyphenylquinazoline*-4-*carboxylic acid*, yellow, m. p. 171° (*ethyl* ester, yellow, m. p. 115°), and 2-p-*hydroxyphenylquinazoline*-4-*carboxylic acid*, yellow, m. p. 251° (*ethyl* ester, yellow, m. p. 159°), obtained analogously, are described. The *disodium* salt of 2-*o*-carboxyphenylquinazoline-4-carboxylic acid (cf. Bogert and Nabenhauer, A., 1924, i, 993) was prepared.

F. G. WILLSON.

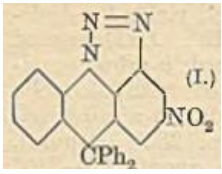
Comparison of heterocyclic systems with benzene. II. Reduction potentials of quinones containing the pyridine, iminazole, triazole, and thiophen rings. L. F. FIESER and L. A. AMES.—See this vol., 1198.

Condensation of nitrobenzene with *o*-phenylenediamine. G. B. CRIPPA and P. CASTELLI (Gazzetta, 1927, **57**, 621—625).—Whereas *p*-phenylenediamine condenses with nitrobenzene to give *p*-aminoazobenzene (this vol., 352), *o*-phenylenediamine gives under the same conditions 2-phenyl-4 : 5-benz-1 : 2 : 3-triazole in 10—15% yield, with *o*-aminoazobenzene. It is suggested that α-2-aminoazoxybenzene, $O{:}NPh.N{\cdot}C_6H_4{\cdot}NH_2$, is an intermediate product. E. W. WIGNALL.

Dicyanotriazole. J. A. FIALKOV (Bull. Soc. chim., 1927, [v], **41**, 1209—1217).—The tetrameride of hydrocyanic acid (Bedel, A., 1923, i, 190) on treatment with nitrous acid gives yellow dicyanotriazole, m. p. 145—150°, which is transformed by sublimination at 140°/20—30 mm. into a colourless *isomeride*. These two substances are strong acids comparable with the mineral acids and form *sodium* salts which may be converted into the original substance. Measurements of the conductivity of the isomerides and their sodium salts show that the colourless modifications have the lower values. It is suggested that the coloured form is 4 : 5-dicyano-1 : 2 : 3-triazole and the colourless, 4 : 5-dicyano-2 : 1 : 3-triazole. The weak acid, m. p. 214—215°, produced by hydrolysis of the yellow form, is probably 4-cyano-1 : 2 : 3-triazole-5-carboxylic acid. G. A. C. GOUGH.

Coloured derivatives of tetraphenylmethane. X. Derivatives of diphenylcarbazine. F. KEHRMANN and M. ROHR (Helv. Chim. Acta, 1927, **10**, 596—603).—When polynitrodiphenyldihydroacridines are partly reduced with alcoholic ammonium or potassium sulphide (A., 1926, 526), 1- and 9-nitro-groups are always attacked first. The constitutions of the resulting nitroamines are established by diazotisation and boiling with alcohol, when 1- or 9-amino-groups give stable yellow *peri*azimines, whilst those in other

positions are eliminated. The azimines are reduced by stannous chloride to amines. In this way 1 : 3-dinitro-5 : 5-diphenylcarbazine (1 : 3-dinitro-5 : 5-diphenyldihydroacridine, A., 1921, i, 600) is reduced to 3-*nitro*-1-*amino*-5 : 5-*diphenylcarbazine*, m. p. 269°, which is converted by nitrous acid into 3-*nitro*-1 : 10-*azimino*-5 : 5-*diphenylcarbazine* (I.), m. p. 216°. 1 : 7-Dinitro-5 : 5-diphenylcarbazine yields 7-*nitro*-1-*amino*-, m. p. 270° (decomp.), and 7-*nitro*-1 : 10-*azimino*-*diphenylcarbazine*, m. p. indef. 3-Nitro-7-aminodiphenylcarbazine is deaminated to 3-nitrodiphenylcarbazine. 3 : 7-Dinitro-1-amino-5 : 5-diphenylcarbazine, obtained together with a little 3 : 7 : 3′ : 7′-*tetranitro*-1 : 1′-*azodiphenylcarbazine* by reducing 1 : 3 : 7-trinitrodiphenylcarbazine, gives with nitrous acid and alcohol 3 : 7-*dinitro*-1 : 10-*azimino*-5 : 5-*diphenylcarbazine* (II), m. p. 300° (decomp.), whilst its reduction product, 7-*nitro*-1 : 3-*diaminodiphenylcarbazine*, decomp. 280°, gives the 7-nitro-1 : 10-azimino-derivative (above). Similarly, nitrous acid and alcohol convert 3 : 7-dinitro-1 : 9-diamino-5 : 5-diphenylcarbazine, m. p. 266° (not 180° as previously stated, A., 1926, 526), into the azimine (II), and 3 : 7-*dinitro*-1 : 9-*diamino*-5 : 5-*dinitrodiphenylcarbazine*, prepared from hexanitrodiphenylcarbazine (A., 1919, i, 551), into 3 : 7-*dinitro*-1 : 10-*azimino*-5 : 5-*dinitrodiphenylcarbazine* (explodes on heating), from which a blue *dye* is obtained by reduction and aerial oxidation.



(I.)

H. E. F. NOTTON.

Synthesis of β-*iso*coproporphyrin and of opsopyrrolecarboxylic acid. H. FISCHER and H. ANDERSAG (Annalen, 1927, **458**, 117—148).—Coproporphyrin (complex *copper* salt; *tetraethyl* ester, m. p. 225—226°) is conveniently separated from ethereal solutions of porphyrins (cf. A., 1926, 1261) by conversion into the *hydrochloride* (crystallographic data by STEINMETZ), from which colloidal solutions of coproporphyrin may be prepared. The residues from the synthesis of *iso*coproporphyrin (complex *copper* salt; *tetramethyl ester hæmin*, $C_{40}H_{44}O_8N_4ClFe$; *tetraethyl* ester, m. p. 258°) contain the isomeric β-*iso*coproporphyrin, isolated as the *tetramethyl* ester, m. p. 135° (complex *copper* salt, m. p. 177°; *hæmin*, $C_{40}H_{41}O_8N_4ClFe$), and traces of a substance with an absorption band at λ 645. The ester is hydrolysed by sodium hydroxide to amorphous β-iso*coproporphyrin* (? a mixture) (*tetraethyl* ester, m. p. 124°; complex *copper* salt). A second synthesis of *iso*coproporphyrin has been effected by brominating cryptopyrrolecarboxylic acid and heating the resulting *bis*-(5-*bromo*-4-*methyl*-3-β-*carboxyethyl*-2-*pyrryl*)*methene hydrobromide*, m. p. 200° (decomp.), with bis-(4 : 5-dimethyl-3-β-carboxyethyl-2-pyrryl)methene and succinic acid at 220°. Bromination of 5-carbethoxy-2 : 4-dimethyl-3-pyrrylpropionic acid (*loc. cit.*) affords a *substance*, m. p. 275°, as well as 5-carbethoxy-4-methyl-2-bromomethyl-3-pyrrylpropionic acid. The latter product is converted by potassium cyanide in aqueous alcohol into 5-*carbethoxy*-4-*methyl*-2-*cyanomethyl*-3-*pyrrylpropionic acid*, m. p. 176°, by aniline into 5-*carbethoxy*-4-*methyl*-2-*anilinomethyl*-3-*pyrrylpropionic acid*, m. p. 162°, and by oxidation with lead nitrate or chromic acid into 2-*aldehydo*-5-*carbethoxy*-4-*methyl*-3-*pyrrylpropionic acid*, m. p. 173°, which is hydrolysed by alcoholic potassium hydroxide to 2-*aldehydo*-5-*carboxy*-4-*methyl*-3-*pyrrylpropionic acid*, decomp. 230° with formation of porphyrin. The synthesis of opsopyrrolecarboxylic acid previously described (*loc. cit.*) has been confirmed. Ethyl 2 : 4-dimethylpyrrole-5-carboxylate condenses with ethyl cyanoformate in ether–chloroform in presence of hydrogen chloride, giving *ethyl* 5-*carbethoxy*-2 : 4-*dimethyl*-3-*pyrrylglyoxylate*, m. p. 127·5°. The methyl esters of copro-, *iso*copro-, and β-*iso*copro-porphyrin are reduced by hydrogen iodide in glacial acetic acid at 100°, giving in each case principally 2 : 3-dimethyl-β-4-pyrrylpropionic acid, identified as the methyl ester picrate (cf. A., 1914, i, 429); uroporphyrin octamethyl ester yields small quantities of the same product. These examples illustrate the tendency to the formation of 2 : 3-dimethylpyrroles in the reduction of pyrrylmethenes (cf. A., 1926, 962). The absorption spectra of the three coproporphyrins, their methyl esters, and of the "hæmins," "phyllins," and complex copper salts of the latter, also of the complex *iron* salt, $C_{40}H_{37}O_{16}N_4Fe$, of uroporphyrin, are tabulated. Evidence in favour of the view that the coproporphyrins differ only in the disposition of the double linkings is furnished by the identity of the absorption spectra of corresponding derivatives.

H. E. F. NOTTON.

Porphyrin syntheses. XI. Ætioxantho- and mesoxantho-porphinogens. H. FISCHER and A. TRIEBS (Annalen, 1927, **457**, 209—248; cf. this vol., 365, 469).—An attempt to obtain an analogue of dehydroindigo (Kalb, A., 1909, i, 966) from ætioporphyrin further confirms the rejection of the "indigoid" structure in favour of Küster's formula. Oxidation of ætioporphyrin in chloroform and acetic acid shaken with lead peroxide gives an intensely yellow compound, *ætioxanthoporphinogen*, $C_{32}H_{38}O_4N_4$, decomp. 318°, crystallising with $6H_2O$ or $3COMe_2$ [crystallographic data by STEINMETZ] (*sodium* and *potassium* salts, *hydrochloride*, and *hydrobromide* described; no metal complex salts, no perchlorate, no picrate). Bromine gives *perbromides* with 4Br and 8Br. The substance is very stable to hydriodic acid (probably owing to the sparing solubility of the *hydriodide*), to water at 220°, and to potassium methoxide at 220°. It does not react with phenylhydrazine, hydroxylamine, benzoyl chloride, acetyl chloride, methyl iodide, methyl sulphate, methyl-alcoholic hydrogen chloride, ethyl mercaptan, keten (at 15°), phosphorus tri- or pentachloride, thionyl chloride, hydrogen cyanide, or nitrous acid. Dry distillation at 320—350° (bath temperature) yields opsopyrrole. The substance is oxidised by ozone to oxalic acid and ammonia, the amount of the latter accounting for half the nitrogen (ætioporphyrin behaves similarly), and by lead peroxide in sulphuric acid, or by nitric acid, to methylethylmaleinimide. The four oxygen atoms of ætioxanthoporphinogen are removed by reduction with sodium amalgam in methyl alcohol and acetic acid, regenerating ætioporphyrin. Magnesium and acetic acid give the same result, but iron and aluminium in boiling acetic acid have no effect, whilst reduction with zinc dust and hot acetic acid removes only two oxygen atoms, forming a

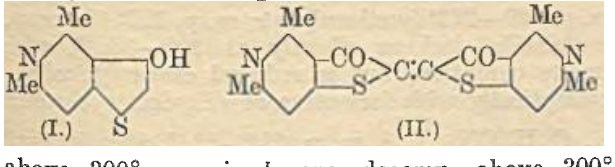
colourless, crystalline *compound*, $C_{32}H_{42}O_2N_4$, decomp. 297° (*hydrochloride*; no sodium salt), which is reduced by sodium amalgam to ætioporphyrin. It is suggested that ætioxanthoporphinogen contains two *N*-oxide groups and two tertiary carbinol groups.

When lead tetra-acetate is used in place of lead peroxide for the oxidation of ætioporphyrin, no xanthoporphinogen can be isolated, and the product is a *dichloroætioporphyrin*, m. p. 305° (Pregl block). A *monobromoætioporphyrin*, m. p. 392° (Pregl block), is isolated by fractionation of Fischer and Klarer's synthetic ætioporphyrin (A., 1926, 962). An analytical method for following the course of bromination of ætioporphyrin and of cryptopyrrole is described.

Oxidation of mesoporphyrin dimethyl ester with lead peroxide in chloroform and acetic acid gives *mesoxanthoporphinogen dimethyl* ester, $C_{36}H_{42}O_8N_4$, which regenerates the same porphyrin ester on reduction with sodium amalgam. The absence of isomerides from the reduction products of both the xanthoporphinogens has an important bearing on the question of constitution. Xanthoporphinogens have also been obtained from coproporphyrin ester and tetramethyltetrapropylporphin.

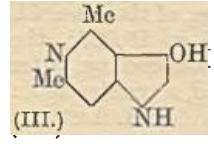
[With P. HALBIG and B. WALACH.]—*Ethyl 2-dibromomethyl-4-hydroxymethylpyrrole-3 : 5-dicarboxylate*, m. p. 130—131°, obtained from the 2 : 4-dimethyl ester using bromine and sodium bromate in acetic acid, gives with phenylhydrazine and hydrazine a bromine-free *phenylhydrazone*, m. p. 199°, and *hydrazone*, m. p. 143°, respectively. Reduction with zinc and acetic acid removes bromine, forming *ethyl 2-methyl-4-hydroxymethylpyrrole-3 : 5-dicarboxylate*, m. p. 132° (*acetate*, m. p. 40°), which is also obtained when ethyl 2 : 4-dimethylpyrrole-3 : 5-dicarboxylate is oxidised with chromic–acetic acid. The compound shows only one reactive hydrogen atom when treated with magnesium methyl iodide. Ætioxanthoporphinogen has according to the same criterion only the same number of active hydrogen atoms as ætioporphyrin. C. HOLLINS.

New "thiopyrindigotin" and a pyrindoxyl. E. KOENIGS and H. KANTROWITZ (Ber., 1927, 60, [*B*], 2097—2105).—Ethyl 4-chloro-2 : 6-dimethylpyridine-3-carboxylate is hydrolysed by a slight excess of dilute aqueous-alcoholic potassium hydroxide at 130° and the resulting solution is treated with potassium hydrogen sulphide at 160—170°, whereby 4-thiol-2 : 6-dimethylpyridine-3-carboxylic acid, m. p. 235°, is obtained in good yield. It is transformed by sodium hydroxide and chloroacetic acid into 3-*carboxy*-2 : 6-*dimethylpyridyl*-4-*thiolacetic acid*, $CO_2H{\cdot}C_5NHMe_2{\cdot}S{\cdot}CH_2{\cdot}CO_2H$, m. p. 247° (*hydrochloride*, m. p. 221°), which, with acetic anhydride, affords 3-*hydroxy*-4 : 6-*dimethylpyridothiophen* (I), m. p. 49° (*hydrochloride*, m. p. 94°; *chloroplatinate*, decomp.



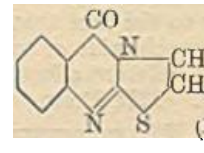
above 300°; *semicarbazone*, decomp. above 300°; *compound*, $C_{16}H_{15}ON_3S$, m. p. 98°, obtained by coupling with diazotised *p*-toluidine). Oxidation of the thiophen derivative in alkaline solution at 70° in the presence of spongy platinum affords "4 : 6 : 4′ : 6′-*tetramethylthiopyrindigotin*" (II) (unstable *hydrochloride*; *chloroplatinate*, decomp. above 300°), which can be reduced by alkaline hyposulphite or tin and hydrochloric acid and dyes cotton a dull pink. The "thiopyrindigotin" is more readily prepared by the action of concentrated sulphuric acid at 210—215° on 3-carboxy-2 : 6-dimethylpyridyl-4-thiolacetic acid (cf. Plazek and Sucharda, A., 1926, 1263).

Ethyl 4-chloro-2 : 6-dimethylpyridine-3-carboxylate is converted by aminoacetonitrile at 150° into the *anhydride* of 3-*carboxy*-2 : 6-*dimethyl*-4-*pyridylaminoacetic acid*, m. p. 100—101° (*hydrochloride*, m. p. 221°); the corresponding *acid*, m. p. 184°, and its *hydrochloride*, m. p. 282°, are described. Acetic anhydride transforms the acid or its anhydride into 4 : 6-*dimethylpyrindoxyl* (III), m. p. 67°, in moderate yield; the *hydrochloride*, m. p. 243°, *chloroplatinate*, decomp. above 300°, *semicarbazone*, m. p. 63°, and *p-toluenesazo*-derivative, m. p. 92°, are described. Attempts to oxidise it to the corresponding "pyrindigotin" were unsuccessful. H. WREN.



Dioximes. XLV. I. DE PAOLINI (Gazzetta, 1927, **57**, 656—660).—3 : 4-Dibenzoyl-1 : 2 : 5-furazan, prepared by Angeli (A., 1893, i, 355) by the action of alcohol on dibenzoylglyoxime, is better obtained from the peroxide of the latter by the action of stannous chloride. When treated with sodium hydroxide it yields oximinobenzoylacetonitrile; the action of nitrogen tetroxide on dibenzoylfurazandioxime, m. p. 180°, yields the *peroxide* of the latter, m. p. 171—172° (decomp.). Similarly, 3 : 4-*di-p-toluoyl*-1 : 2 : 5-*furazan*, m. p. 128—129°, is obtained from di-*p*-toluoylglyoxime peroxide; it yields a *dioxime*, m. p. 181—182° (decomp.), a *diphenylhydrazone*, m. p. 200—201° (decomp.), and, by the action of sodium hydroxide, oximino-*p*-toluoylacetonitrile, m. p. 137° (cf. Lublin, A., 1907, i, 213). E. W. WIGNALL.

Condensation of anthranilic acid with allylthiocarbimide. G. ROSSI (Gazzetta, 1927, **57**, 625—632).—Pawlewski (A., 1906, i, 542) considered the product, m. p. 208—210° (I), of the interaction of anthranilic acid with allylthiocarbimide to be 4-keto-2-thion-1-allyltetrahydroquinazoline, since it was not identical with the 3-allyl compound; when treated with alkaline hydrogen peroxide it gave a product, m. p. 187—189°, (II), regarded as the 2 : 4-diketo-compound. The migration which the formulation of (I) involves is improbable; also the substance $C_{18}H_{15}O_3N_3$, m. p. 211—212°, (III), obtained by the same reaction and wrongly regarded (Rossi, A., 1914, i, 1169; Gazzetta, 1914, **44**, [2], 267) as the dianilide of 3-nitrophthalic acid, would on Pawlewski's scheme be 2-*o*-carboxyanilo-4-keto-1-allyltetrahydroquinazoline, but it contains no carboxyl group. Hydrolysis of (III) by hydrochloric acid yields (II), with a *substance*, $C_{11}H_{12}O_3N_2$, m. p. 180°; hydrolysis by potassium hydroxide solution yields a product $C_{11}H_{10}O_2N_2$, of which part has m. p.



172—174°, and the residue m. p. 194—198°. It is suggested that (I) has the structure formulated.
E. W. WIGNALL.

Volatile alkaloid of pepper. A. PICTET and R. PICTET (Helv. Chim. Acta, 1927, **10**, 593—595).—The alkaloid, C_5H_9N (*hydrochloride*, $[\alpha]_D$ +2·77°; *picrate*, m. p. 165°), obtained by steam-distilling black pepper (A., 1907, i, 954) gives an oily nitroso-derivative, and is reduced by tin and hydrochloric acid to racemic 3-methylpyrrolidine. It is therefore 3-methylpyrroline. H. E. F. NOTTON.

Microchemical reactions of papaverine. M. WAGENAAR (Pharm. Weekblad, 1927, **64**, 1085—1089).—The precipitation of the alkaloid, methods of obtaining it crystalline, and the effect on it of the commoner alkaloid reagents are described. The mercuric iodide test is the most sensitive, a precipitate being obtained with as little as 0·1 mg. of the alkaloid, and in concentrations as low as 1 in 10,000; the precipitate is microcrystalline, but on cooling, after warming with dilute hydrochloric acid, separates again in characteristic four-sided crystals. S. I. LEVY.

Constitution of yohimbine. E. WINTERSTEIN and M. WALTER (Helv. Chim. Acta, 1917, **10**, 577—584).—Yohimbine is decomposed by soda-lime at 250° (cf. Barger and Field, J.C.S., 1915, **107**, 1025) giving a dimethylindole, m. p. 55°, identical with that obtained by Warnat (this vol., 681) from yohimboaic acid, and a mixture of bases. Rapid distillation of small portions of yohimbine with zinc dust yields the same dimethylindole, whilst the following bases are separated as picrates after fractional distillation: (*a*) *iso*quinoline, (*b*) a base, $C_{13}H_{12}N_2$ (picrate, m. p. 268—270°; cf. Warnat, *loc. cit.*), and (*c*) a *base*, $C_{12}H_{10}N_2$ (*picrate*, m. p. 240—250°), probably formed from (*b*) by loss of a methyl group. The base (*b*) is identical in composition with the supposed dimethylquinoline of Barger and Field and is regarded as the dimethyl derivative of a condensed pyrrole-*iso*quinoline nucleus. The same fission products are obtained in high yield when yohimbine hydrochloride is distilled with 2·5 mols. of alkali in superheated steam at 300°.
H. E. F. NOTTON.

Behaviour of ψ-cocaine hydrogen *d*-tartrate and of cocaine hydrochloride towards reagents. M. FERRARIS (Boll. Chim. Farm., 1927, **66**, 577—580).—Towards the ordinary alkaloid reagents, psicaine and cocaine hydrochloride usually react similarly, but with mercuric chloride the former gives no precipitate and the latter a white precipitate. With silver nitrate a similar difference is observed. Cocaine, but not psicaine, blackens when triturated with mercurous chloride. When 0·01 g. of cocaine is heated with 2 drops of alcohol and a little powdered potassium hydroxide, the odour of ethyl benzoate is observed, whereas similar treatment of psicaine gives only a feeble and transitory aromatic odour. Certain other differences exist between the reactions of the two compounds, these being due mostly to the fact that one is a tartrate and the other a hydrochloride or to those conditions which determine the different effects of the two molecules on polarised light. T. H. POPE.

Amine-oxides of alkaloids. II. M. POLONOVSKI and M. POLONOVSKI (Bull. Soc. chim., 1927, [iv], **41**, 1186—1190).—*N*-Methylgranatoline, obtained by the reduction of ψ-pelletierine (Tanret, A., 1923, i, 832), reacts with hydrogen peroxide (30%) at the ordinary temperature to give *N-methylgranatoline oxide*, m. p. 218° (*hydrochloride*, m. p. 210°; *picrate*, m. p. 254°), which may be reduced to the parent substance by sulphur dioxide. Tropinone, best prepared by the oxidation of tropinal in concentrated sulphuric acid solution with potassium dichromate at 0°, yields similarly *tropinone oxide*, m. p. 98° (*hydrochloride*, m. p. 193°; *picrate*, m. p. 210°; *chloroaurate*, m. p. 176—177°). Hydrogen peroxide reacts vigorously with an acetone solution of scopoline to give *scopoline oxide*, m. p. 123° [decomp. 129°; *compound* containing water and hydrogen peroxide of crystallisation, $4C_8H_{13}O_3N,3H_2O_2,3H_2O$ (stable at 100°; decomposed by crystallisation from alcohol), m. p. 110—120°; *hydrochoride*, 175°; *hydrobromide*, m. p. 180—181° (decomp.); *picrate*, m. p. 200° (decomp.)]. Emetine yields amorphous *emetine oxide*, softening at 115°, $[\alpha]_D$ +44·3° in 95% alcohol (*c*=2·5).
G. A. C. GOUGH.

Amine-oxides of alkaloids. III. Action of acid chlorides and anhydrides. Preparation of nor-bases. M. POLONOVSKI and M. POLONOVSKI (Bull. Soc. chim., 1927, [iv], **41**, 1190—1208).—The action of acetyl chloride or of acetic anhydride on the oxides of bases containing an *N*-methyl group results in the elimination of that group as formaldehyde with the formation of the corresponding nor-base. Benzoic anhydride reacts similarly in some cases. The oxide is liable to suffer complete decomposition unless dry materials are used and unless the vigorous reaction is controlled at the first stage. The reaction is completed by heating at 100° for 3 or 4 hrs. In this way the following compounds are prepared: acetylnortropidine (an oil); nortropidine (an oil; chloroaurate, m. p. 187°); acetylnortropinone (an oil); nortropinone (*hydrochloride*, m. p. 201°; *chloroaurate*, m. p. 168°); diacetylnortropanol (an oil); *N*-acetylnortropanol, m. p. 124°; nortropanol (hydrochloride, m. p. 285°; chloroaurate, m. p. 211°; chloroplatinate, m. p. 248—249°); *N*-acetylnor*apo*atropine, m. p. 113—114° [hydrochloride, 140° (darkening at 115°)]; diacetylnorhyoscyamine (*l-O*-acetyltropyl-*N*-acetylnortropanol); *N*-acetylnorscopolamine, m. p. 130°, $[\alpha]_D$ −25° in alcohol; *diacetylgranatoline*, m. p. 80°; *N*-acetylgranatoline, m. p. 120°; N-*acetylnornicotine* (an oil), $[\alpha]_D$ −13·6° in benzene. G. A. C. GOUGH.

Strychnine and brucine. VI. Catalytic hydrogenation of strychnine and some derivatives. A. E. OXFORD, W. H. PERKIN, jun., and R. ROBINSON (J.C.S., 1927, 2389—2410).—The double linking of strychnine is reduced by hydrogen and palladous chloride, giving *dihydrostrychnine*, $C_{20}H_{24}ON\leqslant^{CO}$, m. p. 220—222° [*methosulphate*, m. p. 322° (decomp.); *methiodide*, darkens slightly at 300—330°], which resists oxidation, but is reduced electrolytically or catalytically with formation of dihydrostrychnidine-*A*, $C_{20}H_{24}ON\leqslant^{CH_2}$, m. p. 212—214°, identical with "methyl-ψ-dihydrostrychnidine, $C_{22}H_{28}ON_2$, m. p. 212°," described by Clemo, Perkin, and Robinson

(this vol., 888) [dimethiodide, m. p. 285—290° decomp.), and dimethochloride are identical with methyl*neo*dihydrostrychnidinium iodide and chloride espectively (*loc. cit.*)], and *hexahydrostrychnine*, $_{20}H_{21}ON(CH_2{\cdot}OH){:}NH$, m. p. 197—199° (*nitroso-* nd *diacetyl* derivatives), also obtainable by catalytic reduction of tetrahydrostrychnine. Skita and Franck's "dihydrostrychnine," m. p. 209—210° (A., 1911, i, 1017), on the other hand, is stated to yield tetrahydrostrychnine, *i.e.*, $_{20}H_{22}ON(CH_2{\cdot}OH){:}NH$, by catalytic reduction. When dihydrostrychnidine methochloride is heated with methyl-alcoholic potassium hydroxide at 130° here are formed methoxymethyltetrahydrostrychnidine (cf. Clemo, Perkin, and Robinson, *loc. cit.*) and *ethyldihydrostrychnidine* A, m. p. 178—180°.

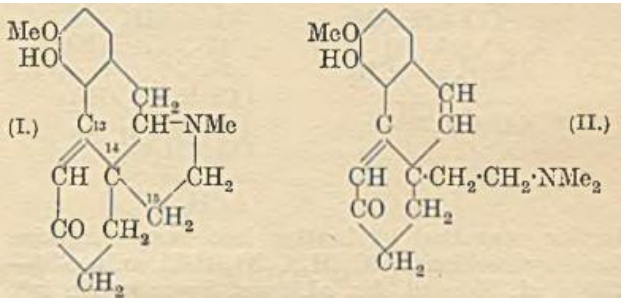
*iso*Strychnine, m. p. 220°, yields an O-*acetyl* derivative, m. p. 133—134°, but no semicarbazone (cf. liveri-Mandala and Comella, A., 1923, i, 1224) or phenylhydrazone was obtained. Catalytic reduction converts *iso*strychnine into *dihydroisostrychnine*, m. p. 244—246° (+3H_2O) or 249—251° (anhyd.) [*methosulphate*; *methiodide*, m. p. 320° (decomp.); O-*acetate*, m. p. 202—204°], obtained from dihydrostrychnine by heating with water at 165—185° or with methyl-alcoholic ammonia; it is prepared more easily by dissolving dihydrostrychnine in hot alcoholic sodium ethoxide and keeping the solution at 44—46° for 6 hrs. The strychnine–*iso*strychnine isomerism is thus proved to be independent of the double linking, which need not even be present. The isomerisation is possibly due to internal condensation between a ketonic carbonyl group and hydrogen atom adjacent to the ·CO·N: group. *iso*Strychnic acid, m. p. 231° decomp.), is not reduced by hydrogen and palladium, and it is therefore probable that the mol. of water it contains is constitutionally bound.

Electrolytic reduction of *iso*strychnine gives *isostrychnidine*, $C_{21}H_{24}ON_2$, m. p. 155—157° (+1·5H_2O) or 163—168° (+0·25H_2O) [*methosulphate*, m. p. 200—205° (decomp.)], which by the action of hydrogen and palladium yields *dihydroisostrychnidine*-b, $_{21}H_{26}ON_2$, m. p. 151—153°, isomeric with *dihydroisostrychnidine*-a, m. p. 191—192° (+0·5H_2O), obtained by electrolytic reduction of dihydro*iso*strychnine.

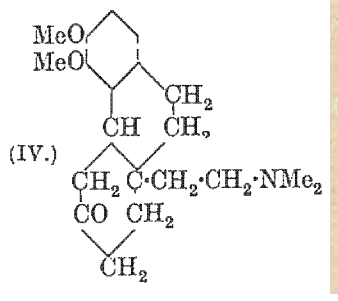
Strychnidine gives no *iso*strychnidine when heated with water, the product being *dioxyhydroxydihydrostrychnidine*, $C_{21}H_{26}O_4N_2$, m. p. 260° (decomp.; +4H_2O). *Dioxyhydroxyhexahydrostrychnine*, $_{21}H_{28}O_5N_2$, has m. p. 201—203° (+2H_2O). Strychnidine couples with diazotised sulphanilic acid to form azo-*compound*, from which by reduction with stannous chloride p-*aminostrychnidine*, decomp. above 330°, is obtained. This amine is diazotisable and gives azo-*dyes* with β-naphthol, H-acid, and J-acid. *p-Sulphobenzeneazomethylstrychnine* is described.

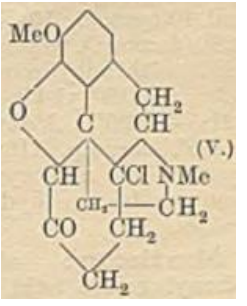
Benzoylation converts strychnic acid into a *mixed anhydride*, m. p. 215—218°. C. HOLLINS.

Acid transformations of morphine alkaloids; constitution of thebainone. C. SCHOPF and F. BORKOWSKY (Annalen, 1927, **458**, 148—174).—Solutions of thebaine and of thebainone in concentrated hydrochloric acid (cf. Howard, A., 1884, 1201) probably contain products of similar constitution, since they have practically the same absorption spectrum. Thebainone and hydroxylamine give, in addition to the oxime, an additive *compound* (also +H_2O), m. p. 173—174°. The isolation from the product of hydrogenation of thebaine with palladium–calcium carbonate (cf. this vol., 472) of *dihydroepithebainoneoxime*, m. p. 228°, $[\alpha]_D^{20}$ −115·8° (the term epi- being used to denote stereoisomerism about C^{14}), which is isomeric but not identical with dihydrothebainoneoxime, $[\alpha]_D^{18}$ +6·6°, and with *thebainoloxime*, m. p. 217—218°, $[\alpha]_D^{18}$ +104·2°, renders the presence of a C^{15}—C^{13} linking in thebainone (Gulland and Robinson, J.C.S., 1923, **123**, 998) impossible. The following facts are adduced in favour of formula (I) for the-



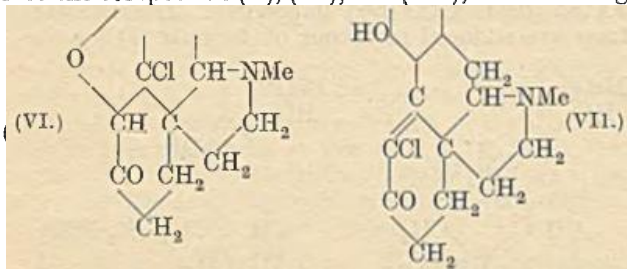
bainone: (*a*) the absence of halochromy in acid solution of hydroxythebainone (Speyer, A., 1923, i, 127), (*b*) the impossibility of hydrogenating the double linking in thebainone, (*c*) the morphol degradation of thebainonemethine derivatives (cf. Knorr and Pschorr, A., 1905, i, 814, 920, 922), and (*d*) the impossibility of displacing the double linking in thebainonemethines into the $\Delta^{13(14)}$-position. Thus, *thebainonemethine* (II), m. p. 170—171° (*methiodide*, m. p. 252°; *oxime*, m. p. 210—211°), prepared from thebainone methiodide and aqueous sodium hydroxide is not isomerised by alkali or dilute acids; it is resinified by concentrated acid. It is hydrogenated to *dihydrothebainonemethine* (*hydriodide*, m. p. 258—259°). Attempts to confirm formula (I) by the preparation of stereoisomeric forms of dihydromethylthebainolmethine were unsuccessful. Methylthebainonemethine (III) is hydrogenated in presence of colloidal palladium to *dihydromethylthebainonemethine* (*methiodide*, m. p. 154—155°), which is reduced by sodium amalgam and alcohol to *dihydromethylthebainolmethine* (IV), oily (*methiodide*, m. p. 115—116°;





methoperchlorate, m. p. 227—228°, $[\alpha]_D^{18}$ 40·7 or −46·6°). The same substance (IV) is obtained by hydrogenating *methylthebainolmethine* (*perchlorate*, m. p. 193—194°), which is prepared by reducing (III)

with sodium amalgam and water, or by treating *methylthebainol methiodide*, m. p. 260° (cf. Hoek, Diss., Munich, 1926), with alkali. (II) is reduced by sodium amalgam to *thebainolmethine*, m. p. 173—174°, which is readily hydrogenated in 10% acetic acid to *dihydrothebainolmethine*, m. p. 119—121°. Methylation of this last by Rodionov's method (A., 1926, 532) again yields the base (IV) (not identical with dihydromethyldihydrothebainonemethine; Cahn, A., 1926, 1264), identified as the methoperchlorate. Accordingly, thebaine is assumed to be transformed successively, on dissolution in cold concentrated hydrochloric acid, into the compounds (V), (VI), and (VII), the last being



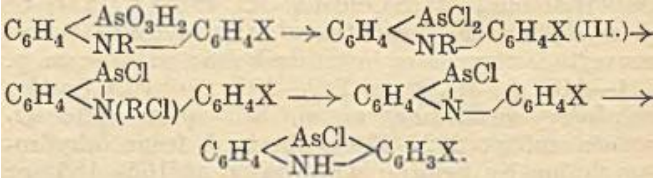
further converted by heating into morphothebaine [acid hydrochloride, $(C_{18}H_{19}O_3N)_2,3HCl$, m. p. 254—255°; cf. Howard, *loc. cit.*], and by reduction into thebainone. The transformations of codeinone into morphothebaine (cf. Cahn and Robinson, A., 1926, 745), of morphine into *apo*morphine, and of codeinone or thebaine into thebenine are explained along similar lines. The nomenclature of thebaine and thebainone derivatives is discussed. H. E. F. Notton.

Microchemical identification of morphine. M. Wagenaar (Pharm. Weekblad, 1927, **64**, 1119—1122).—A summary of the reactions suitable for the microchemical identification of the alkaloid, together with complete references to the literature, is given. The most delicate are those with mercuric bromide and iodide, which are positive at concentrations of 1 in 10,000. S. I. Levy.

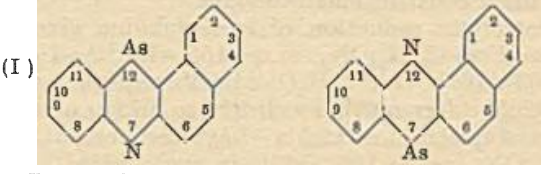
Organic arsenic compounds. Some cyanides and dicyanides. E. Grischkievitch-Trochimovski, L. Mateyak, and Zablotski (Bull. Soc. chim., 1927, [iv], **41**, 1323—1333).—Silver cyanide converts phenyldichloroarsine, α-naphthyldichloroarsine, and 10-chloro-5 : 10-dihydrophenarsazine, in benzene or toluene, into *phenyldicyanoarsine*, m. p. 78·5—79·5°, *α-naphthyldicyanoarsine*, m. p. 159—160° (decomp.), and 10-*cyano*-5 : 10-*dihydrophenarsazine*, m. p. 227—228° (decomp.), respectively. Di-α-naphthylarsenious oxide with anhydrous hydrogen cyanide in a sealed tube at 100° yields *di-α-naphthylcyanoarsine*, m. p. 191·5—192·5°. *Methyldicyanoarsine*, m. p. 115·5—116·5°, decomp. 118°, is obtained from dimethylcyanoarsine and cyanogen bromide. The cyano-compounds are hydrolysed to the corresponding oxides. H. Burton.

Manufacture of 4-formamido-2-hydroxyphenylarsinic acid and salts. Établ. Poulenc Frères and E. Fourneau.—See B., 1927, 892.

10-Chloro-5 : 10-dihydrophenarsazine and its derivatives. V. General method of synthesis and determination of constitution. C. S. Gibson and J. D. A. Johnson (J.C.S., 1927, 2499—2516; cf. Burton and Gibson, this vol., 264).—Diphenylamine-*o*-arsinic acids are obtainable both from an aniline-*o*-arsinic acid and a bromobenzene, and from an *o*-bromophenylarsinic acid and an arylamine, the yields being dependent on the reactivity of the bromine atom, which increases in the order: bromobenzene, *o*-bromophenylarsinic acid, *o*-bromonitrobenzene. With the exception of the *N*-methyl compound, all the diphenylamine-*o*-arsinic acids may be converted into phenarsazinic acids by boiling with concentrated hydrochloric acid, or into 10-chloro-5 : 10-dihydrophenarsazines by reduction with sulphur dioxide and a little iodine in presence of alcoholic hydrochloric acid, the 10-chloro-compounds being oxidisable to the phenarsazinic acids (from which they may be regenerated by reduction). Ring-closure by reduction probably proceeds by way of the dichloroarsine, *e.g.*,



When R=Me, a small amount of 10-chloro-8 : 10-dihydrophenarsazine is obtained. When X=*o*- or *p*-NO_2 and R=H, the decreased basicity of the nitrogen atom tends to prevent cyclisation. The intermediate dichloroarsine (III) is isolable only in the case where X=*o*-NO_2. The probable intermediate compound $C_6H_4X{\cdot}NH{\cdot}C_6H_4{\cdot}AsO(OH)Cl$, in the cyclisation by hydrochloric acid, appears transiently as an oil in most cases, but is not isolable. These reactions are also extended to the synthesis of benzophenarsazines (I) and *iso*benzophenarsazines (II).



o-Bromophenylarsinic acid (prepared by an improved method) and bromobenzene condense with aniline and with *o*-aminophenylarsinic acid, respectively, to give *diphenylamine-2-arsinic acid*, m. p. 166° (slight decomp.), from which phenarsazinic acid hydrochloride, m. p. 203—205° (decomp.), and 10-chloro-5 : 10-dihydrophenarsine, m. p. 191°, are obtained. 4-*Methyldiphenylamine-2'-arsinic acid*, m. p. 160—165° (decomp.), prepared from *p*-toluidine or *p*-bromotoluene, behaves similarly; 2-*methylphenarsazinic acid hydrobromide*, m. p. 208—210° (decomp.), and 10-*bromo*-2-*methyl*-5 : 10-*dihydrophenarsazine*, m. p. 180° (decomp.), are described. 2-*Methyldiphenylamine-2'-arsinic acid*, m. p. 130—140°, prepared from *o*-toluidine, gives 4-*methylphenarsazinic acid*, m. p. 309—310° [*hydrochloride*, m. p. 199° (decomp.)], and 10-*chloro*- [m. p. 191° (decomp.)] and 10-*bromo*- [m. p. 190° (slight decomp.)] -4-*methyl*-5 : 10-*dihydrophenarsazines*. N-*Methyldiphenylamine*-2-*arsinic acid*, m. p. 182—184° (decomp.), obtained from methylaniline, is not cyclised by hydrochloric acid, but by the reduction method yields a small

amount of impure 10-chloro-5 : 10-dihydrophenarsazine.

α-Naphthylamine condenses with *o*-bromophenylarsinic acid to form 2-α-*naphthylaminophenylarsinic acid*, m. p. 165°, which is converted into 7-*chloro*-7 : 12-*dihydroisobenzophenarsazine* (as II), m. p. 219°, and 7 : 12-*iso*benzophenarsazinic acid [*hydrochloride*, m. p. 232° (decomp.)]. β-Naphthylamine similarly gives 2-β-*naphthylaminophenylarsinic acid*, m. p. 181°, 12-chloro-7 : 12-dihydrobenzophenarsazine (as I), the 12-*bromo*-compound, m. p. 251—252° (decomp.), and 7 : 12-*benzophenarsazinic acid*, m. p. above 325° [*hydrochloride*, m. p. 234° (decomp.); *sodium*, *ammonium*, *barium*, *silver*, *mercuric*, *ferric*, *copper*, *cobalt*, and *calcium* salts described.]

The constitutions of several nitro- and amino-derivatives are confirmed by synthesis. 2-*Nitrodiphenylamine*-2′-*arsinic acid*, m. p. 238—240° (decomp.), prepared from *o*-bromonitrobenzene or from *o*-nitroaniline, gives 10-chloro-4-nitro-5 : 10-dihydrophenarsazine, m. p. 165° (Wieland and Rheinheimer, A., 1921, i, 371); 4-aminophenarsazinic acid is unaffected by nitrous acid at 5°. 3-*Nitrodiphenylamine*-2′-*arsinic acid*, m. p. 202°, from *m*-bromonitrobenzene, gives a single product of cyclisation, 10-*chloro*-3(or less probably 1)-*nitro*-5 : 10-*dihydrophenarsazine*, m. p. 258—259° (decomp.), which is oxidised to 3(or 1)-*nitrophenarsazinic acid*, not melted at 320° (*sodium* salt described); 10-*bromo*-3(or 1)-*nitro*-5 : 10-*dihydrophenarsazine* melts at 234° (decomp.). From 4-*nitrodiphenylamine*-2′-*arsinic acid*, m. p. 223° (decomp.), prepared from *p*-bromonitrobenzene, 10-*chloro*-2-*nitro*-5 : 10-*dihydrophenarsazine*, m. p. 276—278° (decomp.), is obtained, identical with the product of reduction of nitrated phenarsazinic acid (Burton and Gibson, A., 1926, 1162; Wieland and Rheinheimer, *loc. cit.*) in presence of hydrochloric acid; nitration of phenarsazinic acid therefore gives, as the more easily isolable product, the 2-nitro-compound.

C. Hollins.

Germanium. XVIII. Further organic compounds of germanium. W. R. Orndorff, D. L. Tabern, and L. M. Dennis (J. Amer. Chem. Soc., 1927, 49, 2512—2516; cf. A., 1926, 924).—Conversion of germanium tetraphenyl by bromine into triphenylgermanium bromide (m. p. 134°) takes place more readily in ethylene dibromide than in carbon tetrachloride solution (cf. Kraus and Foster, this vol., 268). *Triphenylgermanium chloride*, m. p. 117—118°, is obtained from triphenylgermanium oxide and hydrogen chloride in light petroleum, from the oxide and concentrated hydrochloric acid in boiling alcohol, or from a solution of triphenylgermanium bromide and hydrogen chloride. Diphenylgermanium dibromide could not be obtained by direct action of bromine on germanium tetraphenyl; direct hydrolysis of the reaction mixture yielded two *substances*, m. p. 147° and 210°, respectively, probably complex dehydration products of diphenylgermanic acid (cf. Morgan and Drew, A., 1925, i, 1197). *Triphenyl*-p-*tolylgermane*, m. p. 123—124°, is obtained from triphenylgermanium bromide and excess of magnesium *p*-tolyl bromide. *Triphenylanisylgermane*, m. p. 158—159°, and *triphenylethylgermane*, m. p. 75—76°, are obtained analogously. Treatment of triphenylgermanium bromide and *p*-bromodimethylaniline with sodium in boiling xylene affords *triphenyldimethylanilinogermane*, m. p. 140—141° [*hydrochloride*, m. p. 105—110° (decomp.)]. *Germanium tetrabenzyl*, m. p. 107—108°, obtained from magnesium benzyl chloride and germanium tetrachloride in ether–xylene, affords a *tetrasulphonic acid* (*barium* salt) when treated with 25% oleum at below 35°. Treatment of mercury diphenyl with germanium tetrachloride in xylene at 140° for 2 days, with subsequent hydrolysis, affords *phenylgermanic acid anhydride* $(GePhO)_2O$ (cf. Morgan and Drew, *loc. cit*). p-*Tolylgermanic acid anhydride* and *benzylgermanic acid anhydride* are obtained analogously, whilst *dimethylaminophenylgermanic acid anhydride* is obtained similarly from dimethylaniline and germanium tetrachloride at 100—110°. None of the above anhydrides has a definite m. p. *Germanium tetra*-n-*butyl*, b. p. 178—180°/733 mm., was prepared.

F. G. Willson.

Phosphorylation of proteins. C. Rimington (Compt. rend. Lab. Carlsberg, 1927, **17**, No. 2, 1—13).—Phosphorylation of proteins is readily effected by the slow addition of an ice-cold solution of phosphorus oxychloride in carbon tetrachloride to a rapidly stirred solution of the protein in the requisite quantity of dilute alkali, the reaction mixture being kept just alkaline by addition of 4*N*-sodium hydroxide and at a temperature below 5°. Caseinogen, serum-globulin, and dephosphorised casein (Rimington and Kay, A., 1926, 970) have been treated in this manner and the action of acid, alkaline, and enzyme hydrolysing agents on the products has been investigated. Phosphorised caseinogen contains 1·77% of phosphorus, the ratio P/N being 0·130, whilst for rephosphorised caseinogen the corresponding values are 1·75% and 0·124, respectively. Both products are coagulated by rennin. Phosphorised globulin contains 0·71% of phosphorus, the P/N ratio being 0·051. Under the action of pepsin and 0·25*N*-hydrochloric acid the phosphorised proteins slowly lose phosphorus as phosphoric acid, but 0·25*N*-sodium hydroxide at 37° liberates the whole of the phosphorus in 24 hrs. Trypsin causes a rapid separation of the whole of the phosphorus of phosphorised globulin in the form of an organic, acid-soluble substance, but liberates phosphoric acid from this compound only extremely slowly. Bone phosphatase, which liberates no phosphoric acid from the original phosphorised protein, rapidly liberates the whole of the phosphorus from this organic compound as phosphoric acid. The nature of the linking involved in proteins containing phosphorus is discussed, the author being of the opinion that a phosphoric ester of a hydroxyl group is formed.

J. W. Baker.

Phosphorus of caseinogen. I. Isolation of a phosphorus-containing peptone from tryptic digests of caseinogen. II. Constitution of phosphopeptone. C. Rimington (Biochem. J., 1927, **21**, 1179—1186, 1187—1193; cf. Rimington and Kay, A., 1926, 970; Rimington, this vol., 272, 581).—I. A peptone, $C_{37}H_{62}O_{33}N_9P_3$, named *phosphopeptone*, was isolated from tryptic digests of caseinogen in a yield corresponding with 50% of the organic phosphorus of the digest. The filtrate from a 38 hr. digest

was precipitated with lead acetate and ammonia. The precipitate was then decomposed with hydrogen sulphide, and after removing the inorganic phosphorus the peptone was precipitated with uranium acetate. The *copper* and *barium* salts each containing nine equivalents of the metal and a *brucine* salt were prepared. The free acid has $[\alpha]_{5461}^{15}$ −80·53° and gives the biuret and ninhydrin reactions, but not the usual colour reactions for amino-acids. A primary colour reaction is also given with diazobenzenesulphonic acid, but there is no secondary colour after reduction. The peptide linkings of phosphopeptone are slowly attacked by trypsin, which also slowly liberates phosphorus as phosphoric acid.

II. Phosphopeptone was hydrolysed with hydrochloric acid and the resulting amino-acids were converted into their calcium salts. The concentrated salt solution was then treated with 97% alcohol, the precipitate dissolved in water and decomposed with oxalic acid, and converted into a copper salt which was found to be that of β-hydroxyglutamic acid. From the alcoholic solution of the calcium salts, α-amino-β-hydroxybutyric acid and serine were isolated. A hypothetical structural formula which is in agreement with the known chemical properties of the peptone is advanced. Posternak's work (this vol., 273, 581) is criticised. S. S. Zilva.

Racemisation. V. Action of acid and alkali on gelatin. P. A. Levene and L. W. Bass (J. Biol. Chem., 1927, **74**, 715—725).—The average rotation of the mixture of amino-acids resulting from acid hydrolysis of gelatin was α_{5461} −0·23° to −0·38° (4 dm. tube); after preliminary treatment of the gelatin for 24 hrs. at 25° with 0·1, 1·0, and 3·0*N*-alkali, the corresponding rotations were −0·69°, −1·13°, and −0·2°, respectively. The results indicate that racemisation (principally of the *d*-amino-acids) is more complete in the dilute alkali, probably owing to the rapidity of hydrolysis in the concentrated alkali. The results agree with those of Dakin (A., 1913, i, 208). C. R. Harington.

Constitution of the diazo-compounds of silk fibroin. A. Morel and P. Sisley (Bull. Soc. chim., 1927, [iv], **41**, 1217—1224).—Fibroin, after treatment with nitrous acid at 10—12° for 24 hrs. in the absence of light, becomes yellow and couples slowly with certain amines and phenols with the production of bright colours, which, whilst fast to washing and light, are changed in tint by acids and alkalis. Many amines and phenols will not couple with the diazotised fibroin. The general properties of the colours are analogous to those of the azo-dyes, and it is suggested that the nitrous acid reacts with the tyrosine of the fibroin (Abderhalden, A., 1905, i, 75; 1922, i, 784) to produce an *o*-quinone-oxime which is reduced by further nitrous acid to form a diazonium nitrate. This view is supported (i) by the production of similar colours from tyrosine and (ii) by the preparation of phenolazo-β-naphthol from phenol, nitrous acid, and β-naphthol. According to this view diazotised fibroin, after reduction with stannous chloride, contains a free amino-group which accounts for its rapid diazotisation in contrast to the slow diazotisation of fibroin. G. A. C. Gough.

Hydrolysis of silk by 25% formic acid. N. D. Zelinski and K. P. Lavrovski (J. Russ. Phys. Chem. Soc., 1927, **59**, 423—426).—The action of 25% formic acid on silk fibre, freed from gum, at 180°/10 atm. was investigated, to determine whether hydrolysis was complete, or whether, as in the action of 10% acid on proteins, very stable condensation products of the amino-acid were formed.

On treatment for 3 hrs., a 10% yield of tyrosine was obtained. No basic products of reduction, such as piperazine, but only small quantities of ammonia and methylamine, were obtained from the decomposition of the amino-acids. The solid separated from the aqueous solution on esterification in the presence of hydrochloric acid gave glycine ester hydrochloride, whilst from the mother-liquor, on further esterification, alanine ester, b. p. 49—50°, was obtained. Formic acid (25%) under similar conditions also hydrolysed pure glycine anhydride and so behaved like 4—5% solutions of mineral acids. M. Zvegintzov.

Osmometric method of determining the mol. wt. of proteins. G. Adair (J. Amer. Chem. Soc., 1927, **49**, 2524—2525).—A reply to Svedberg and Nichols (this vol., 99), and a summary of arguments in support of results obtained by the osmometric method of determining mol. wt. of proteins (cf. Adair, A., 1926, 21; 1925, ii, 965). The provisional estimate of the average mass of the protein particles in serum is raised from 80,000 to 100,000. F. G. Willson.

Effect of radium radiation on pseudoglobulin. A. Fernau (Biochem. Z., 1927, **189**, 172—174).—Pseudoglobulin on irradiation with radium is denatured as with serum- and egg-albumin (cf. A., 1926, 367), the coagulation temperature being first decreased and the globulin finally separating as a powder. The time of irradiation necessary for the commencement of precipitation is influenced both by the presence of salts and by the concentration of the solution, but pseudoglobulin solutions obtained by ordinary dialysis behaved similarly to those which were made completely salt-free by electrodialysis. P. W. Clutterbuck.

Combination between acid dyes and proteins. R. A. Gortner (J. Biol. Chem., 1927, **74**, 409—413).—A discussion of the results of Chapman, Greenberg, and Schmidt (this vol., 686). C. R. Harington.

Sulphur in proteins. III. Derivatives of *l*- and *i*-cystine. E. Abderhalden (J. Biol. Chem., 1927, **75**, 195—197). R. A. Gortner (*ibid.*, 199—200).—Polemical (cf. Gortner and Hoffman, this vol., 581; Abderhalden, A., 1903, ii, 564). C. R. Harington.

Halogenated proteins. VIII. Chlorogluten. A. J. J. Vandevelde (Rec. trav. chim., 1927, **46**, 590—593; cf. A., 1925, i, 92; this vol., 474).—A solution of chlorine in carbon tetrachloride converts gluten into chlorogluten (N 10·6; Cl 23·2%), partly soluble in water and apparently a mixture; it is more resistant to reagents than other chlorinated proteins. E. W. Wignall.

Micro-method for the determination of "hydrogen number." S. Ogawa (Sci. Rep. Tohoku Imp. Univ., 1927, **16**, 671—676).—Precise details of apparatus and experimental technique are

given of a modification of Fokin's method (B., 1908, 878) of determining "hydrogen number" as a measure of unsaturation; it is possible to test 5—20 mg., depending on the degree of unsaturation, of various fatty materials. E. HOLMES.

Volumetric determination of alkoxy-groups. E. P. EATON and E. S. WEST (J. Biol. Chem., 1927, 75, 283—288).—The compound is boiled with hydriodic acid and the alkyl iodide absorbed in pyridine at 80°; the pyridinium alkyl iodide is treated with excess of sulphuric acid and potassium iodate and the liberated iodine distilled into potassium iodide and titrated. The method is applicable to methoxyl and ethoxyl groups and to compounds containing sulphur.
C. R. HARINGTON.

Copper number for dextrose. C. A. AMICK (J. Physical Chem., 1927, 31, 1441—1477).—The use of alkaline copper solutions is invalidated by the facts that the amount of oxidation depends on the alkalinity and concordant results differing greatly from series to series can be obtained according to conditions. Further, solutions made alkaline by carbonates give higher copper numbers than those made alkaline by alkali hydroxide. The volumetric method of Bertrand (A., 1907, ii, 136) is inaccurate because of adsorption of Fehling's solution by the asbestos mat or filter-paper used. The adsorbed material cannot be removed by washing but dissolves in the acidified iron alum solution used. Further, ferric salts catalyse the oxidation of the adsorbed tartrates by the permanganate. Iron salts, however, can be used when sodium fluoride is added to remove the excess of ferric iron by forming a complex, Na_3FeF_6, which is unstable in solutions of 2·5% acidity. Iron salts may also be used with sodium pyrophosphate if the acidity is kept low. In a new volumetric method, filtration is eliminated, and the cuprous oxide is oxidised by a phosphomolybdic reagent, the blue colour which is formed being discharged in the cold, by titration with permanganate. The reducing action of sugar is not due to carboxyl formation from the carbonyl group, as generally supposed. The results support the views of Nef for the formation, with subsequent fission, of enediols by the reducing sugars in alkaline solution.
L. S. THEOBALD.

Microchemical reactions for citric acid. M. WAGENAAR (Pharm. Weekblad, 1927, 64, 1135—1138).—The formation of the anhydride and of the various salts does not afford satisfactory tests. Oxidation to acetone and conversion of this into iodoform can be effected, but malic and lactic acids give this compound also under the conditions employed. Oxidation in presence of hydrobromic acid yields pentabromoacetone, which can be brought to characteristic crystallisation by addition of ether; the corresponding iodine compound crystallises more readily, and is more suitable for the test. The reaction is not given by tartaric, succinic, lactic, malic, or oxalic acids. S. I. LEVY.

Characteristic colour reactions for lactic acid, methylglyoxal, and carbohydrates with carbazole and sulphuric acid. Z. DISCHE (Biochem. Z., 1927, 189, 77—80).—The method of carrying out the carbazole reaction is described and tables indicate the colours obtained with a large number of aldehydes, ketones, hydroxy- and amino-acids, etc.
P. W. CLUTTERBUCK.

Colorimetric determination of *o*-dihydroxy-derivatives of benzene. H. SCHMALFUSS, K. SPITZER, and H. BRANDES (Biochem. Z., 1927, 189, 226—228).—A method is described for the colorimetric determination of dihydroxybenzene derivatives, based on the colour obtained with ferric chloride, and applied to solutions of pyrocatechol, protocatechuic acid, protocatechualdehyde, adrenaline, and *l*-3 : 4-dihydroxyphenylalanine. The limits of the method are from $1{\cdot}12\times10^{-5}$ to $7\times10^{-7}M$ solutions and the error is +3%. P. W. CLUTTERBUCK.

Evaluation of ethyleosin. W. C. HOLMES and J. T. SCANLAN (Stain Tech., 1927, 2, 101—103).—Methods for the determination of eosin and ethyleosin in samples of the latter are described. The great difference in solubility of the two dyes in water makes this possible; at 26° 100 c.c. of water dissolve 44·2 g. of eosin and only 0·0312 g. of ethyleosin.
H. W. DUDLEY.

Extinction coefficients of dyes. R. W. FRENCH (Stain Tech., 1927, 2, 124—125).—The extinction coefficients of seven acid and nine basic dyes are tabulated. H. W. DUDLEY.

Biochemistry.

Colloidal properties of the surface of the living cell. J. F. MCCLENDON (Fourth Colloid Symposium Monograph, 1926, 224—233).—Experiments on the conductivity of the corpuscle-interior of laked blood support the selective semipermeability of the colloidal cell surface. CHEMICAL ABSTRACTS.

Effect of certain dyes on blood *in vitro*. H. WALES, J. C. MUNCH, and E. W. SCHWARTZE (J. Pharm. Exp. Ther., 1927, 31, 473—479).—The extinction coefficients of solutions of the following dyes in diluted blood have been determined in the range of the visible spectrum: guinea-green-B., light-green-S.F. yellowish, fast-green-F.C.F., indigotin, erythrosin, amaranth, ponceau-3R, orange-I, orange-II, naphthol-yellow-S., and tartrazine. Immediate readings show no diminution in intensity of the oxyhæmoglobin bands; on keeping, however, a diminution takes place and the band of reduced hæmoglobin appears (5450 Å.). Since in no case was a band at 4950 Å. detected it is concluded that no methæmoglobin was formed. E. A. LUNT.

Specific refraction of whole [plasma-]protein. K. RECKNAGEL (Arch. exp. Path. Pharm., 1927, 125, 257—268).—The specific refractive index of the total plasma-protein shows marked variation even in one individual and is related to the specific viscosity, both values being dependent on the colloidal condition of the protein. W. O. KERMACK.

Quantitative micro-method for the fractionation of serum-proteins by electrodialysis. A. Tóth (Biochem. Z., 1927, **189**, 270—293).—By using a centrifugable membrane for electrodialysis, the serum-protein can be separated immediately by centrifuging. The loss of protein during dialysis is usually less than 1% and never more than 2%. The changes of reaction, the separation of salts, and the formation of precipitate during electrodialysis were followed in parallel experiments, in one case with a combination of a chromed gelatin and collodion and in the other of a pair of collodion membranes. With the former pair, the reaction passed from that of the diluted serum to that of the isoelectric point of globulin, whilst with the latter pair the reaction was acid and then drew near to the isoelectric point of globulin. The decrease in electrolytes shows initially a rather steep and uniform fall, then a period of no further decrease, and finally a considerable decrease. The conductivity curve follows the same course with both pairs of membranes but the removal of electrolytes is quicker with the chromed gelatin–collodion pair. The precipitation curve is also of the same type for the chromed gelatin–collodion pair and reaches its maximum after 40 min., whereas with the pair of collodion membranes it remains steady where the conductivity curve shows its maximum, the high point being attained after 50 min. The course of electrodialysis is divided into three phases. In the first those electrolytes not combined or loosely combined with protein are removed and about 50% of the precipitation occurs, whilst in the second phase those crystalloids bound to the protein are removed, and in the third phase the conductivity again falls. The effect of age on the chromed gelatin membranes in respect to its nitrogen permeability is investigated with human sera. The pair of collodion membranes is recommended for quantitative investigation because of their easier preparation and their greater trustworthiness. P. W. Clutterbuck.

Preparation of serum-globulin and its definability. L. Reiner (Magyar Orvosi Arch., 1927, **28**, 288—303).—Serum-euglobulin is not an additive product of protein and lipin. Globulin, which has a broad isoelectric zone, is not a homogeneous substance. Proteins with different isoelectric points cannot be isolated from so-called euglobulin.

Chemical Abstracts.

Normal bilirubin content of human sera. R. Sivó (Biochem. Z., 1927, **189**, 159—161).—The normal bilirubin content of serum is 0·80—1·10 mg. % and values above 1·20 mg. % are regarded as pathological. The occurrence of a low bilirubin content in certain diseases could not be confirmed.

P. W. Clutterbuck.

Existence of lactacidogen in blood. (Mme.) A. Roche and J. Roche (Compt. rend., 1927, **185**, 873—875).—Determinations of the lactic acid–phosphorus ratio for defibrinated dog's blood, diluted with twice its volume of sterile distilled water and maintained at 38—40°, indicate the presence of a hexose-diphosphoric acid. The lactacidogen probably undergoes degradation by a phosphatase analogous to that found in muscle juices. J. Grant.

Reducing non-sugars and true sugar in human blood. M. Somogyi (J. Biol. Chem., 1927, **75**, 33—43).—Fermentative removal of dextrose from blood is complete if, in the preparation for the precipitation of proteins by tungstic acid, the blood be diluted with a 10% aqueous suspension of washed yeast. The non-dextrose reducing substances of human blood amount almost constantly to 27 mg. per 100 c.c. (expressed as dextrose), whatever may be the total concentration of sugar, but are increased in amount in cases of nitrogen retention; they are unequally distributed between the red blood-corpuscles and the plasma, amounting to 47 mg. % in the former and 10 mg. % in the latter; part of the non-dextrose reducing power is due to ergothioncine.

C. R. Harington.

Preservation of blood for chemical analysis. F. F. Schwentker (Arch. Path. Lab. Med., 1927, **3**, 410—413).—If the Lewis–Benedict method is employed, variably high results are obtained when sodium fluoride and thymol are used as preservatives.

Chemical Abstracts.

Concentration of urea in normal [human] blood. E. M. MacKay and L. L. MacKay (J. Clin. Invest., 1927, **4**, 295—306).—The blood-urea varies between 11·0 and 48·0 mg. per 100 c.c., being higher in males than in females; there is a diurnal fluctuation. Chemical Abstracts.

Micro-determination of blood-sugar. Blood-sugars of insects. R. Blumenthal (Science, 1927, **65**, 617—619).—The method of Folin and Wu is applied to the manipulation of 0·03 c.c. of material. The following average and extreme values for the blood-sugar (mg. per 100 c.c.) were obtained: *Romelea microptera* (nymph) 41·7, 34·2—49·4; *Melanoplus femur rubrum* 35·3, 30·6—41·9; *Melanoplus diffentialis* 36·5, 31·0—45·9; *Chortophaga viridifasciata* 34·0; *Encoptolophus sordidus* 36·4; *Popellia japonica* (larva) 63·0, 56·3—69·2. A. A. Eldridge.

Action of powdered metals on blood-catalase. G. Lio (Arch. Farm. sperim., 1927, **43**, 218—224).—Finely-divided silver, nickel, copper, and cobalt have no action on hydrogen peroxide solution but gradually weaken and ultimately abolish the activity of blood-catalase. Powdered quartz is without influence in this direction. T. H. Pope.

Determination of calcium in whole blood. W. R. Caven and A. Cantarow (J. Lab. Clin. Med., 1926, **12**, 76—77).—The calcium is determined volumetrically as oxalate, the blood being hæmolysed by distilled water. Chemical Abstracts.

Electrometric determination of iron in blood. J. F. King and F. H. Howard (J. Biol. Chem., 1927, **75**, 27—32).—Blood was incinerated with sulphuric and perchloric acids and the solution of the residue titrated electrometrically with titanous sulphate against a standard solution of ferric sulphate by the method of King and Washburne (this vol., 24); with 5 c.c. of blood the error of the method is 0·2%.

C. R. Harington.

Manganese content of plants and animals. C. W. Lindow and W. H. Peterson (J. Biol. Chem., 1927, **75**, 169—175).—Figures are given for the

manganese content of numerous food materials of plant and animal origin. C. R. HARINGTON.

Constituents of *Laganum* (*echinoidea*). I. M. KOTAKE (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1927, 6, 49—51).—Cholesterol is isolated from the ethereal extract of the dry, powdered horny covering of *Laganum*. The ethereal extract of the inner portion after hydrolysis yields more cholesterol and an unsaturated fatty acid which on reduction (without purification) with palladium-black and hydrogen in alcohol yields *dihydrolaganic acid*, $C_{20}H_{40}O_2$, m. p. 68·5—70° (*amide*, m. p. 104—105°), which is not identical with either stearic or arachic acids and probably contains a branched carbon chain.

J. W. BAKER.

Nitrogenous extractives of ox liver. Y. HIWATARI (J. Biochem. [Japan], 1927, 7, 161—167).—An extract obtained from 14 kg. of ox liver yielded uric acid 5; guanine 0·7; adenine 1·5; xanthine 0·45; hypoxanthine 0·6; choline 3 g., and a small quantity of carnosine. CHEMICAL ABSTRACTS.

Determination of carnosine. F. M. KUEN (Biochem. Z., 1927, **189**, 60—76).—Carnosine was determined by seven methods in the muscle of the ox, horse, pig, calf, and rabbit. Horse muscle contains 0·3% of carnosine when determined as the characteristic copper compound or after hydrolysis as histidine picrolonate, the value being practically constant for the different samples. Diazo-colorimetric and copper-colorimetric methods gave values which were too high. Frozen meat contained much less carnosine than fresh meat. Smoked flesh contains either no carnosine or histidine, or else only traces, but a substance is present which gives the diazo-reaction but is not precipitated by mercuric sulphate.

P. W. CLUTTERBUCK.

Colloidal characteristics of muscle proteins. III. Physico-chemical constants for myogen. H. H. WEBER (Biochem. Z., 1927, **189**, 407—450).—Myogen solutions purified by electrodialysis contain 1—6% of myogen, only 5—10% of the total nitrogen of such solutions being present as other proteins (albumin). Pure myogen has *d* 1·35, and fresh electrodialysates in the absence of carbon dioxide have $[\alpha]_D$ +31°, but this increases threefold by acid ionisation. Hydrolysis of protein in very alkaline solution causes the concentration of hydroxyl ions obtained by electrotitration to appear 20% too high, and in very acid solutions the concentration of hydrogen ions 10% too low. The union of myogen with hydrogen and hydroxyl ions increases at a given p_{ah} (negative exponent of the hydrogen-ion activity) proportionally with the myogen concentration. The bound $H^{\cdot}$–p_{ah} curve (with 1 millimol. of myogen nitrogen) may be represented (apart from the isoelectric zone) by the dissociation curve of a univalent base with a dissociation constant at $K_B=3{\cdot}5\times10^{-11}$ and a total acid-binding power of 115×10^{-3} millimol. $H^{\cdot}$, the base equivalent being 750. The bound OH'–p_{ah} curve (with 1 millimol. of myogen nitrogen) is described (apart from the isoelectric zone) by the addition of the dissociation curves of two univalent acids with dissociation constants $K_{a_1}=6{\cdot}3\times10^{-9}$ and $K_{a_2}=10^{-11}$ and a total base-binding power of $17—89\times10^{-3}$ millimol. OH'. The equivalent weight of the substance first dissociated is 5100 and the total base equivalent 815 (by electrotitration) and 1027 (by Willstatter's titration). For myogen chloride in pure hydrogen chloride solution, the activity, measured by the calomel electrode, shows an increase from 0·5 at p_{ah} 1·5 to 0·7 at p_{ah} 3, whilst in hydrogen chloride and $M/30$-sodium chloride it is only 0·4 at

3. The "non-dissolving space" (cf. Polanyi, A., 1920, ii, 604) for 1 g. of acid-ionised myogen is only 2·7 cm., a figure much lower than the volume of myogen (disperse phase) as calculated from viscosity measurements (which at p_{ah} 1·5 is 12·4 cm.), and this discrepancy is of importance in view of Pauli's hydration theory of protein ions which depends on viscosity measurements. The alkaline ionisation of myogen at the p_{ah} of resting muscle is as high as the acid ionisation at p_{ah} 5·5, *i.e.*, at a p_{ah} almost never attained in muscle. Since myogen on account of its isoelectric point at p_{ah} 6·3 is the only muscle protein which is concerned in acid-swelling, the acid-swelling theory of contraction must be discarded. The total muscle myogen can neutralise only one fifth of the lactic acid arising in muscular fatigue, and since under these conditions one to two thirds of the lactic acid is neutralised by protein, a protein of much greater buffering power must be present (cf. A., 1925, i, 995).

P. W. CLUTTERBUCK.

Lens protein and its fractions. A. C. WOODS and E. L. BURKY (J. Amer. Med. Assoc., 1927, **89**, 102—110).—New methods of preparation yield a larger ratio of α- to β-crystallin. Serologically pure fractional antigens were obtained by a method utilising the isoelectric points of the crystallins.

CHEMICAL ABSTRACTS.

Isolation of a substance with carcinolytic properties from the reticulo-endothelial system. N. WATERMAN and L. DE KROMME (Proc. K. Akad. Wetensch. Amsterdam, 1927, **30**, 499—501).—Normal blood-serum and normal organs contain a substance capable of dissolving cancer cells. This property disappears on the appearance of carcinoma, and it may be increased or diminished by *X*-rays according to the length of time of irradiation. Ether extracts of almost all organs possess a more or less lytic action, but the extracts of the lymphatic glands, spleen, and thymus are most active. The extraction is made with 10—15 times the volume of ether under a reflux condenser for 8 hrs. The ether is removed and the aqueous residue treated with excess of acetone. The white flocculent precipitate is washed with acetone, dried, ground with 96% alcohol, filtered, and the whitish-grey residue dried and shaken with a mixture of one part of phosphate buffer, p_H 7·7, with five parts of physiological sodium chloride solution, which dissolves the active matter. The lytic power of the product depends on the p_H of the environment. An acid reaction counteracts lysis, whilst an alkaline one promotes it. A lytic power of 81% has so far been obtained. The product contains neither tryptic nor lipolytic enzyme, and is free from protein. Its lytic power is affected by *X*-rays.

M. S. BURR.

Presence of acetaldehyde in cerebrospinal fluid. P. THOMAS and E. MAFTEI (Bull. Sci.

Roumaine, 1927, **10**, 16—20).—Small quantities of acetaldehyde have been detected in human cerebrospinal fluid. Cerebrospinal fluid is shown to contain neither decarboxylase nor an alcohol oxidase and so it is concluded that the acetaldehyde does not originate in the fluid itself, but in the blood. W. O. KERMACK.

Chlorides of gastric contents in relation to free acidity. S. MILLER and F. B. SMITH (Lancet, 1927, i, 593—595).—The mean curves of the total chlorides in all grades of gastric acidity are similar in shape, and differ only in magnitude. The mean curves of the inorganic chlorides have the same general form and relation to time of digestion as those of the total chlorides, but agree more closely in magnitude. In hyperchlorhydria the inorganic chlorides tend to remain low, or rise only slightly.
A. A. ELDRIDGE.

Relation of p_H to titratable acidity of milk. P. F. SHARP and T. J. MCINERNEY (J. Biol. Chem., 1927, **75**, 177—184).—In fresh milk the p_H varied from 6·0 to 7·73 and the titratable acidity from 0·05 to 0·5%, expressed as lactic acid; a curve is given by means of which the p_H can be deduced from the titratable acidity over the range of 0·1—0·5% of the latter. The relation between p_H and titratable acidity in sour milk is of a different character.
C. R. HARINGTON.

Determination of calcium in human milk. C. S. ROTHWELL (J. Biol. Chem., 1927, **75**, 23—26).—By treatment of the material with sodium chloride to make a concentration of 5% of the latter, the author's direct precipitation method (A., 1925, i, 1350) becomes applicable to human milk. C. R. HARINGTON.

Chlorides and non-protein nitrogenous constituents of the sweat, urine, and blood as affected by heat and work. G. A. TALBERT, E. E. HARRIS, J. R. FINKLE, and S. H. SILVERS (Amer. J. Physiol. Proc., 1926, **76**, 185—186).—Sweat contained 3·2—6·5 mg. of chlorine, 0·338—1·625 mg. of nitrogen, 0·05—1·12 mg. of urea, and 0·04—0·211 mg. of ammonia per c.c. Generally, the chlorides and total nitrogen vary directly. A. A. ELDRIDGE.

Physico-chemical properties of bilirubin in body-fluids. E. FORRAI and R. SIVÓ (Biochem. Z., 1927, **189**, 162—167).—Bilirubin, although readily ultrafiltrable, becomes completely unable to pass the ultrafilter in presence of colloids. Caffeine destroys the bilirubin–colloid union. P. W. CLUTTERBUCK.

Instability of bilirubin and detection of bilirubin in urine. R. SIVÓ and E. FORRAI (Biochem. Z., 1927, **189**, 168—171).—Fresh urine must be used for the detection of bilirubin on account of the instability of bilirubin. Union with colloid (see preceding abstract) increases the stability of bilirubin.
P. W. CLUTTERBUCK.

Relation of inorganic iron to nutritional anæmia. H. S. MITCHELL and M. VAUGHN (J. Biol. Chem., 1927, **75**, 123—137; cf. A., 1926, 1269).—Whilst not all soluble iron salts are equally effective in the relief of nutritional anæmia, it remains true that no insoluble iron compound is satisfactory in this respect. No relationship could be observed between vitamin-*E* and the assimilation of iron.
C. R. HARINGTON.

Blood-sugar curves in non-diabetic subjects. W. G. LENNOX [with M. BELLINGER] (J. Clin. Invest., 1927, **4**, 331—352).—A progressive lowering of successive curves follows the ingestion or injection of dextrose; hence a single curve has little diagnostic significance. CHEMICAL ABSTRACTS.

Utilisation of protein, carbohydrate, and fat in hypoglycæmia in diabetics requiring insulin. Dextrose content of blood-plasma and corpuscles, and effect of insulin and dextrose on the acid–base balance of the blood. R. B. GIBSON, L. GREER, and A. BARER (Amer. J. Physiol. Proc., 1926, **76**, 188).—At high blood-sugar levels the metabolism is of the diabetic type; at hypoglycæmic levels the fat metabolism is augmented. Blood-sugar levels are incidental to, and not the cause of, the metabolic changes. Pre-operative administration of insulin and dextrose produces a shift of the acid-base balance further to the alkaline side.
A. A. ELDRIDGE.

Fat metabolism in diabetes. I. Blood-lipins in experimental diabetes. W. R. BLOOR, E. M. GILLETTE, and M. S. JAMES (J. Biol. Chem., 1927, **75**, 61—83).—Experimental diabetes, produced in dogs by removal of the greater part of the pancreas, resulted, whatever the nature of the diet, in an increase in the fasting concentration of lipins in the blood and a still greater increase in the response of the blood-lipins to a fat meal. The variation was most marked in the fats and least in the lecithin; the increase in cholesterol was variable and usually less marked than that observed in human diabetics.
C. R. HARINGTON.

Effect of the administration of sodium β-hydroxybutyrate on the glycosuria of phloridzin diabetes. N. MORRIS and S. GRAHAM (Lancet, 1927, i, 1020—1021).—With dogs there was no appreciable rise in the D : N ratio. A. A. ELDRIDGE.

Optical activity and reducing power of dextrose excreted by renal diabetics. E. J. MAGERS and R. B. GIBSON (J. Biol. Chem., 1927, **75**, 299—304).—The sugar excreted by renal diabetics was of the same character in the fasting condition and after ingestion of dextrose, and had, in all cases, the specific rotation of ordinary dextrose. C. R. HARINGTON.

Epilepsy. Rational treatment by production of ketosis. F. B. TALBOT, K. M. METCALF, and M. E. MORIARTY (Amer. J. Dis. Children, 1927, **33**, 218—225).—In epileptic children treated by fasting or with ketogenic diet there is an increased blood-acetone concentration, and a marked excretion of acetone substances in the breath and urine. The alkaline reserve is lowered and the blood-sugar decreased.
CHEMICAL ABSTRACTS.

Changes in plasma-proteins of hæmatoporphyrin rabbits. M. KOMATSU (J. Biochem. [Japan], 1927, **7**, 1—17).—The albumin/globulin ratio in the plasma of hæmatoporphyrin rabbits exposed to sunlight is considerably diminished, owing to an increase in the globulin and a diminution of the albumin content. The rise in globulin content of the plasma runs more or less parallel to the developing anæmia, but it is not known whether the globulin owes its origin to the destruction of red blood-cells. There is

a notable increase in the urobilin content of the urine of the hæmatoporphyrin rabbits.

CHEMICAL ABSTRACTS.

Lævulose tolerance test for hepatic efficiency. G. KING (Lancet, 1927, i, 385—388).—Normally, the rise in blood-sugar after ingestion of 45 g. of lævulose is 8 mg. per 100 c.c.; there is a return to the fasting level in 1·5—2 hrs. In liver disease the reaction is atypical. A. A. ELDRIDGE.

Comparative sugar content of blood and of cerebrospinal fluid in various conditions. A. LEVINSON (Amer. J. Dis. Children, 1925, **30**, 774—779).—No direct relation was observed in meningitis. Ingestion or injection of dextrose usually raised the cerebrospinal-fluid value, which is low in meningitis.

CHEMICAL ABSTRACTS.

Blood as a physico-chemical system. VI. Terminal chronic nephritis. L. J. HENDERSON, A. V. BOCK, D. B. DILL, L. M. HURXTHAL, and C. VAN CAULAERT (J. Biol. Chem., 1927, **75**, 305—313).—A nomographic representation is given of the condition of the blood immediately preceding death from chronic nephritis, the most conspicuous features being reduction in the hæmoglobin, increase in acidity, and a profound change in the distribution of electrolytes between red blood-corpuscles and plasma.

C. R. HARINGTON.

Chemical aspects of the toxæmias of pregnancy. J. N. CRUICKSHANK (Glasgow Med. J., 1927, 26, 1—11).—In pre-eclamptic toxæmia there is no gross retention of nitrogen. The composition of the blood and urine characteristic of the later months of normal pregnancy is maintained in the toxæmias. The hydræmia characteristic of late pregnancy and the œdema of certain toxæmic cases are not related to the blood- or urine-chlorides.

CHEMICAL ABSTRACTS.

Changes in oxygen capacity of rabbit hæmoglobin following splenectomy. B. B. STIMSON (J. Biol. Chem., 1927, **75**, 95—99).—Splenectomy in rabbits was followed by a greater fall in oxygen capacity than in hæmoglobin content of the blood; no spectroscopic evidence of the presence of methæmoglobin could be obtained, but, after treatment with a reducing agent, the combining capacity of the blood for carbon monoxide was increased. The presence is therefore assumed of some oxidation product of hæmoglobin similar to, but not identical with, methæmoglobin. C. R. HARINGTON.

Respiratory metabolism following administration of various carbohydrates. H. J. DEUEL, jun. (J. Biol. Chem., 1927, **75**, 367—391).—Ingestion of lævulose and sucrose leads to an immediate rise in the respiratory quotient; the rise is slightly slower with lactose and galactose, whilst with dextrose and maltose it is delayed for 45 min., and with starch for 1—2 hrs. The specific dynamic effects of all the carbohydrates were closely similar to one another, and approximated to the effects already observed in dogs. The maximum heat production occurred usually about 2 hrs. after ingestion of the carbohydrate and was not necessarily coincident with the highest respiratory quotient.

C. R. HARINGTON.

Metabolism of dihydroxyacetone in normal and diabetic individuals. I. M. RABINOWITCH (J. Biol. Chem., 1927, **75**, 45—60).—Further evidence is given in support of the previous suggestion (A., 1925, i, 1352; cf. also Kermack and others, A., 1926, 861) that, in the normal and diabetic individual, dihydroxyacetone can be oxidised directly, and, unless administered in large excess, is not converted into dextrose. The opposite conclusions of Campbell and others (A., 1926, 1272) are perhaps accounted for by technical errors in the determination of dihydroxyacetone. C. R. HARINGTON.

Distribution and recovery of dextrose injected into animals. O. FOLIN, H. C. TRIMBLE, and L. H. NEWMAN (J. Biol. Chem., 1927, **75**, 263—281).—Dextrose injected intravenously into nephrectomised dogs disappears very rapidly from the blood-stream, but cannot be accounted for after 30 min. by the increase in the dextrose content of the muscles and the glycogen of the liver. Similar experiments with guinea-pigs showed, however, that by analysis of the whole animal 30 min. after the injection the whole of the dextrose could be accounted for; it was then found that such injections led at first to rapid accumulation of dextrose in the skin and glandular organs; in the course of 3—4 hrs. the dextrose content of these tissues and of the blood had returned to the normal, and there could then be detected the increase in the glycogen of the muscles and the liver as observed by other workers (cf. Cori and Cori, A., 1926, 1271).

C. R. HARINGTON.

Behaviour of the glycæmic curve in the child during a prolonged fast. I and II. I. G. TOSI (Clin. pediatr., 1926, **8**, 577—591, 592—603).—With infants on a tea-"saccharin" diet the minimal blood-sugar (0·05—0·06%; normal 0·06—0·10%) is attained in 24 hrs., with older children in 48 hrs. The decrease is followed by a rise which is apparently caused by the mobilisation of the glycogen reserves. Addition of fat to the diet does not essentially influence the glycæmic curve, but caseinogen does so. It is concluded that sugar can be formed from protein, but not from fat. CHEMICAL ABSTRACTS.

Sugar and cholesterol in the blood-serum in relation to fasting. R. E. SHOPE (J. Biol. Chem., 1927, **75**, 101—113).—In man, the pig, the cat, and the guinea-pig, fasting causes a fall in the sugar and an increase in the free cholesterol and cholesterol esters of the blood; on resumption of food the reverse changes take place. In the rabbit, on the other hand, fasting is accompanied by an increase in the blood-sugar as well as in the cholesterol of the blood. The relationship between the sugar and cholesterol is regarded as indicating that the latter plays a part in the metabolism of fats. C. R. HARINGTON.

Effect of addition of alkali [to the diet] on alimentary hyperglycæmia during starvation. G. HIRSCH (Biochem. Z., 1927, **189**, 451—459).—Administration to starving rabbits, dogs, and men of dextrose on the one hand and of the same amount of dextrose with alkali (sodium hydrogen carbonate and acetate) on the other showed that with alkali the specific dynamic action was decreased and the

respiratory quotient increased, the blood-sugar curve was lower and after 4 hrs. hypoglycæmia intervened, and the increased sugar tolerance obtained by repeating the administration of sugar fell away.

P. W. CLUTTERBUCK.

Lactate metabolism in infants. M. B. BRAHDY (Amer. J. Dis. Children, 1927, **33**, 451—457).—The lactate ion does not influence the peripheral metabolism. CHEMICAL ABSTRACTS.

Ketosis in the rat. H. LEVINE and A. H. SMITH (J. Biol. Chem., 1927, **75**, 1—22).—Variations in the fat, carbohydrate, or protein fractions of the diet of adult rats caused no corresponding fluctuations in excretion of ketones, nor could ketosis even be produced by sudden change from a diet rich in carbohydrate to one rich in fat. The mechanism of ketosis must therefore be different in man and in the rat, and the theory of Shaffer is not applicable to rats. Excretion of acetone substances in the rat was increased by injection of phloridzin or by addition of sodium carbonate to the diet rich in fat; under almost all conditions, β-hydroxybutyric acid represented about 70% of the total excretion of acetone substances. C. R. HARINGTON.

Pasteurised and dried milk as source of calcium, phosphorus, and nitrogen. A. C. WILLARD and K. BLUNT (J. Biol. Chem., 1927, **75**, 251—262).—Positive balances of calcium, phosphorus, and nitrogen were observed in children when these elements were supplied principally in the form of dried or pasteurised milk, the former being slightly the more satisfactory. C. R. HARINGTON.

Purine metabolism. I. Distribution of uric acid in blood and lymph of the dog following intravenous injection of uric acid. A. A. CHRISTMAN and H. C. ECKSTEIN (J. Biol. Chem., 1927, **75**, 201—206).—Following intravenous injection of uric acid into dogs there was found a considerable increase in the uric acid content of the lymph obtained from the thoracic duct; this may account in part for the rapid disappearance of uric acid after injection, observed by Folin and others (J. Biol. Chem., 1924, **60**, 361). C. R. HARINGTON.

Action of ammonium benzoate on the urine. J. M. JOHNSTON (Edinburgh Med. J., 1927, **34**, 223—230).—When ammonium benzoate is fed to normal persons, there is diuresis with increase in the ammonia content; urines originally giving abnormal reactions due to drugs quickly revert to normal reaction. Hippuric acid output was first increased, and then unchanged benzoic acid appeared.

CHEMICAL ABSTRACTS.

Chemical changes during the life cycle of the tent caterpillar (*Malacosoma americana*, Fab.). I. Moisture and fat. II. Nitrogen and its relation to moisture and fat. W. RUDOLFS (J. N.Y. Entomol. Soc., 1926, **34**, 249—256, 319—330).—The moisture content is lowest in the newly hatched larvæ and highest during the third to fifth larval instars. The fat content is lowest at hatching and highest when the larvæ have just pupated. The egg-mass contains 13% of nitrogen, and the growing larva 10·2% (average), decreasing from hatching to the last instar. The composition of the egg-mass was investigated in detail. CHEMICAL ABSTRACTS.

Intracellular oxidation-reduction potential. L. RAPKINE and R. WURMSER (Proc. Roy. Soc., 1927, **B**, **102**, 128—137).—Micro-injection of indicators into the cells of the salivary glands of *Chironomus* or *Calliphora* larvæ or into the oocytes of the sea-urchin or of the star-fish shows that cytoplasm and nucleus are at p_H 7·2 and r_H 19—20. In the case of *Spirogyra* the p_H is 6 and r_H is 14—16. Injection of dextrose, lævulose, sodium succinate, and sodium pyruvate into the cells of the salivary gland of *Chironomus* does not change the r_H.

W. O. KERMACK.

Effect of cold on animals. I. Chemical changes in the blood. S. YAMAGUCHI (J. Orient. Med., 1926, **5**, No. 6, 71).—When the body temperature of rabbits cannot be maintained, there is a decrease in the blood carbon dioxide, ammonia, urea, and amino-acids, and an increase in the dextrose, acetone, and lactic acid. CHEMICAL ABSTRACTS.

Behaviour of acetoacetic acid in the organism, compared with that of ethyl acetoacetate and ethyl sodioacetoacetate. E. PACE (Arch. Farm. sperim., 1927, **43**, 145—162).—In the frog, ethyl acetoacetate exerts a depressing action on the central nervous system, a dose of 0·05—0·06 g. causing temporary paralysis, and one of 0·1 g. death, with a frog weighing 20 g. Sodium acetoacetate produces in the frog nothing more than a slight torpor, even when 0·3 g. is administered to a frog of 20 g. The action of ethyl sodioacetoacetate on the frog is similar to, but less intense than, that of ethyl acetoacetate, 0·15 g. causing paralysis and 0·25 g. death. Although the elimination of these compounds from the organism occupies 24—36 hrs., the duration of the paralysis is only 2—5 hrs.

In the rabbit, ethyl acetoacetate has a weak depressing action and also induces albuminuria; the compound is completely decomposed in the organism, and the urine contains acetone and acetoacetic acid and a slightly increased proportion of ammonia, but no alcohol. Sodium acetoacetate produces no marked effects; it partly decomposes giving acetone and partly passes unchanged into the urine, which shows also increased excretion of ammonia. Ethyl sodioacetoacetate gives no acetone but is eliminated as sodium sodioacetoacetate, the alkyl group being completely oxidised in the organism; albuminuria and increase in the ammonia of the urine are also observed. T. H. POPE.

Pharmacological action of diaminoacetone. J. H. WADIA (J. Pharm. Exp. Ther., 1927, **31**, 481—483).—Diaminoacetone is pharmacologically almost inert. Following subcutaneous injection into the guinea-pig about 17% of the amount injected is excreted unchanged. E. A. LUNT.

Specific action of ketonic substances on respiration. K. GOLLWITZER-MEIER (Arch. exp. Path. Pharm., 1927, **125**, 278—286).—β-Hydroxybutyric acid and acetoacetic acid do not appear to influence respiration apart from their effect on the p_H of the blood. Acetone seems to have a specific stimulating action on the respiratory centre. W. O. KERMACK.

Mechanism of the action of iodides on nitrogen metabolism. G. P. Grabfield, C. Gray, B. Flower, and E. Knapp (J. Clin. Invest., 1927, 4, 323—329).—Increase (27%) in the nitrogen excretion of dogs follows the subcutaneous injection of sodium iodide without an increase in the sulphur excretion or change in the fluid intake and urine output.

Chemical Abstracts.

Blood-fat variations after iodine administration to rabbits. W. Büssem (Arch. exp. Path. Pharm., 1927, 126, 63—76).—Intravenous injection into rabbits of large amounts of an iodine solution (Pregl's "septoiodine") results in considerable increases in the neutral blood-fat and the free blood-cholesterol. The increase in the latter is most marked a few hours after the injection and usually the value soon returns to the original level. An organic iodine preparation ("Jodisan-Bayer") gives similar results. Small doses of iodine injected intravenously cause a fall in the neutral blood-fat but a rise in the free blood-cholesterol. After the administration *per os* of a dose of thyroxine (0·6 mg.) there is a temporary small fall in the neutral fat and a corresponding rise in the free cholesterol of the blood. A. Wormall.

Detoxication of nitrites. E. Hesse (Arch. exp. Path. Pharm., 1927, 126, 209—221).—Animals poisoned by sodium nitrite are protected by administration of a mixture of a suitable phenol and iron salt, such as orcinol and ferric chloride or guaiacol and Prussian-blue. This effect is due partly to the formation of an insoluble compound between the iron and the nitrosophenol which is produced and partly by the action of the phenol in inhibiting the production of methæmoglobin by the nitrite.

W. O. Kermack.

Fluid and chloride exchange between blood and cells after administration of theophylline. K. O. Möller (Arch. exp. Path. Pharm., 1927, 126, 143—158).—Independently of its action on the kidneys theophylline causes water and chlorides to pass from the tissues into the blood.

W. O. Kermack.

Sulphate diuresis and combined sulphate–theophylline diuresis. K. O. Möller (Arch. exp. Path. Pharm., 1927, 126, 159—179).—Intravenous administration of sodium sulphate has a marked diuretic action and lowers the concentration of chlorides in the blood. Simultaneous administration of theophylline and sodium sulphate causes a much more marked diuresis and a much larger excretion of chlorides than does either separately. The excretion of sodium sulphate administered intravenously is markedly increased by the administration of theophylline. W. O. Kermack.

Action of theophylline on the excretion of chlorides and water. K. O. Möller (Arch. exp. Path. Pharm., 1927, 126, 180—203).—The essential action of theophylline on the kidneys is to cause an increase in the excretion of chlorides. This is accompanied by an increase in the excretion of water dependent on the amount of water present in the organism. W. O. Kermack.

Activity of heart-specific glucosides of the second order. P. Haupstein (Arch. exp. Path. Pharm., 1927, 126, 121—128).—Glucosides acting on the heart are divided into two groups, the first containing the glucosides of *Digitalis purpurea*, whilst the second group contains all the others. The lethal doses for rabbits of *Adonis* glucoside I, *Adonis* glucoside II, scillarin, *Convallaria* glucoside, and "*g*-strophanthin" have been determined, using intravenous injection, slow and rapid intravenous infusion, subcutaneous injection, and introduction into the stomach. With intravenous injection it is found that the potency (reciprocal of the lethal dose) increases from *Adonis* glucoside I to "*g*-strophanthin" in the order given, and that the time between the injection and death decreases in the same order. The action of these drugs on the heart and the absorption of the glucosides after subcutaneous injection and oral administration are discussed.

A. Wormall.

Velocity of action of various narcotics. L. Lendle (Arch. exp. Path. Pharm., 1927, 125, 287—300).—The rate of action of various narcotics has been determined by a new method. No relation appears to exist between the reaction time and the velocities of diffusion of these compounds *in vitro*.

W. O. Kermack.

Comparative pharmacology of certain trialkyl- and dialkyl-barbituric acids. A. W. Dox and A. M. Hjort (J. Pharm. Exp. Ther., 1927, 31, 455—472).—A comparison has been made, mainly on mice, of numerous dialkyl and trialkyl derivatives of barbituric acid with particular reference to minimum anæsthetic dose and minimum lethal dose. Of the dialkyl derivatives studied 5-ethyl-5-*iso*butyl-, 5-ethyl-5-*n*-butyl-, 5-ethyl-5-*iso*amyl-, and 5-ethyl-5-hexyl-barbituric acids are most suitable as hypnotics, and of the trialkyl series studied only 1-methyl-5-ethyl-5-*iso*amylbarbituric acid is suitable.

E. A. Lunt.

Elimination and toxicology of veronal. G. Sensi (Annali Chim. Appl., 1927, 17, 447—456).—Determinations made by the author's method (this vol., 173) show that from 70 to 85% of the veronal administered to dogs is eliminated in the urine. The extent of the elimination depends on the method of its introduction into the organism, and on the quantity and solubility of the compound administered, and also varies with different animals. Animal metabolism undoubtedly exerts a destructive action on veronal, and putrefaction of the organs results in gradual disappearance of the drug; the nature of the resultant products is unknown. These results contradict those of Ipsen (Wien. Med. Wochenschr., 74, 2025). In toxicological cases, veronal is best sought in the urine and kidneys. T. H. Pope.

Alkaloid trichloroacetates. Use of trichloroacetic acid in toxicology. II. Detection of alkaloids in viscera. M. G. Florence (Bull. Soc. chim., 1927, [iv], 41, 1242—1244).—Small amounts of alkaloids in viscera and in other organic matter may be isolated by extraction with a 20% aqueous solution of trichloroacetic acid at 35°. The filtrate from the coagulated protein is extracted with light petroleum to remove neutral substances, basified, and re-extracted separately with different solvents to remove

the alkaloids. A partial separation of the latter is obtained by this method. The method has been applied to the detection of alkaloids in milk, blood, and the viscera of poisoned animals; in some cases the recovery amounts to 91%. G. A. C. GOUGH.

Pharmacological action of certain quinine derivatives. W. E. DIXON and P. DE (J. Pharm. Exp. Ther., 1927, **31**, 407—432).—Quitenine, *iso*propylhydrocupreine, benzoyl*iso*propylhydrocupreine, *iso*amylhydrocupreine, benzoyl*iso*amylhydrocupreine, eucupinotoxin, *iso*octylhydrocupreine, and allylhydrocupreine have been compared with quinine, with reference to their action on *Paramœcia*, ciliary movement, isolated plain and striated muscle, isolated frog's heart, red blood-corpuscles, and as local anæsthetics. The most toxic of the substances examined is cucupinotoxin, which causes acute œdema on intravenous injection. The local anæsthesia produced by these drugs is due to their action on the nerve endings. E. A. LUNT.

Blood-gases in strychnine poisoning. W. LUDWIG and H. EBSTER (Arch. exp. Path. Pharm., 1927, **126**, 245—254).—Decrease of oxygen in the blood during strychnine poisoning is attributable to the paralysis of the respiratory system. Strychnine has no effect *in vitro* on the blood dissociation curves of oxygen or carbon dioxide. W. O. KERMACK.

Action of ergotamine ("gynergen") on the blood-sugar level in rabbit and man. W. SEIDEL (Arch. exp. Path. Pharm., 1927, **125**, 269—277).—Administration of ergotamine tartrate lowers the blood-sugar but the duration of the hypoglycæmia is too short to be of therapeutic value in diabetes. W. O. KERMACK.

Physiological antagonism between calcium ions and ergotamine. R. AGNOLI (Arch. exp. Path. Pharm., 1927, **126**, 222—234).—Ergotamine exercises an inhibitory action on the heart and the smooth muscle in the absence of calcium ions but this effect disappears in their presence. W. O. KERMACK.

Chemotherapy. II. Internal antisepsis by means of sulphato-compounds. M. COPLANS and A. G. GREEN (J. Pharm. Exp. Ther., 1927, **31**, 433—443; cf. this vol., 172).—Preliminary experimental evidence is cited for the use of sulphato-green, sulphato-violet, and their leuco-compounds as internal antiseptics by virtue of the generation by hydrolysis, *in vivo*, from such substances of basic compounds with a bactericidal action. This is due to the relative instability of the sulphato-group in the side-chain of these compounds, in comparison with the stability of the sulphonic groups attached to the nucleus in the ordinary triphenylmethane series of acid-greens and acid-violets. E. A. LUNT.

Action of caffeine on micro-organisms. G. B. ZANDA (Arch. Farm. sperim., 1927, **43**, 277—288).—In the proportion of 1 g. per 100 c.c., caffeine prevents putrefaction of albumin solutions and destroys or inhibits the development of pathogenic organisms. T. H. POPE.

Pharmacological action of some compounds related to camphor. I. J. ISCHIKAWA (Arch. exp. Path. Pharm., 1927, **126**, 41—47).—ω-Aminopinane, ω-aminopinene, and *r*-homocamphenilone have very little antiseptic action against *B. coli*, but with Metschnikoff's *vibrio* the antiseptic value is more marked and is greatest in the case of ω-aminopinane. The effect of these substances on the isolated frog's heart has been determined. A. WORMALL.

Germicidal effect of staining solutions. G. A. ECKFELDT and S. A. KOSER (Stain Tech., 1927, **2**, 109—114).—Gentian-violet, crystal-violet, and carbol-fuchsin generally destroy the majority of non-spore-forming bacteria and yeasts in cover-slip preparations. Non-spore-forming organisms never survive the Gram staining process. Methylene-blue stains exert very little, if any, germicidal power and "Indian ink" is entirely without action. H. W. DUDLEY.

Effect of neutral-red preparations on *Paramœcium caudatum*. C. N. WILSON (Stain Tech., 1927, 2, 115—123).—Various commercial samples of this dye varied in physical properties and toxicity to *Paramœcium* owing to impurities. Neutral-red was toxic in a concentration of 1 : 100,000. H. W. DUDLEY.

Influence of sodium acetate, borate, citrate, and phosphate on the activity of pancreatic amylase. H. C. SHERMAN, M. L. CALDWELL, and J. E. DALE (J. Amer. Chem. Soc., 1927, **49**, 2596—2598).—In presence of 0·05*M*-sodium chloride and 0·004*M*-sodium borate, citrate, or phosphate, for ½ hr. periods at 40°, pancreatic amylase exerts its optimum activity at p_H 7·0—7·2. These activities are the same in presence of the citrate or phosphate, and slightly less in presence of borate or acetate, but this is probably due to a lowering of the buffering effect rather than to specificity of the acetate or borate ions. In presence of 0·05*M*-sodium chloride, the activity is independent of the concentration of the phosphate from 0·0005*M* to 0·05*M*, and of the borate from 0·001*M* to 0·01*M*, provided optimal p_H is maintained. Under the latter condition, the activity in starch solutions containing 0·05*M*-sodium chloride is unaffected by phosphate. It is concluded that acetate, borate, citrate, and phosphate have no marked specific effect on the enzyme. F. G. WILLSON.

Human fructosediphosphatase. II. E. FORRAI (Biochem. Z., 1927, **189**, 155—158).—Saline extracts of human liver, muscle, and kidney contain fructosediphosphatase, and after inactivation by heating are not reactivated by addition of insulin. Insulin has no effect on the hydrolysis *in vitro* of fructosediphosphoric acid by such extracts. P. W. CLUTTERBUCK.

Enzymic synthesis of protein. P. RONA and F. CHROMETZKA (Biochem. Z., 1927, **189**, 249—264).—The formation of sparingly soluble products by the action of pepsin on concentrated aqueous solutions of protein decomposition products at p_H 4—5 or by the action of trypsin at p_H 5·5 as reported by Wasteneys and Borsook (A., 1925, i, 97, 102, 472, 865) is completely confirmed, but the conclusion of the latter that this represents synthesis of protein is contested, the sparingly soluble products being

formed in the case of pepsin by deamination and of trypsin by further hydrolysis of the substrate.
P. W. CLUTTERBUCK.

Separation of trypsin and enterokinase by ultrafiltration. H. BECHHOLD and L. KEINER (Biochem. Z., 1927, **189**, 1—17).—Enterokinase is completely retained by a 4% acetic acid–collodion membrane, whilst trypsin still passes even a 10% membrane. Addition of the filtrate to the residue results in complete reactivation. The kinase particles must be greater than those of albumin or hæmoglobin, and about equal to those of glutin, whereas trypsin is extremely finely dispersed (semi-colloid). Neutralisation or making faintly alkaline with potassium hydroxide, but not with ammonia, increases the dispersion of the kinase. Kinase obtained by ultrafiltration contains proteins but is free from ash, carbohydrates, and protein decomposition products. The kinase and protein fraction is, by weight, 2·8% of the crude trypsin. Trypsin ultrafiltrates are proteolytically completely inactive, whereas the kinase fraction retains about 16% of the original activity and this "residual activity" cannot be reduced by exhaustive washing with water, 0·05*N*-ammonia solution, or with 0·01% hydrogen chloride solution. Separated trypsin is completely destroyed by keeping for 2·5 days, but the kinase and the trypsin which gives its residual activity retain their activity completely for at least 8 days. Addition of albumin inhibits tryptic activity and its removal by ultrafiltration leads to reactivation. Tryptic activity cannot be reduced by albumin, however, below the value of the residual activity (16%) and the residual activity of the kinase is not affected by addition of albumin. There is, therefore, no dynamic equilibrium between kinase and trypsin, but a part of the trypsin is free and removable by ultrafiltration, whilst 16% is bound to the kinase and cannot be detached either by ultrafiltration or by albumin. The inhibitory action of albumin is not due to any power to adsorb trypsin. P. W. CLUTTERBUCK.

Philothion. II. G. ROSSI (Zymologica, 1927, **2**, 105—115).—Experiment shows that the hydrogenation of sulphur by extracts of brewers' yeast, and of horse's liver and kidneys, at 40° (cf. Biochem. Terap. sperim., 1924, 351) does not take place if these extracts are previously heated at temperatures which enzymes are unable to withstand. The evolution of hydrogen sulphide observed by Abelous and Ribaut when such extracts, after being heated to boiling, act on sulphur at 40° (A., 1904, i, 704) either results from the insufficiency of the heating or represents the liberation of gas formed during the heating and adsorbed by the constituents of the extracts.
T. H. POPE.

Metabolism of yeast. O. WARBURG (Biochem. Z., 1927, **189**, 350—353).—Commercial bakers' yeast respires 8—10 times as strongly as pure laboratory cultures, the respiration being a property not determined by the type of yeast but one arising during manufacture and decreasing again under other conditions of growth. P. W. CLUTTERBUCK.

Action of carbon monoxide and nitric oxide on respiration and fermentation. O. WARBURG (Biochem. Z., 1927, **189**, 354—380).—Regarding iron as the respiratory enzyme, its distribution between oxygen and carbon monoxide is mathematically and experimentally investigated. It is shown that the mechanisms of fermentation and respiration are related processes. The disturbances of such distribution by respiration and irradiation are examined. The distribution of hæmoglobin between oxygen and carbon monoxide shows that hæmoglobin is related to but not identical with the respiratory enzyme. Cytochrome does not combine with carbon monoxide. Carbon monoxide inhibits the rate of multiplication of yeast cells and fermentation increases more slowly in carbon monoxide than in nitrogen, but with the same number of cells the rate is the same. Carbon monoxide does not inhibit formation of lactic acid or alcoholic fermentation. Nitric oxide forms a dissociating compound with the fermentation enzyme but with yeast cells it has also an irreversible side-reaction whereby cells are killed, the more quickly the higher the temperature. This side-reaction is not obtained with tumour cells (cf. A., 1926, 434, 1277). P. W. CLUTTERBUCK.

Biochemical conversion of oximinopyruvic acid into alanine. K. MAURER (Biochem. Z., 189, 216—219).—Pyruvic acid oxime is reduced in a fermenting sugar solution to alanine, identified as the α-naphthylcarbimide and as the benzoyl derivative. A control experiment indicated that the alanine did not arise from yeast protein during autolysis. P. W. CLUTTERBUCK.

So-called co-enzyme of alcoholic fermentation. A. J. KLUYVER and A. P. STRUYK (Proc. K. Akad. Wetensch. Amsterdam, 1927, **30**, 569—575).—Theoretical. The so-called co-enzyme of zymase is considered to be a complex with a number of factors each essential to the alcoholic fermentation of hexoses by zymase: (1) with an introductory hydrogen acceptor such as acetaldehyde which, when Harden's technique (A., 1917, i, 501) is employed, will reactivate washed zymase, (2) with hexosephosphate which is the missing factor when Buchner and Haehn's technique (A., 1910, i, 648) is employed, (3) with antiprotease when Meyerhof's technique (A., 1919, i, 57) is employed. The restoration of the activity to inactivated zymase as prepared by Meyerhof and thought by him to be due to the existence of a widely distributed co-enzyme is due to the protective action exerted on the zymase by the preferential reaction of the proteolytic enzymes, always present, with smaller protein complexes than those usually associated with the zymase. Thus the partial hydrolysate from inactivated zymase acts as a co-enzyme for unhydrolysed inactivated zymase. E. A. LUNT.

Modifications in the course of alcoholic fermentation by the action of the oscillating electromagnetic field on yeast. E. BENEDETTI (Atti R. Accad. Lincei, 1927, [vi], **5**, 1029—1034).—The fermentative activity of yeast, exposed to the action of an oscillating electromagnetic field, is first diminished to a minimum, then increased, and again diminished to a second minimum.
T. H. POPE.

Poisonous action of quinine compounds on the power of fermentation of living yeast. P. Rona and H. W. Nicolai (Biochem. Z., 1927, **189**, 331—347).—A method is given for investigating separately the effect of the concentration of alkaloid and of the duration and p_H of the reaction on the poisoning of fermentation by quinine compounds. Poisoning was maximal after 30—60 min. The optimal poisoning effect was obtained at the p_H at which the alkaloidal base was set free. This p_H for vucine and eucupine is 4·4—5·3, and these substances, in distinction from quinine and optoquin, have considerable toxic action at this p_H. P. W. Clutterbuck.

Action of electric current on proteins and enzymes. V. Sadikov (Bull. Acad. Sci. U.R.S.S., 1927, 5—6, 385—396).—When an electric current is passed through dilute sodium hydroxide solution in which protein is suspended or dissolved, proteolysis appears to take place. Fats and polysaccharides are also decomposed under similar conditions. A whole animal, *e.g.*, a frog or mouse, immersed in sodium hydroxide solution through which a current is passed is largely dissolved. The effects of an electric current on bacteria, diphtheria toxin, and enzymes are also described. W. O. Kermack.

Chemical analysis of the tubercle bacillus. T. B. Johnson and R. D. Coghill (Amer. Rev. Tuberculosis, 1927, **15**, 494—499).—All cellular changes caused by autolysis must be minimised; heating is avoided, and fat is extracted with cold ether. Attempts to isolate a globulin fraction were unsuccessful. Most of the protein is soluble in 0·5% sodium hydroxide solution, although insoluble in water, but this fraction gives a low tuberculin reaction. The cold-water extracts contain a potent tuberculin. Chemical Abstracts.

Growth of the typhoid bacillus. A. Doskocil (Biochem. Z., 1927, **189**, 314—321).—Ammonium salts and amino-acids serve as a source of nitrogen for *B. typhosus* but amido- and imido-nitrogen (except of bile salts) is not generally accessible. Dextrose, lactic acid, the carbon chain of alanine, asparagine, and glutamic acid serve as a source of carbohydrate but not so the carbon chains of tyrosine, lysine, and glycine. The alanine chain probably passes through the stages of lactic, pyruvic, and glyoxylic acids. The bacillus is found in man to the greatest extent in the small intestine, blood, and gall-bladder. In late summer it thrives greatly in streams in virtue of the ammonium salts of organic acids arising from decaying vegetation. P. W. Clutterbuck.

Bacterial proteins. Presence of alcohol-soluble proteins in bacteria. K. Goadby (Proc. Roy. Soc., 1927, **B**, **102**, 137—142).—Bacteria suspended in sodium chloride solution (0·85%) when shaken with ether containing benzoyl chloride for 1—3 days are deprived of the carbohydrate material, which passes into the ethereal solution. The bacteria washed with acetone and dried are extracted at 37° with sodium chloride solution (0·85%) for 24 hrs., when some protein is removed. They are then suspended in 70% alcohol for 24 hrs. at 37°, which extracts a protein in the case of a large number of bacteria. The protein gives most of the usual protein reactions, and is similar to alcohol-soluble proteins from the seeds of cereals. W. O. Kermack.

Imitation of organic forms by means of sodium stearate. L. A. Herrera (Atti R. Accad. Lincei, 1927, [vi], 6, 18—22; cf. A., 1926, 244, 435; this vol., 279).—When added to a dilute solution of stearic acid in ordinary petrol, drops of 14% sodium hydroxide solution coloured with soap-black simulate a number of organisms, both in form and in their pulsations and changes of shape. The results are regarded as indicative of the importance of the fatty acids in morphogenesis. T. H. Pope.

Blood-sugar. VIII. Blood-sugar and -phosphorus curves. VI. Adrenaline. H. K. Barrenscheen, A. Eisler, and L. Popper (Biochem. Z., 1927, **189**, 119—124).—After subcutaneous and intravenous injection of adrenaline, the inorganic phosphate of blood and the urinary phosphate are decreased, the latter considerably, the effect being the reverse of that due to insulin (cf. A., 1926, 1270). P. W. Clutterbuck.

Diabetes and the action of insulin. XI. The organ secreting glycæmin. XII. Direct proof of the secretion of insulin by the pancreas. S. Dietrich (Arch. exp. Path. Pharm., 1927, **125**, 326—335, 336—342; cf. this vol., 795).—XI. The isolated frog's liver treated with ergotamine yields dextrose under the action of glycæmin but not of adrenaline. From this and other evidence it is concluded that the liver is the only source of glycæmin.

XII. After subcutaneous administration of dextrose or after vagus stimulation, insulin may be detected in the pancreatico-duodenal vein when it cannot be found in the carotid blood. W. O. Kermack.

Action of insulin. I. Inhibition of phosphate excretion by insulin. H. K. Barrenscheen and R. Berger (Biochem. Z., 1927, **189**, 302—307).—The power of the kidney of a mouse poisoned with insulin to hydrolyse sodium hexosediphosphate is considerably less than that of a normal mouse. This inhibition of kidney phosphatase possibly explains the decreased urinary phosphate excretion under the action of insulin. P. W. Clutterbuck.

Insulin and fructosephosphoric acid. E. Forrai (Biochem. Z., 1927, **189**, 150—154).—Insulin has no action on the hydrolysis, *in vitro*, of fructose-diphosphoric acid by the enzymes of muscle pulp, blood, or liver, whilst, in rabbits, injection of fructose-diphosphoric acid does not alleviate hypoglycæmic convulsions. P. W. Clutterbuck.

Insulin and fat metabolism. J. Hepner and O. Wagner (Biochem. Z., 1927, **189**, 322—330).—The effect of insulin on the liver-fat in rats, dogs, and guinea-pigs is investigated and the decrease in iodine value obtained under insulin is regarded as due to decreased desaturation of fat, it being assumed that fat transport from the periphery is inhibited by insulin. P. W. Clutterbuck.

Absence of hypoglycæmia after intraperitoneal administration of insulin to well-fed rabbits. F. M. Hoskins and F. F. Snyder (J. Biol. Chem.,

1927, 75, 147—155).—Intraperitoneal administration of insulin causes hypoglycæmia in fasting but not in well-fed rabbits. It is thought that the difference is due to the passage of the insulin through the liver when administered by the intraperitoneal route.
C. R. HARINGTON.

Thyroxine in intermediate metabolism. A. SIMON (Biochem. Z., 1927, 189, 265—269).—Addition of thyroxine to rabbit's liver pulp generally caused increased (11—247%), but sometimes decreased acetaldehyde formation, and glycogen determinations suggest that this change is due to the decomposition of carbohydrate. P. W. CLUTTERBUCK.

Antimony trichloride as a possible quantitative reagent for vitamin-*A*. F. WOKES and S. G. WILLIMOTT (Analyst, 1927, 52, 515—524).—The reaction between antimony trichloride and cod-liver oil is a chemical one with a temperature coefficient of 2. It is probably of a condensation type and may be retarded by dehydration of the solvents. The conditions suggested for the test are : 2 c.c. of a decanted solution of antimony trichloride (recrystallised from chloroform) in anhydrous chloroform (concentration 26 or 27% wt./vol.) mixed in a ½ in. cell with a freshly-prepared solution of oil in chloroform (dried over calcium chloride), of such a concentration that 0·1—0·3 c.c. is used. The colour is read 30 sec. after mixing, in Lovibond blue units (the reading should be below 18) at 16°, a divergence of more than 1° requiring a correction. Since the blue colour rapidly changes to yellow, red, and reddish-brown, the time factor is important. D. G. HEWER.

Reaction of fatty extracts of certain organs with the antimony trichloride test for "vitamin-*A*." W. H. WILSON (Biochem J., 1927, 21, 1054—1058).—By this colour reaction it is shown that fatty extracts from the human liver may contain 25 times as much vitamin-*A* as a good sample of cod-liver oil. The intensity of the reaction varies within wide limits in different livers and may in some cases be no more than 1/250 of the maximum recorded. The substance responsible for the colour reaction is present in considerable amount in the liver at birth, but is not present in the placenta. The ether extract of livers of healthy animals slaughtered for food was found to contain from 6 to 12·5 times the amount of vitamin-*A* present in cod-liver oil. S. S. ZILVA.

Vitamin-*A* of irradiated milk. G. C. SUPPLEE and O. D. DOW (J. Biol. Chem., 1927, 75, 227—239).—Milk (dried or fresh) which has been irradiated with ultra-violet light in order to induce in it antirachitic activity, has neither suffered any loss of vitamin-*A* nor acquired toxic properties. C. R. HARINGTON.

Separation of a substance from oils which inhibits destruction of vitamin-*A* by ferrous sulphate. H. W. ESTILL and E. V. MCCOLLUM (J. Biol. Chem., 1927, 75, 157—162).—On mixing a pyridine solution of lithium chloride with a light petroleum solution of cod-liver oil, a precipitate was obtained, which, on stirring with light petroleum, could be separated into a light and a heavy portion. Both fractions, after removal of lithium chloride, were free from vitamin-*A* and -*D*, but the light fraction, which is regarded as being perhaps vitamin-*E*, when added to the diet containing ferrous sulphate (J. Amer. Med. Assoc., 1927, 88, 1047) prevented the occurrence of ophthalmia. C. R. HARINGTON.

Relation of inorganic dietary constituents to production of ophthalmia in rats. J. H. JONES (J. Biol. Chem., 1927, 75, 139—146).—The diet described by McCollum and others (J. Biol. Chem., 1922, 53, 313) leads to ophthalmia in rats only when it is made up at long intervals, and in this case the rapidity of appearance of the ophthalmia is proportional to the amount of ferrous sulphate in the diet; a catalytic effect of the latter salt on the oxidation of vitamin-*A* is therefore the probable explanation of the results. C. R. HARINGTON.

Multiple nature of vitamin-*B*. H. C. SHERMAN and J. H. AXTMAYER (J. Biol. Chem., 1927, 75, 207—212).—Autoclaving caused destruction of almost all the antineuritic activity of bakers' yeast; a mixture of such material with ground whole wheat gave, however, better growth than an equal amount of fresh yeast or of whole wheat. Vitamin-*B* is therefore divided into vitamin-*F* (heat-labile antineuritic) and vitamin-*G*, both factors being necessary for growth. On this basis, whole wheat is richer in vitamin-*F* than in vitamin-*G*, and the reverse is true of milk. C. R. HARINGTON.

Extraction of vitamin-*B* from wheat germ. E. V. MCCOLLUM and H. D. KRUSE (Amer. J. Hyg., 1926, 6, 197—200).—The efficiency of 95% alcohol containing 1% of various organic and inorganic acids or salts as an extractive for vitamin-*B* with minimal contamination by other substances was examined. The best results were obtained with alcohol containing tannic or gallic acid.
CHEMICAL ABSTRACTS.

Relation between the vitamin-*B* content of the ration eaten [by cows] and of the milk produced. S. I. BECHDEL and H. E. HONEYWELL (J. Agric. Res., 1927, 35, 283—288).—Three cows were fed for more than 2 yrs., throughout their growth period, on a ration proved to be decidedly deficient in vitamin-*B* by experiments with rats. The milk from these cows, fed to rats as a supplement to a basal ration free from vitamin-*B*, was equal to milk from normally fed cows in supplying the deficiency. It would appear that cows, and possibly other ruminants, possess the power to synthesise vitamin-*B* and are not dependent on its presence in the ration eaten.
C. T. GIMINGHAM.

Effect of administration of active iron compounds on the course of avitaminosis in pigeons. P. M. SUSKI (Biochem. Z., 1927, 188, 459—464).—In pigeons on a polished rice diet, a daily dose of 5 mg. of active iron oxide prevented loss in weight but did not retard death. A daily dose of 50 mg. of unirradiated or irradiated ferrous sulphate retarded the fall in weight and the irradiated material also retarded death. Active iron carbonate acted unfavourably on the course of avitaminosis (cf. this vol., 382). P. W. CLUTTERBUCK.

Nutrition. VIII. Comparative vitamin-*B* value of foodstuffs. Cereals. I. R. H. A.

PLIMMER, J. L. ROSEDALE, W. H. RAYMOND, and J. LOWNDES (Biochem. J., 1927, 21, 1141—1161).—The estimations were carried out on pigeons by administering diets containing various quantities of the foodstuffs tested mixed with other ingredients (rice or flour and fish-meal) free from vitamin-*B*. The percentage of the foodstuffs necessary for maintenance was taken as a standard. The following substances were investigated and are arranged in order of activity: dried yeast, wheat germ, marmite, bakers' yeast, bran, middlings, whole wheat flour, rye (whole), millet, dari, maize (kibbled), barley (whole), buckwheat, whole oats, Sussex ground oats, and oatmeal. The last three were protective in diets containing 95% of the substance, whilst in the case of dried yeast 4% was sufficient. Maize germ and maize gluten contained little of the vitamin. The quantities of some of the above substances required to enable the birds to rear their young were also ascertained. These were higher than those required for maintenance.

S. S. ZILVA.

Experiments with Jansen and Donath's antiberiberi vitamin. C. EYKMAN (Proc. K. Akad. Wetensch. Amsterdam, 1927, 30, 376—382).—Investigations with pigeons and cocks demonstrate that the vitamin isolated by Jansen and Donath (this vol., 382) has the power to prevent and to cure polyneuritis gallinarum. H. F. GILLBE.

Synthesis of antineuritic vitamin by yeast. G. L. PESKETT (Biochem. J., 1927, 21, 1102—1103).—Yeast grown on a synthetic medium containing very little antineuritic vitamin and under conditions excluding bacterial contamination produced considerably more of the vitamin than the amount present in the medium. Synthesis is thus definitely established (cf. Hawking, this vol., 796). S. S. ZILVA.

Alkali reserve and p_H in avitaminosis-*C*. G. MOURIQUAND, A. LEULIER, and P. SÉDALLIAN (Compt. rend., 1927, 185, 551—553).—In avitaminosis-*C* (guinea-pigs) no lowering of the blood-p_H occurs, whilst the fall in alkaline reserve is slow and appears only after the 27th day. The scorbutic lesions are not a function of the acidosis. The development of experimental scurvy takes place in two stages. In the first, the predystrophic, typical osteohæmorrhagic manifestations are seen, whilst in the second, the dystrophic, loss of weight takes place together with a fall in the blood-iron, the cholesterol of the suprarenals, and the alkaline reserve. The two phases appear to exist in other diseases besides scurvy.

W. ROBSON.

Antiscorbutic fraction of lemon juice. VI. E. HOYLE and S. S. ZILVA (Biochem. J., 1927, 21, 1121—1127; cf. Daubney and Zilva, A., 1926, 871).—The concentrated antiscorbutic fraction from lemon juice does not contain any manganese, but contains traces of iron, phosphorus, and sulphur. These elements of the active fraction behave on dialysis like the active principle. S. S. ZILVA.

Vitamin-*D*. I. Activation of cholesterol. A. JENDRASSIK and A. G. KEMENYFFI (Biochem. Z., 1927, 189, 180—190).—The view that ergosterol is the activatable substance is confirmed, but the authors disagree with the suggestions that the activity of irradiated cholesterol is due to ergosterol present merely as an impurity, and also that removal of this impurity gives a cholesterol which is no longer activatable. The authors suggest that provitamin can be re-formed from that part of the cholesterol which contains so-called water of crystallisation. By withdrawing the last traces of water from cholesterol the provitamin present is destroyed and the possibility of re-formation is lost, and the characteristic provitamin absorption bands between 280 and 300 μμ disappear. Fractionation of irradiated cholesterol with ethyl alcohol shows that cholesterol is only partly activated, but after removal of the active material an inactive substance is left which can always, under suitable conditions, be reactivated. The bromination experiments of Windaus could not be confirmed, reduction of the bromination product always giving an activatable cholesterol. The difference is supposed to be due to the fact that the authors, after bromination and reduction, treated their cholesterol with water to make possible the re-formation of provitamin. Windaus' result that boiling cholesterol with animal charcoal completely removes the activatable substance is confirmed.

P. W. CLUTTERBUCK.

Antirachitic value of irradiated cholesterol and phytosterol. VIII. Activation of sterol fractions by ultra-violet irradiation. A. F. HESS and R. J. ANDERSON (J. Biol. Chem., 1927, 74, 651—657).—α-Sitosterol (when freshly prepared) was rendered strongly antirachitic by irradiation with ultra-violet light, whilst β- and γ-sitosterols, which had been purified by bromination and subsequent reduction, could not be so activated. C. R. HARINGTON.

Photochemical production of vitamin-*D* from ergosterol. O. ROSENHEIM and T. A. WEBSTER (Lancet, 1927, ii, 622—625).—The lowest protective dose of irradiated ergosterol (vitamin-*D*) for the rat is 0·0001—0·00005 mg. per day. The maximum activity was produced within 30 min. by the radiations of the mercury vapour lamp and remained constant up to 4 hrs.' irradiation, although decomposition of the ergosterol proceeded throughout this period. Probably, after a short initial period, the formation and destruction of the vitamin take place at the same rate, so that the activity remains constant until the ergosterol is exhausted. Ergosterol is activated by sunlight; this is significant in connexion with the known curative effect of sunlight in rickets.

H. W. DUDLEY.

Relation of vitamin-*E* to iron assimilation. N. SIMMONDS, J. E. BECKER, and E. V. MCCOLLUM (J. Amer. Med. Assoc., 1927, 88, 1047—1050).—The death of rat-fœtuses by deficiency in vitamin-*E* is due to a crisis in their assimilation of iron. Ferrous sulphate (0·2% of the diet) is harmful, but not ferric citrate or wheat-germ oil. Liver contains much iron, and liver fats contain much vitamin-*E*.

CHEMICAL ABSTRACTS.

Manifestations of life in fruit and foliage and their detection by means of the potentiometer. F. SCURTI and D. CORTESE (Annali Chim. Appl., 1927, 17, 407—414).—All fruits, foliage, and vegetables contain well-defined electrical systems, which may

be measured with the electrometer by immersing two platinum electrodes in two different tissues of the same plant or of the same organ. In such systems the *P.D.* varies greatly with the tissues connected, and any tissue may act as either positive or negative pole. The electrical potential is always greatest with the fresh material. T. H. POPE.

Chemical composition of plants in relation to photoperiodic changes. G. T. NIGHTINGALE (Wisconsin Agric. Exp. Sta. Res. Bull., 1927, No. 74, 1—63).—Tomato and salvia plants may store nitrate for subsequent conversion into other nitrogen compounds. Hemicellulose is utilised as a source of sugar. When there is no external supply of nitrogen or opportunity for carbohydrate synthesis, and reserve carbohydrates are depleted, there is decomposition of protein and increase in amino-acids, amide-nitrogen, and proteose-nitrogen. Salvia, unlike tomato, is limited in the assimilation of nitrate by a 7 hr. day, even although carbohydrate is available. Carbohydrates accumulated in the short-day plants. Plants subjected to a short photo-period gained more in total nitrogen than those subjected to a long photo-period.
CHEMICAL ABSTRACTS.

Photosynthesis of naturally occurring compounds. I. E. C. C. BALY, J. B. DAVIES, M. R. JOHNSON, and H. SHANASSY. **II.** E. C. C. BALY, W. E. STEPHEN, and N. R. HOOD. **III.** E. C. C. BALY and J. B. DAVIES.—See this vol., 1040, 1041.

Photochemical formation of peroxides during oxygen transport by chlorophyll. H. GAFFRON (Ber., 1927, **60**, [*B*], 2229—2238).—Attempts to isolate peroxides of fluorescent dyes which are active in promoting transport of oxygen have been unsuccessful. Acceptor peroxides are, however, produced during the photo-oxidation of aliphatic amines in the presence of chlorophyll. If a solution of chlorophyll in amylamine is exposed to light and then placed in the dark, the quantity of peroxidic oxygen is approximately equal to the amount of molecular oxygen absorbed. This oxygen is quantitatively evolved when a catalyst, such as manganese dioxide, is added to the darkened solution; it can be determined quantitatively by the iodometric method. Photochemical action depends greatly on the solvent used, increasing more than one hundredfold when solutions in acetone or pyridine are used in place of aqueous solutions; the absorption of oxygen ultimately reaches 2 mols. for each mol. of primary or secondary amine. Tertiary and aromatic amines are more stable after illumination; a proportion of the oxygen is evolved spontaneously when the solution is placed in the dark, but this can be reduced to 2—3% by dilution of *iso*amylamine with dioxan. Addition of a molecular proportion of water to *iso*amylamine causes only one half of the absorbed oxygen to be subsequently removable; further addition of water up to 50% has no further effect and the peroxide produced is completely stable (hence probably hydrogen peroxide). In di*iso*butylamine and in ethylamine dissolved in dioxan photo-oxidation proceeds much more slowly and 65% and 50% of the absorbed oxygen respectively is subsequently recoverable as such. H. WREN.

Aspect of the biochemistry of sugars. P. A. LEVENE (Nature, 1927, **120**, 621).—Polemical against Robinson (this vol., 960). A. A. ELDRIDGE.

Biochemistry of the sugars. R. ROBINSON (Nature, 1927, **120**, 656).—A reply to Levene (see preceding abstract). A. A. ELDRIDGE.

Correlation of chemical composition with hardiness in brambles. R. V. LOTT (Missouri Agric. Exp. Sta. Res. Bull., 1926, No. 92, 1—22).—The hardiness is related to the percentage of bound water, as determined by the dilatometer method. The correlation coefficient between the bound water and pectin is $0{\cdot}67 \pm 0{\cdot}06$, and between the protein-nitrogen and bound water $0{\cdot}60 + 0{\cdot}07$.
CHEMICAL ABSTRACTS.

Hydrogen-ion concentration of plant tissues. I. Method. J. SMALL. **II. Flowering and other stems.** M. W. REA and J. SMALL (Protoplasma, 1926, **1**, 324—333, 334—344).—I. A micro-colorimetric indicator method is described.
II. The plant families are classified according to the reaction of the tissue of the young flowering stem.
CHEMICAL ABSTRACTS.

Adaptability of the quinol electrode to the determination of p_H in expressed plant saps. M. DOMONTOVICH (Nauch. Agron. Zhur., 1925, **2**, 700—712).—The results are in fair agreement with those obtained with the hydrogen electrode.
CHEMICAL ABSTRACTS.

Influence of reaction of culture medium on growth of strawberry plants. L. S. MORRIS and J. W. CRIST (Mich. Agric. Exp. Sta. Tech. Bull., 1927, No. 77, 1—16).—The range for survival is p_H 4·0—8·0, for satisfactory growth 5·0—7·0, for optimal growth 5·7—6·0. Absorption of iron and aluminium was greater from the more acid solutions.
CHEMICAL ABSTRACTS.

Antagonistic influence of hydrogen and calcium on the development of *Saprolegnia*. M. F. LILIENSHTERN (Trav. Soc. Nat. Leningrad, 1925, **55**, No. 3, 3—16).—Calcium (1—2% at p_H 3·6; 0·2% at p_H 4·6) neutralises the limiting influence of hydrogen ions. CHEMICAL ABSTRACTS.

Essential nature of aluminium and silicon for plant growth. A. L. SOMMER (Univ. Calif. Pub. Agric. Sci., 1926, **5**, 57—81).—Addition of aluminium (1 in 10^6) to culture solutions somewhat increased the yield of seed with peas, and the growth and yield of seed with millet. Addition of gelatinous silicic acid improved the growth of rice and millet.
CHEMICAL ABSTRACTS.

Action of rare-earth [and other] elements on plants. (SIGNA.) M. ARENA (Rend. Acad. Sci. fis. mat. Napoli, 1927, [iii], **33**, 37—39).—Small quantities of salts of uranium, zirconium, beryllium, cerium, tungsten, and rubidium stimulate the growth of roots in slips of *Alternanthera spathulata* in Pfeffer's solution. Ammonium molybdate has a feeble action, and vanadium oxychloride poisons the plant.
E. W. WIGNALL.

Effect of nutrient conditions on activity of oxidase and catalase. B. D. EZELL and J. W. CRIST (Mich. Agric. Exp. Sta. Tech. Bull., 1927, No. 78, 1—24).—For lettuce, radish, and spinach, the

correlation between catalase activity and growth was better than that between oxidase activity and growth, both being negative. CHEMICAL ABSTRACTS.

Influence of age on the composition of the wood of the maritime pine. M. H. PATY (Chim. et Ind., 1927, **18**, 204—210).—In a study of the variation of the composition of wood with the age of the tree, the three classes of compounds considered were pentosans, lignin, and celluloses. The first were determined by conversion into furfuraldehyde (and methylfurfuraldehyde) by hydrolysis, lignin by extraction of the wood with dilute sulphuric acid, total cellulose by chlorination. Pentosans and methylpentosans were found to reach a maximum at 5 years (10%) and then decrease slowly. Lignin showed a very slight continuous increase. α-Cellulose and total cellulose increased rapidly up to 20 years, then slowly. The content of oleoresins increased slowly but never exceeded 2%. The effect of tapping and of air-drying after cutting was also studied.

C. IRWIN.

Fruit-spur composition in relation to fruit-bud formation. G. F. POTTER and H. R. KRAYBILL (Proc. Amer. Soc. Hort. Sci., 1925, **22**, 146—150).—Similar carbohydrate : nitrogen relations in spurs are not always accompanied by similar degrees of fruit-bud formation. CHEMICAL ABSTRACTS.

Evolution of tannin in fruits. Kaki. E. BOTTINI (Annali Chim. Appl., 1927, **17**, 415—425).—The fruits of *Diospyros lycopersicon* and *D. kirakaki* contain considerable proportions of tannin and acids, and a small amount of reducing sugars, but no pectin. As the fruits mature, the tannin disappears almost entirely, the acids diminish in quantity, and appreciable amounts of sugars and of pectin are formed. The presence of ozone in the air favours the oxidation of the tannin and the formation of carbohydrates, but does not affect the organic acids, the pectin, or the colouring material. Formaldehyde, on the other hand, produces no change in the proportions of any of these constituents. A low temperature (1—2°) does not prevent the disappearance of the tannin or organic acids, but modifies sensibly the ripening process, diminishing the proportions of reducing sugars and of pectin. The results are explainable on the assumption that the gradual disappearance of the tannin during ripening is the result of the joint action of a condensing enzyme, which determines the formation of colouring matter, and an oxidising enzyme, which, as in the respiratory process, transforms the tannin into carbon dioxide and water.

T. H. POPE.

Decomposition of hexoses in plants. I. Zymase apparatus of seed. V. ZALESKI [with O. PISARSHEVSKI]. **II. Condition and activity of the zymase apparatus in seed.** V. ZALESKI [with L. NOTKINA] (Biochem. Z., 1927, **189**, 39—48, 101—113).—I. The view of Bodnar (cf. A., 1926, 438, 439) that pea-zymase requires for its activity the presence of an activator is confirmed. Boiled extract of peas, however, can be replaced by boiled extract of yeast or muscle, and extracts of yeast, pea, and muscle all accelerate alcoholic fermentation of pea-meal. The activator plays no role in the formation of hexose-phosphates nor can it be replaced by any usual hydrogen donator or acceptor. Assumption of the existence of a zymase zymogen is unnecessary, the stimulatory action of oxygen on the alcoholic fermentation of pea-meal depending not on the conversion of zymogen into active zymase but on the liberation of the activator.

II. Further evidence is given in support of the authors' view that the increase of the activity of zymase during the first stages of germination of peas is due not to an increased formation of zymase nor to the oxidative conversion of zymogen into zymase, but to the formation of an activator which is also an unknown activator of the alcoholic fermentation of carbohydrates. P. W. CLUTTERBUCK.

Enzyme content of resting wheat grains. A. OPARIN and N. POSPELOVA (Biochem. Z., 1927, **189**, 18—25).—The enzyme content of resting seeds depends on the kind of seed and differs for each year of harvesting. Seeds which have lost their power to germinate still contain some catalase, peroxidase, and amylase. The annual variation in catalase content runs parallel with the variations in germinating power.

P. W. CLUTTERBUCK.

Galactoaraban of lupin seeds. A. HEIDUSCHKA and H. TETTENBORN (Biochem. Z., 1927, **189**, 203—207).—Potassium galactoaraban, $C_{16}H_{28}O_{14}$,KOH is prepared from seeds of *Lupinus luteus* by the method of Schulze, Steiger, and Maxwell (A., 1890, 283). Various preparations always gave the same specific rotation, mean $[\alpha]_D^{20}$ +76·98±1·83°, and the same *copper* salt, $C_{16}H_{28}O_{14}$,$CuSO_4$. Galactoaraban, when boiled with hydrochloric acid, gave considerable amounts of furfuraldehyde. Galactoaraban, $C_{16}H_{28}O_{14}$, appears to contain one molecule of galactose and two molecules of pentose.

P. W. CLUTTERBUCK.

Blackening of the pods of the broom, *Sarothamnus scoparius*, Wimm. H. SCHMALFUSS, H. BARTHMEYER, and H. BRANDES (Biochem. Z., 1927, **189**, 229—232).—The melanogen of *Sarothamnus scoparius*, Wimm. is identified as a pyrocatechol derivative. The pods blacken when sufficient oxygen penetrates the epidermis and chlorophyll-containing layer in which the melanogen is found, and this occurs either during drying of the pods or after injury of their cuticle. P. W. CLUTTERBUCK.

North American Sarraceniaceæ. Review. Nectar. J. S. HEPBURN. **Pitcher liquor.** F. M. JONES and J. S. HEPBURN. **Enzymes of the pitcher liquor. Chemistry of pitcher liquor.** J. S. HEPBURN and F. M. JONES. **Bacteriology of pitcher liquor.** J. S. HEPBURN and E. Q. ST. JOHN. **Absorption of nutrients in the pitchers.** J. S. HEPBURN, E. Q. ST. JOHN, and F. M. JONES. **Composition of tissues.** J. S. HEPBURN and E. Q. ST. JOHN. **Bibliography.** J. S. HEPBURN (Trans. Wagner Free Inst. Sci., 1927, **11**, 3—30, 31—33, 35—48, 49—68, 69—73, 75—83, 85—86, 87—91, 93—95).—The nectar of *Darlingtonia californica* and *Sarracenia flava* contains *d*-lævulose, and of *S. minor*, *S. sledgei*, *S. drummondii*, and *S. purpurea* a reducing sugar. The reaction towards litmus and p_H values of the pitcher liquor were investigated, and

the behaviour of the proteases present was examined. The pitcher liquor did not contain reducing sugar, but hydrogen sulphide was sometimes present. The bacteria present in the open pitchers were able to use amino-acids, amides, and ammonium salts of organic acids as their sole source of carbon and nitrogen. The following data for the chemical composition of the pitchers (leaves) and rhizomes are recorded: moisture, crude fat, crude protein, crude fibre, ash (soluble and insoluble) and its alkalinity, and nitrogen-free extractives. CHEMICAL ABSTRACTS.

Production of nitrites by *Verticillium* in pure culture. J. DUFRÉNOY (Bull. Soc. Chim. biol., 1927, 9, 935—936).—Nitrite was detected in a culture medium, originally containing nitrate but no nitrite, after *Verticillium* (isolated in pure culture from apricot, plum, or cherry tree) had been grown on it for 15 days. W. O. KERMACK.

Isolation of the oil and alkaloids of stavesacre seed (*Delphinium staphisagria*). L. N. MARKWOOD (J. Amer. Pharm. Assoc., 1927, 16, 928—932).—Extraction of the seeds of *D. staphisagria* with light petroleum yields the alkaloid, delphinine, and an oil having d_4^{20} 0·891, n^{20} 1·462, acid value 92·8, iodine value (Hanus) 80·2, saponification value 190·0, acetyl value 12·8, and unsaponifiable matter 2·92%. The purification and crystallographic examination of the alkaloid are described. E. H. SHARPLES.

Ether-soluble substances of cabbage leaf cytoplasm. IV. Diglyceridephosphoric acid. H. J. CHANNON and A. C. CHIBNALL (Biochem. J., 1927, 21, 1112—1120; cf. this vol., 386).—From the products of hydrolysis of the diglyceridephosphoric acid with barium hydroxide an ether-insoluble fraction of lead salts was obtained which behaved like a mixture of salts from about equal parts of stearic and palmitic acids. The ether-soluble fraction of the lead salts from the unsaturated acids yielded hexabromostearic and tetrabromostearic acids on bromination, showing the presence of linolenic and linoleic acids in the original mixed fatty acids. Small quantities of oleic acid may have been present; arachidonic acid was absent. The greater part of the acids formed on hydrolysis were found in the unsaturated acid fraction. The name *phosphatidic acid* is assigned to the diglyceridephosphoric acid. S. S. ZILVA.

Glutelins. II. Glutelin of rice (*Oryza sativa*). D. B. JONES and F. A. CSONKA (J. Biol. Chem., 1927, 74, 427—431).—Rice endosperm differs from wheat endosperm (this vol., 799) in containing only one glutelin, which was prepared by extracting the rice with 0·2% sodium hydroxide and treating the extract with ammonium sulphate to 3% saturation. The preparation so obtained shows a higher content of nitrogen and certain differences in the nitrogen distribution as compared with the preparations of other workers. C. R. HARINGTON.

Glutelins. III. Glutelin of oats (*Avena sativa*). F. A. CSONKA (J. Biol. Chem., 1927, 75, 189—194).—Oat flour was extracted with 0·2% sodium hydroxide and the filtrate treated with ammonium sulphate to 10% saturation; the crude glutelin was purified by repeated dissolution in dilute sodium hydroxide and precipitation with alcohol and ammonium sulphate, the final yield being 1·9% of the flour; the material had its isoelectric point at p_H 6·45 and contained total N 17·53%, of which 13·46% was amide-N, 1·99% cystine-N, 15·30% arginine-N, 3·49% histidine-N, and 5·45% lysine-N. C. R. HARINGTON.

Globulins of rice (*Oryza sativa*). D. B. JONES and C. E. F. GERSDORFF (J. Biol. Chem., 1927, 74, 415—426).—Rice endosperm, on extraction with 5% sodium chloride, yielded 0·09% of a globulin coagulating at 74° and 0·07% of a second globulin coagulating at 90°. The residue from the sodium chloride extraction, on treatment with dilute sodium hydroxide, gave 2·4% of a glutelin. From rice bran there was obtained 2·88% of globulin, 0·13% of albumin, and no glutelin. Figures are given for the nitrogen distribution of the various proteins. C. R. HARINGTON.

Proteins of sesame seed, *Sesamum indicum*. D. B. JONES and G. E. F. GERSDORFF (J. Biol. Chem., 1927, 75, 213—225).—Fat-free sesame seeds were extracted with 10% sodium chloride solution. On heating the extract at 68° a precipitate was obtained, containing about 40% of ash (magnesium, sodium, potassium, and phosphorus); there were further isolated an α-globulin, coagulation temperature 95°, which could be crystallised from 2% sodium chloride, and a smaller amount of a β-globulin, coagulation temperature 84°. Figures are given for the nitrogen distribution of the various fractions. C. R. HARINGTON.

Nitrogenous components from the fruit of *Citrus grandis*, Osbeck, form. Buntan Hayat. Y. HIWATARI (J. Biochem. [Japan], 1927, 7, 169—173).—From 27 kg. of macerated juice sacs of the *Citrus* fruit of Buntan were obtained: 2·2 g. of glycine-betaine, 8·5 g. of stachydrine, and 0·2 g. of putrescine. CHEMICAL ABSTRACTS.

Nitrogenous constituents of maize pollen. C. G. VINSON (J. Agric. Res., 1927, 35, 261—278).—The nitrogenous compounds extractable from finely-ground maize pollen by dilute sodium hydroxide solution have been studied. The pollen contains very little, if any, globulin. A substance resembling glutelin was precipitated on neutralisation of the alkaline extract with sulphuric acid, and constituted 9·9% of the air-dry pollen. The following substances were detected in the filtrate from the glutelin fraction, after extraction with ether and hydrolysis: adenine, arginine, lysine, tyrosine, choline, and β-hydroxyglutamic acid. Aspartic and glutamic acids were not present. Proteolytic enzymes were not found, but carbohydrases and a pectase were present. A compound believed to be a flavone or flavonol was also isolated. The use of Neuberg's reagent for precipitating amino-nitrogen compounds proved unsatisfactory. C. T. GIMINGHAM.

Phosphorus compounds of plants. II. Solubility of phosphorus compounds of barley flour. S. MINKOVSKA (Bull. Acad. Polonaise, 1926, *B*, 1007—1039; cf. Koehler, this vol., 798).—The results obtained in the extraction of phosphorus compounds from barley flour by water, and by hydrochloric acid,

acetic acid, and sodium hydroxide solutions agree with those obtained by Koehler with maize. The amounts of total soluble phosphoric acid and inorganic phosphate extracted are determined principally by the final reaction of the extract. Barley flour contains enzymes which can rapidly liberate inorganic phosphoric acid from organic phosphorus compounds. The optimum reaction for these enzymes is p_H 5·4—4·7. On long keeping, dry barley flour shows an increase in inorganic phosphoric acid. Freshly-prepared barley flour contains 0·076% inorganic P_2O_5, 0·59% phytic P_2O_5, and 0·20% P_2O_5 in other organic combinations. G. W. Robinson.

Phosphorus compounds of plants. III. Solubility of phosphorus compounds of oat flour and ability of phytic acid to combine with protein substances of flour. S. Lindenbaum (Bull. Acad. Polonaise, 1926, *B*, 1041—1098).—The results obtained for oat flour resemble those obtained by Minkovska (cf. preceding abstract) for barley flour. The optimum reaction for the enzyme in oat flour transforming organic into inorganic phosphoric acid is p_H 5·75—4·9. Oat flour contains 0·084% mineral P_2O_5, 0·573% phytic P_2O_5, and 0·133% P_2O_5 in other organic combinations. Oat flour contains certain substances one of which is a protein with isoelectric point at p_H 5·8—6·8. In media on the acid side of its isoelectric point this compound forms an insoluble compound with phytic acid. G. W. Robinson.

Phosphorus compounds of plants. IV. Phosphorus compounds of the mycelium of *Aspergillus niger*. W. Vorbrodt (Bull. Acad. Polonaise, 1926, *B*, 1099—1108).—A preliminary note. The results obtained by extracting the mycelium of *Aspergillus niger* with varying concentrations of hydrochloric acid, acetic acid, and sodium hydroxide resemble those obtained by other workers for maize, barley, and oat flour (cf. preceding abstracts).
G. W. Robinson.

Distribution of potassium and sodium in lants. G. Andre and E. Demoussy (Bull. Soc. him. biol., 1927, 9, 861—866).—See this vol., 798.

Absorption of potassium salts by the root system of plants. K. Lemanczyk (Bull. Acad. Polonaise, 1926, *B*, 1109—1155).—Experiments on the absorption of potassium salts from nutrient solutions by the roots of barley plants are described. Absorption is considered to consist of two phases, viz., equivalent absorption, including absorption of salt molecules as such, and ionic absorption. The former phase predominates. Changes in the reaction of the nutrient solution are due to the second type of absorption. In ionic absorption, the exchange is between potassium ions in the solution and calcium and magnesium ions in the root-cells, and between the anions of the solution and hydrogen carbonate ions in the root-cells. Time-concentration curves show a periodicity, due to the interference of absorption and swelling. Absorption from solutions of electrolytes is influenced by the nature of the electrolytes, by the ratio of the concentrations of equally charged ions, and by the antagonistic action of ions.
G. W. Robinson.

Alleged occurrence of creatine and creatinine in soil and in plants. W. Linneweh (Z. Biol., 1927, 86, 345—350).—A series of substances giving the same colour reactions as creatinine is tabulated. The formation of a crystalline salt with zinc chloride is not conclusive without analysis, since betaine gives a similar salt. The formula of betaine–zinc chloride is not, as given by Liebreich, $(C_5H_{11}O_2N)_n,ZnCl_2$, but $(C_5H_{11}O_2N)_2,3ZnCl_2,H_2O$. Moreover, the nitrogen contents of arginine monopicrate and creatinine picrate agree within the limits of experimental error. The occurrence of creatine or creatinine in soil, in plants, and in bacterial cultures is not proven.
W. Robson.

Electrodialysis in biochemistry. Technical processes. J. Reitstotter.—See B., 1927, 849.

Determination of carbon dioxide and oxygen by the Haldane apparatus with automatic mixing. G. Gmeiner (Biochem. Z., 1927, 188, 285—289).—The raising and lowering of the mercury container of the Haldane apparatus are effected by attaching it to a rotating lever, the excursion being regulated by the distance of the container from the axis of rotation. P. W. Clutterbuck.

Gasometric micro-determination of iodate and sulphate. Determination of total base in blood-serum. D. D. Van Slyke, A. Hiller, and K. C. Berthelsen (J. Biol. Chem., 1927, 84, 659—675).—The solution of sulphates is shaken for 1 hr. with barium iodate; the resulting solution of iodates is transferred to the apparatus of Van Slyke and Neill (A., 1924, ii, 872), treated with excess of hydrazine, and the nitrogen evolved is measured. An empirical correction is applied for the incompleteness of the reaction between barium iodate and the soluble sulphates. The method is applicable to the determination of total base in 0·1 c.c. of blood-serum with an error of 0·8%, after preparation of the material by the method of Stadie and Ross (A., 1926, 100).
C. R. Harington.

Electrolytic determination of sodium plus potassium. J. L. Stoddard (J. Biol. Chem., 1927, 74, 677—688).—Biological material is incinerated by the method of Fiske (A., 1922, ii, 408). The resulting solution is subjected to electrolysis in a special apparatus with mercury electrodes; the sodium and potassium amalgam formed is determined by titration, a positive correction of 1·2% being applied to the results. C. R. Harington.

Determination of cyanogenetic glucosides. L. R. Bishop (Biochem. J., 1927, 21, 1162—1167).—A satisfactory method is described which is based on the decomposition of most of the glucoside by heating the leaf in water and decomposition of the remainder by added emulsin. The liberated hydrocyanic acid is aspirated, absorbed by potassium hydroxide, and titrated with silver nitrate.
S. S. Zilva.